Benzil Derivatives as Trapping Reagents for the Monomeric Alkylindium(I) Compound In–C(SiMe$_3$)$_3$

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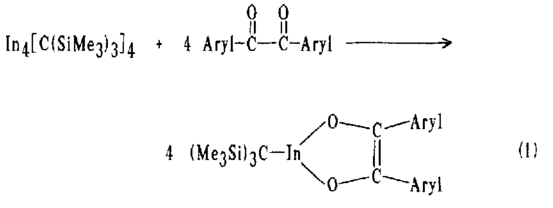
The tetrahedral cluster compound tetrakis{[tris(trimethylsilyl)methyl]indium(I)} (**1**) reacts in boiling *n*-hexane with benzil derivatives (p-X-C_6H_4)C(O)C(O)(p-X-C_6H_4) (X = H, OMe, Br), to yield the 1,4-cycloaddition products of the monomeric alkylindium(I), In–C(SiMe$_3$)$_3$, in which the In atoms are coordinated by a chelating enediolato ligand, to form a five-membered InO_2C_2 heterocycle. As shown by two crystal structure determinations (X = H, OMe), the products are dimeric in the solid state, with a four-membered In_2O_2 heterocycle in the molecular center and both C(SiMe$_3$)$_3$ groups, as well as both enediolato substituents in a *cis* arrangement.

Tetrakis[tris(trimethylsilyl)methyl]tetragallane(4), with an undistorted tetrahedron of four Ga atoms in the solid state, gradually monomerizes with increasing dilution of its solutions in benzene[1]. The monomeric alkylgallium(I) derivative Ga–C(SiMe$_3$)$_3$ is formed, which exhibits strong coordinative and electronic unsaturation, and could also be detected by an electron diffraction experiment in the gas phase[2]. The In_4 analogue **1** shows, however, a much lower tendency to monomerize and remains a tetramer in dilute benzene solution[3]. Although the monomeric formula unit is detected as the highest mass peak in conventional mass spectroscopy, we were not able to determine its structure in the gas phase due to decomposition and quantitative formation of HC(SiMe$_3$)$_3$ upon heating[2]. **1** is easily synthesized by the reaction of InBr with the THF adduct of LiC(SiMe$_3$)$_3$[3,4] and shows an unprecedented chemical reactivity. For instance, heterocubane-type molecules are formed with an excess of the elements sulfur, selenium and tellurium[3,5]. These reactions probably proceed by the gradual occupation of the faces of the In_4 cluster, and an In_4S intermediate with only one face of the tetrahedron occupied by a chalcogen atom could be synthesized by the treatment of **1** with propylene sulfide, and could be characterized by a crystal structure determination[6]. While in boiling *n*-hexane those reactions are usually finished in a short reaction time, solutions of **1** are unreactive towards most reagents at room temperature. This remarkable difference may be interpreted in terms of a partial dissociation of **1** in hot solvents, accompanied by the formation of the reactive monomer In–C(SiMe$_3$)$_3$, which needs to be formed in only trace amounts to account for the enhanced reactivity. The monomeric fragment InR is isolobal to carbon monoxide, and we indeed succeeded in replacing CO ligands in transition metal carbonyls, but the InR ligand exclusively occupies bridging positions between two metal centers[7]. Reactive intermediates like silylenes SiR_2 or stannylenes SnR_2 could be trapped by the 1,4-cycloaddition reaction with heterobutadiene derivatives like 1,4-diazabutadienes[8]. We hoped to realize a similar reaction with tetraindane(4) **1** and to detect the monomeric fragment InR as a cycloaddition product. However, these experiments did not succeed with diazabutadiene compounds[9], and we treated **1** with benzil derivatives[10] in order to use the high In–O bond energy as a driving force.

Reactions of Tetraindane(4) 1 with Benzil Derivatives

The solid benzil derivatives 4,4′-dimethoxy-, 4,4′-dibromo-, and unsubstituted benzil were added to deep violet solutions of **1** in *n*-hexane at room temperature in a molar ratio of 4:1 (eq. 1). The mixtures were refluxed for about one hour, and the color changed from violet to yellow or brown. The products (**2** to **4**) crystallized from the reaction mixtures after concentration and cooling to −50°C, as yellow solids in yields of 65 to 75%, and could be recrystallized from cyclopentane. With the exception of the phenyl derivative **2**, the crystals included solvent molecules (hexane or cyclopentane) in different amounts: **3** (R = OMe) about 1/3 and **4** (R = Br) about one molecule per formula unit of the monomer after evaporation. While crystals of **2**, **3** and **4** decomposed only very slowly in air, the solutions of all three products were extremely air-sensitive, and on contact with air they became deep violet, before an excess of oxygen led to colorless decomposition products. The constitution of the deeply colored intermediates could not be clarified by spectroscopic methods, and they could not be isolated in a pure form.



(1)

Aryl = $-C_6H_5$ (**2**); $-4\text{-MeO-}C_6H_4$ (**3**); $-4\text{-Br-}C_6H_4$ (**4**)

As shown by the cryoscopically determined molar mass, compound **3** (R = OMe) is monomeric in benzene, while the unsubstituted derivative **2** (R = H) gives only a partial monomerization under the same conditions. All products show sharp singlets for the $SiMe_3$ groups in the ^1H and ^{13}C NMR spectra. The carbon atoms bound to indium have resonances at δ = 24.0 (**2**), 23.2 (**3**) and 25.4 (**4**), which lie in the range normally observed for tricoordinated In atoms[11,12]; chemical shifts of about δ = 15 are usually detected with a coordination number of four[13]. The ethylene carbon atoms show signals with expected chemical shifts[14] of δ = 127.0, 113.9 and 121.4.

Crystal Structures of 2 and 3

Because the crystal structure of **3** could not be refined satisfactorily due to strong disorder of the cyclopentane molecules (see below), an additional compound was also characterized by crystal structure determination (**2**). The molecular structures of compounds **2** and **3** are almost indistinguishable; Figure 1 shows the structure and the numbering scheme of a complete molecule of **2**, while part of a molecule of compound **3** in Figure 2 gives a more detailed insight into the molecular center. Five-membered InO_2C_2 heterocycles were formed by the cycloaddition reaction between the benzil derivatives and the monomeric fragment of **1**, In–C$(SiMe_3)_3$; the benzil derivatives contribute enediolato ligands, coordinated by both oxygen atoms of the diketo groups to one indium atom. The In atoms become coordinatively saturated by dimerization of the molecules via In–O bridges and formation of an additional central In_2O_2 heterocycle with distorted tetrahedral coordination of the In atoms and pyramidal coordination of the oxygen atoms. The compounds have a *syn*-configuration with both enediolato groups on one side of the four-membered ring and both C$(SiMe_3)_3$ groups on the other. Thus, the arrangement of the heterocycles could be described as an open cage, and the molecular symmetry is approximately C_2 with the twofold rotation axis perpendicular to the In_2O_2 ring. This structure is probably caused by steric restrictions, because each of the bulky C$(SiMe_3)_3$ groups must come very close to an OC–phenyl group of an enediolato ligand in a hypothetical centrosymmetric molecule.

Figure 1. Molecular structure and numbering scheme of **2** (X = H); the thermal ellipsoids are drawn at the 40% probability level; hydrogen and methyl carbon atoms are omitted for clarity. Only one position of the disordered $SiMe_3$ substituents is drawn. Selected bond lengths [pm] and angles [°]: In1–O1 214.8(3), In1–O3 217.4(3), In1–O4 202.7(4), In1–C1 216.1(5), In2–O1 218.2(3), In2–O2 203.6(3), In2–O3 215.3(3), In2–C2 216.5(5), O1–In1–O3 80.3(1), O1–In1–O4 103.6(1), O3–In1–O4 80.7(1), O1–In1–C1 128.5(2), O3–In1–C1 125.6(1), O4–In1–C1 122.4(2), O1–In2–O2 80.3(1), O1–In2–O3 80.0(1), O2–In2–O3 102.5(1), O1–In2–C2 127.5(1), O2–In2–C2 121.0(1), O3–In2–C2 130.1(1)

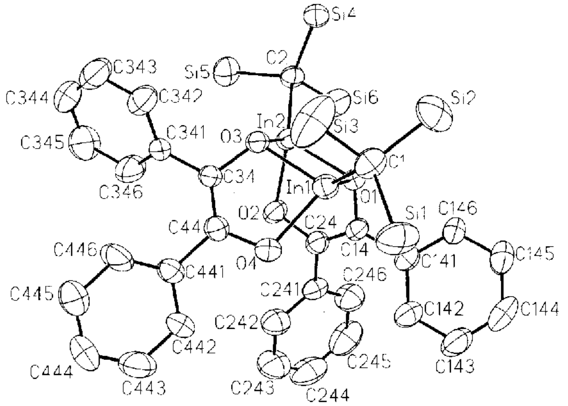
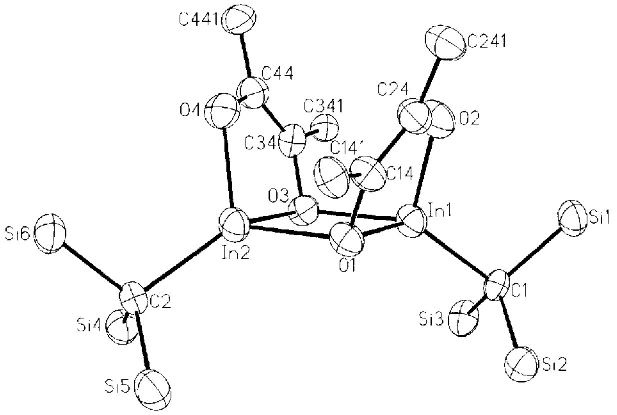


Figure 2. Central part of the molecular structure of **3**; the thermal ellipsoids are drawn at the 40% probability level; methyl and phenyl groups with the exception of the ipso-C atoms are omitted. Selected bond lengths [pm] and angles [°]: In1–O1 219.3(3), In1–O2 203.7(5), In1–O3 216.7(5), In1–C1 216.4(5), In2–O1 216.6(5), In2–O3 217.7(4), In2–O4 202.5(5), In2–C2 216.2(5), O1–In1–O2 81.1(2), O1–In1–O3 79.8(1), O2–In1–O3 105.6(2), O1–In1–C1 128.8(2), O2–In1–C1 119.5(2), O3–In1–C1 128.1(2), O1–In2–O3 80.2(1), O1–In2–O4 105.1(2), O3–In2–O4 80.9(2), O1–In2–C2 128.7(2), O3–In2–C2 127.2(2), O4–In2–C2 120.1(2)



As expected, we observe two significantly different In–O distances. Lengths of 203.2 (**2**) and 203.1 (**3**) pm on average are detected for the terminal In–O bond with a bicoordinated O atom; these distances are among the shortest described in literature and only few compounds could be found with comparable short In–O distances below 210 pm[15,16]. In contrast, the In–O bonds of the In_2O_2 heterocycle with tricoordinated oxygen atoms are very elongated (216.4 and 217.6 pm) and are in the range normally observed for alkoxides, hydroxides and peroxides of organo indium derivatives[16,17]; most of these derivatives show In–O bond lengths between 216 and 220 pm[18]. The In–O bond lengths mainly depend on the coordination number of the oxygen atoms, where smaller bond lengths belong to lower coordinated atoms; similar conditions have been observed before in several other compounds with bonds between the elements of the third main group and chalcogen atoms[11,19]. The transannular In···In (331.2 and 333.3 pm) and O···O distances (287.6 and 279.8 pm) are shorter than the sum of the van der Waals radii (In: 380 pm; O: 300 pm[20]), and the most acute angles of the ring are found at the indium atoms (80.1 and 80.0°). The In–C distances (216.3 pm in both derivatives) are shortened compared to that of the starting compound **1** (224.9 pm), which might be caused by the higher oxidation state of In in **2** and **3** and a stronger electrostatic attraction between In and C; similar effects have often been observed before in the reaction products of **1**[5,7]. The C=C double bond lengths (133.7 and 133.8 pm on average) correspond to standard values[21], the C–O distances depend on the coordination number of the oxygen atom: shorter bonds (136.8 and 137.2 pm) are observed for the bonds including the bicoordinated oxygen atoms (O2–C24, O4–C44), whereas slightly longer bonds are found (142.8 and 141.2 pm on average) for the tricoordinated, bridging oxygen atoms (O1–C14, O3–C34). The bonding situation in this part of the molecule is similar to that in several other enediolato complexes described in the literature[22].

The normals of the planes of the four- and five-membered heterocycles enclose angles of about 71° in **2** and 69° in **3**. While the In_2O_2 heterocycles are almost ideally planar with a maximum deviation of 1.3 and 1.0 pm, respectively, the five-membered rings are folded with the In atoms 42 and 31 pm above the almost ideally planar (maximum deviation 0.4 and 2.5 pm) enediolato groups. The *ipso* carbon atoms of the phenyl groups are at most 4.8 and 6.8 pm above these planes. The phenyl groups are twisted relative to the C=C double bonds by 39 to 59°, so that no significant mesomeric interactions are to be expected. The In–C bonds are almost coplanar, with small C–In–In–C torsional angles (6.6 and –1.5°). As expected from the molecular constitution, much larger torsional angles are observed between the bicoordinated oxygen atoms (O2–In–In–O4; –35.3° and 38.4°).

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Experimental Section

General: All procedures were carried out under an atmosphere of purified argon in dried solvents (*n*-hexane and cyclopentane over $LiAlH_4$). Compound **1** was prepared according to ref.[3], the benzil derivatives from Aldrich-Chemie were used without further purification.

Synthesis of **2** *(Benzil):* 450 mg (0.325 mmol) of tetraindane(4) **1** and 273 mg (1.299 mmol) of benzil are dissolved in 50 ml of *n*-hexane and refluxed for 15 min, until the deep violet color of **1** disappears and a reddish-brown solution has formed. The mixture is concentrated and cooled to –50°C. Yield: 0.54 g (75%) yellow, slightly air-sensitive crystals. – M.p. (argon; closed capillary) 218°C. – ^1H NMR (C_6D_6, 300 MHz): δ = 7.64 (4H, multiplett, *m*-H of phenyl), 7.09 (4H, pseudo-t, *o*-H of phenyl), 6.97 (2H, pseudo-t, *m*-H of phenyl), 0.21 (27H, $SiMe_3$). – ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 129.9 (broad, phenyl), 127.0 (C=C), 24.0 (InC), 5.6 ($SiMe_3$). – IR (paraffin, CsBr plates): $\tilde{\nu}$ = 1602 cm^{-1} m νC=C; 1593 m, 1568 w phenyl; 1464 vs, 1377 vs paraffin; 1319 m, 1305 m, 1288 w, 1263 s, 1254 s δCH_3; 1171 w, 1161 vw, 1155 w, 1115 m, 1069 m, 1051 w, 1036 m, 1009 s, 995 m νCO, νCC; 920 m, 907 m, 858 vs, 847 sh, 764 s, 721 s ρCH_3(Si); 694 s, 677 sh ν_{as}SiC; 615 m ν_sSiC; 557 m, 530 m, 497 w, 463 m, 427 w νInC, νInO; 383 vw, 364 vw δSiC. – $C_{24}H_{37}InO_2Si_3$ (556.63): calcd. C 51.8, H 6.7; found C 51.8, H 6.8.

Synthesis of **3** *(4,4'-Dimethoxybenzil):* 0.370 g (0.267 mmol) of **1** and 0.288 g (1.068 mmol) of 4,4'-dimethoxybenzil are dissolved in 50 ml of *n*-hexane and refluxed for 1 h. The color changes from deep violet of **1** to reddish-brown. The mixture is filtered to separate traces of elemental indium, concentrated up to the beginning of crystallization and cooled to –50°C. Yield: 0.49 g (71%) yellow, slightly air-sensitive crystals, which, after evacuation, include 0.33 molecules of *n*-hexane per formula unit of the monomer after evaporation. – M.p. (argon; closed capillary) 238°C. – Molar mass (cryoscopically in benzene): obs. 446; calc. 470 g/mol for the monomer and an NMR spectroscopically determined content of 0.36 cyclopentane molecules per formula unit. – ^1H NMR (C_6D_6, 300 MHz): δ = 7.63 and 6.74 (both: 4H, d, J_{HH} = 8 Hz, phenyl), 3.26 (6H, OCH_3), 0.27 (27H, $SiMe_3$). – ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 159.2, 131.8 and 130.8 (phenyl), 113.9 (C=C), 54.7 (OMe), 23.2 (InC), 5.7 ($SiMe_3$). – IR (paraffin, CsBr plates): $\tilde{\nu}$ = 1597 cm^{-1} m, 1567 w, 1508 m νC=C, phenyl; 1462 vs, 1377 vs paraffin; 1298 s, 1262 s, 1244 vs δCH_3; 1169 s, 1113 m, 1096 s, 1040 s, 1017 s, 993 s νCC, νCO; 912 m, 858 vs, 847 sh, 828 sh, 779 m, 721 m ρCH_3(Si); 677 m, 658 m ν_{as}SiC; 648 m, 637 m, 619 m, 606 m ν_sSiC; 588 w, 559 m, 530 w, 513 w, 465 w, 427 w νInC, νInO; 392 vw, 360 vw, 338 w δSiC. – $C_{26}H_{41}InO_4Si_3 \cdot 0.36\ C_5H_{10}$ (641.9): calcd. C 52.0, H 7.0; found C 51.7, H 6.8.

Synthesis of **4** *(4,4'-Dibromobenzil):* 0.300 g (0.217 mmol) of **1** and 0.319 g (0.868 mmol) of 4,4'-dibromobenzil are dissolved in 50 ml of *n*-hexane and refluxed for 10 min. The color changes from dark violet of **1** to reddish-brown. The mixture is concentrated and cooled to –50°C. Yield: 0.45 g (65%) yellow, slightly air-sensitive crystals, which include up to one molecule of *n*-hexane (or cyclopentane) per formula unit of the monomer. – M.p. (argon; closed capillary) 162°C (dec.). – ^1H NMR (C_6D_6, 300 MHz): δ = 7.26 and 7.17 (AB spectrum, 8H, phenyl), 0.14 (27H, $SiMe_3$). – ^{13}C NMR (C_6D_6, 75.5 MHz): δ = 131.7 (broad, phenyl), 121.4 (C=C), 25.4 (InC), 5.5 ($SiMe_3$). – IR (paraffin, CsBr plates): $\tilde{\nu}$ = 1626 cm^{-1} w, 1584 m, 1566 vw, 1541 vw νC=C, phenyl; 1462 vs, 1377 vs paraffin; 1314 m, 1277 m, 1263 s, 1254 s δCH_3; 1171 w, 1144 w, 1119 m, 1096 m, 1072 s, 1044 m, 1011 s, 999 s νCC, νCO; 912 m, 858 vs, 829 sh, 779 w, 770 sh, 721 m ρCH_3(Si); 677 w, 658 w ν_{as}SiC; 617 w ν_sSiC; 558 w, 532 w, 521 w, 482 m, 465 m, 427 νInC, νInO, νCBr; 379 vw, 347 vw δSiC. – UV/Vis (*n*-pentane) (ε): 240 (12000), 350 nm (1200). – $C_{24}H_{35}Br_2InO_2Si_3 \cdot C_6H_{14}$ (800.6): calcd. C 45.0, H 6.2; found C 44.6, H 6.0.

Crystal Structure Determinations: Single crystals of **2** and **3** were obtained by recrystallization from cyclopentane; the crystals of **3** were not evacuated after isolation. Crystal data and structure refinement parameters are given in Table 1[25]. Compound **3** crystallizes with solvent molecules, which are strongly disordered and were refined with restraints of bond length and angles and occupancy factors of 0.25 and 0.5. The cyclopentane content determined by the structure refinement is 1.25 molecules per formula unit of the dimeric compound **3**. A further disorder is observed for one of the C($SiMe_3$)$_3$ groups and for the methoxy groups, which could however be satisfactorily resolved. **2** crystallizes without solvent molecules, but shows a rotational disorder of both C($SiMe_3$)$_3$ substituents with occupancy factors of 0.8 and 0.2 for the trimethylsilyl groups Si1, Si2 and Si3, and 0.68 and 0.32 for Si4, Si5 and Si6; such disorder has often been observed before with the axially symmetrical substituent[5,7]. The bond lengths and angles of the disordered groups are refined with restrictions to ideal values. The carbon atoms of the disordered groups are isotropically refined. Despite the disorder, and in contrast to **3**, the structure of **2** could be refined to low *R*-values and satisfactory standard deviations.

Table 1. Crystal data and data collection parameters for **2** and **3**[a]

Formula	$C_{48}H_{74}In_2O_4Si_6$	$C_{58.25}H_{94.5}In_2O_8Si_6$
Z	4	4
Temperature (K)	300(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$; No. 14[23]	$P2_1/c$; No. 14[23]
$d_{\mathrm{calc.}}$ ($\mathrm{g \cdot cm^{-3}}$)	1.305	1.208
a (pm)	1548.0(2)	2400.6(1)
b (pm)	1535.6(1)	1196.76(5)
c (pm)	2493.0(3)	2581.7(1)
β (°)	107.06(1)	101.766(7)
V (10^{-30} m^3)	5665(1)	7261.2(5)
μ (mm^{-1})	0.978	0.777
Crystal size (mm)	0.5 × 0.5 × 0.4	0.5 × 0.4 × 0.4
Diffractometer	Stoe-IPDS	AED 2
Radiation	Mo-K_α; graphite monochromator	
2Θ range (°)	$3.7 \le 2\Theta \le 48.2$	$3 \le 2\Theta \le 48$
Index ranges	$-17 \le h \le 16$	$-27 \le h \le 26$
	$0 \le k \le 17$	$0 \le k \le 13$
	$0 \le l \le 28$	$0 \le l \le 29$
Reflections measured	30117	12003
Independent reflections	8884	11373
Reflections $F > 4\sigma(F)$	6543	7710
Parameters	597	791
$R = \Sigma\lVert F_o\rvert - \lvert F_c\rVert/\Sigma\lvert F_o\rvert$ ($F > 4\sigma(F)$)	0.041	0.0986
$wR^2 = \{\Sigma_w(F_o^2-F_c^2)^2/\Sigma_w(F_o^2)^2\}^{1/2}$	0.091	0.1675
Max./min. residual electron density (10^{30} e/m^3)	0.753/−0.490	0.663/−0.458

[a] Programmes SHELXL-93, SHELXTL[24]; solutions by direct methods; full matrix refinement with all independent structure factors.

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[25] Further details of the crystal structure determinations are available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406856 (**2**) and -406855 (**3**).

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