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On the chemistry of fluoroorgano derivatives of Group 13 elements Part 3. Syntheses of pentafluorophenylindium dibromide, $In(C_6F_5)Br_2 \cdot 2D$ ($D = THF, C_5H_5N$), and related compounds—single crystal structure analyses of $In(C_6F_5)Br_2 \cdot 2THF$ and $In(acac)Br_2 \cdot 2THF$☆

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Abstract

$In(C_6F_5)Br_2 \cdot 2D$ ($D = THF$, pyridine) are selectively and almost quantitatively formed through oxidative addition of C_6F_5Br to InBr in THF solution or dichloromethane–pyridine mixtures. The constitution of $In(C_6F_5)Br_2 \cdot 2THF$ is confirmed by a single crystal structure analysis (monoclinic, $P2_1/c$, $Z = 4$, $a = 1694.3(2)$, $b = 1421.5(2)$, $c = 813.42(9)$ pm, $\beta = 100.3(1)°$, $R_{all} = 0.1072$). Reactions of $In(C_6F_5)Br_2 \cdot 2THF$ and $Mg(C_6F_5)Br$ in diethylether after addition of 4-dimethylaminopyridine (DMAP) yield $In(C_6F_5)_3 \cdot DMAP$. $In[SC(S)N(C_2H_5)_2]_3$ is formed by treatment of $In(C_6F_5)Br_2 \cdot 2THF$ with $NaSC(S)N(C_2H_5)_2$ while acidic hydrolysis with aqueous HBr quantitatively gives $InBr_3 \cdot nH_2O$ and C_6F_5H. Reactions of $In(C_6F_5)Br_2 \cdot 2THF$ with an aqueous solution of pentane-2,4-dione (acetylacetone, Hacac) in THF quantitatively yield $In(acac)Br_2 \cdot 2THF$ and C_6F_5H. The constitution of this compound is established by a single crystal structure analysis (orthorhombic, $Pbcn$, $Z = 4$, $a = 1314.9(2)$, $b = 928.5(1)$, $c = 1468.4(2)$ pm, $R_{all} = 0.0347$).

Keywords: Acetylacetonate; Crystal structure; Indium; Pentafluorophenyl

1. Introduction

Pentafluorophenylindium derivatives were first reported in 1965 [3]. In the early 70s of last century, Deacon and Parrott developed different methods for their syntheses [4–8]. In our systematic studies [1,2,9,10] on the synthesis of pentafluorophenylindium compounds, we found that derivatives of the general formula $In(C_6F_5)Br_2 \cdot 2D$ ($D = THF, C_5H_5N$) are conveniently accessible. In this paper, synthesis, characterisation and reactions of $In(C_6F_5)Br_2 \cdot 2THF$ are described.

2. Results and discussion

2.1. Reactions of bromopentafluorobenzene and indium(I) bromide and mixtures of bromopentafluorobenzene, indium and bromine

Reactions of C_6F_5Br and elemental indium at ambient temperature gave no ^{19}F-NMR spectroscopic for the formation of InC_6F_5 derivatives. By contrast, reactions of C_6F_5Br and InBr or 2:1 mixtures of elemental indium and bromine (Eq. (1)) proceeded selectively in THF with nearly quantitative formation of $In(C_6F_5)Br_2 \cdot 2THF$. Similar results were obtained using 1:4 mixtures of CH_2Cl_2 and pyridine. Both derivatives, $In(C_6F_5)Br_2 \cdot$

☆ For Part 2 see [Z. Anorg. Allg. Chem. 625 (1999) 1287]. This work was presented in part on the 15th Winter Fluorine Conference, St. Petersburg, FL, USA, 14-1-2001 to 19-1-2001, cf. [J. Fluorine Chem. 112 (2001) 119].

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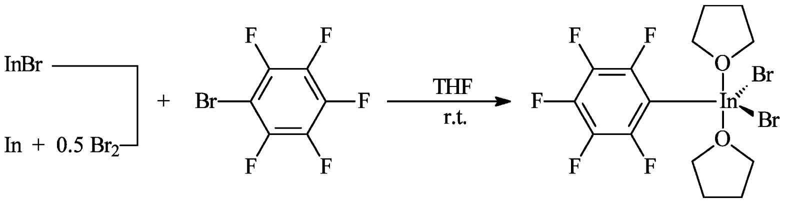
$2THF$ and $In(C_6F_5)Br_2 \cdot 2C_5H_5N$, were isolated as pale yellow, respectively, colourless air and water insensitive solids in nearly quantitative yields.



1 (1)

These reactions might be interpreted in terms of an oxidative addition of C_6F_5Br to InBr or the formal insertion of InBr into the carbon–bromine bond of C_6F_5Br and are best described via the SET mechanistic approach [11] (Scheme 1).

$$\begin{array}{lcl} InBr & \longrightarrow & InBr^{\bullet +} + e^- \\ e^- + C_6F_5Br & \longrightarrow & C_6F_5Br^{\bullet -} \\ C_6F_5Br^{\bullet -} & \longrightarrow & C_6F_5^{\bullet} + Br^- \\ Br^- + InBr^{\bullet +} & \longrightarrow & InBr_2^{\bullet} \\ InBr_2^{\bullet} + C_6F_5^{\bullet} & \longrightarrow & In(C_6F_5)Br_2 \\ \hline InBr + C_6F_5Br & \longrightarrow & In(C_6F_5)Br_2 \end{array}$$

Scheme 1.

2.2. Reactions of $In(C_6F_5)Br_2 \cdot 2THF$

Halide substitution reactions of $In(C_6F_5)Br_2 \cdot 2THF$ and $Mg(C_6F_5)Br$ were carried out in diethylether (Eq. (2)).

$$In(C_6F_5)Br_2 \cdot 2THF + 2Mg(C_6F_5)Br \underset{-2MgBr_2}{\overset{(C_2H_5)_2O}{\rightarrow}} \underset{-2THF}{\overset{+DMAP}{\rightarrow}} In(C_6F_5)_3 \cdot DMAP \qquad (2)$$

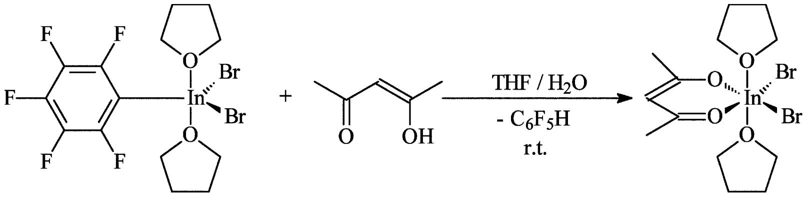
The reaction proceeded to the corresponding substitution product $In(C_6F_5)_3$. Addition of 4-dimethylaminopyridine (DMAP) allowed the isolation of $In(C_6F_5)_3 \cdot DMAP$ [1] in moderate yield. In contrast, treatment of $In(C_6F_5)Br_2 \cdot 2THF$ with $(C_2H_5)_2Zn$ after addition of $(C_2H_5)_3N$ did not selectively give the expected product, $(C_2H_5)_2InC_6F_5 \cdot N(C_2H_5)_3$ [10] but a product mixture of at least four InC_6F_5 compounds (^{19}F-NMR control).

Also reactions of $In(C_6F_5)Br_2 \cdot 2THF$ and $NaSC(S)N(C_2H_5)_2 \cdot 3H_2O$ in aqueous THF did not give the desired complex compounds $\{In(C_6F_5)[SC(S)N(C_2H_5)_2]\}Br$ or $In(C_6F_5)\{[SC(S)N(C_2H_5)_2]_2\}$ but $In[SC(S)N(C_2H_5)_2]_3$ and C_6F_5H (Eq. (3), idealised). Single crystals of $In[SC(S)N(C_2H_5)_2]_3$ were grown from toluene solutions of the raw material showing an identical structure as determined previously [12].

$$In(C_6F_5)Br_2 \cdot 2THF + 3Na[SC(S)N(C_2H_5)_2] + H_2O \overset{THF/H_2O}{\rightarrow} In[SC(S)N(C_2H_5)_2]_3 + 2NaBr + NaOH + C_6F_5H \qquad (3)$$

Reactions of $In(C_6F_5)Br_2 \cdot 2THF$ and aqueous HBr (48%), the H-acidic compounds acetylacetone (pentane-2,4-dione, Hacac), 2,2,6,6-tetramethylheptane-3,5-dione and 1,1,1,5,5,5-hexafluoropentane-2,4-dione proceeded selectively in the cases of the two former. These reactions gave $InBr_3 \cdot nH_2O$ (Eq. (4)) and $In(acac)Br_2 \cdot 2THF$ (Eq. (5)) after extended reaction times (up to 1 week at room temperature).

$$In(C_6F_5)Br_2 \cdot 2THF + HBr \underset{-C_6F_5H}{\overset{THF}{\rightarrow}} InBr_3 \cdot nH_2O \qquad (4)$$



5 (5)

However, reactions with further α,γ-diketones gave complex product mixtures. ^{19}F-NMR spectra reveal that the In–C bond had not completely been cleaved even after extremely prolonged reaction times of up to 6 weeks.

As mentioned before, the reaction of pentane-2,4-dione (acetylacetone, Hacac) and In(C_6F_5)Br_2·2THF proceeded smoothly and selectively to give In(acac)Br_2·2THF in good yield. This method offers a third approach to prepare In(acac)Br_2 different from the previously described pathways starting from indium(I) halides and pentane-2,4-dione yielding mixtures of In$(acac)_3$ and In(acac)X_2. The In(acac)X_2 was converted into octahedral complexes ($InX_2O_2N_2$ moieties) after addition of 2,2′-bipyridine, 1,10-phenantroline, pyridine or pyridine-D_5 [13]. Compounds In(acac)X_2·D (X = Cl, Br; D = 2,2′-bipyridine, 1,10-phenantroline) were alternatively prepared from InX_3, the donor and pentane-2,4-dione in methanol solutions [14].

Single crystals of In(acac)Br_2·2THF were grown on storing the mother liquor for several months at ambient temperature. The results of single crystal analyses are given in the following section.

2.3. Results of crystal structure analyses

2.3.1. Single crystal structure of In(C_6F_5)Br_2·2THF

In the crystal structure of In(C_6F_5)Br_2·2THF, the indium atom is surrounded by one carbon atom of the C_6F_5 group, two oxygen atoms of the THF molecules and two bromine atoms (Fig. 1). The co-ordination polyhedron is a nearly ideal trigonal bipyramid with the bromine atoms and the carbon atom forming the equatorial plane, while the oxygen atoms occupy apical sites. The shortest distance is found for the In–C bond (218.7 pm). This value corresponds well with distances found for other crystallographically characterised pentafluorophenyl indium compounds, i.e. $(C_6F_5)_2$-In$(CH_2)_3N(CH_3)_2$ [15] and [$(C_6H_5)_3PNP(C_6H_5)_3$][In-$(C_6F_5)_4$] [1].

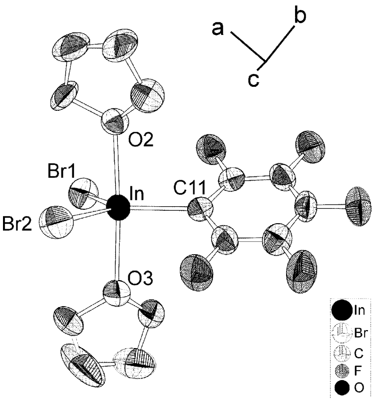


Fig. 1. Molecular structure of In(C_6F_5)Br_2·2THF.

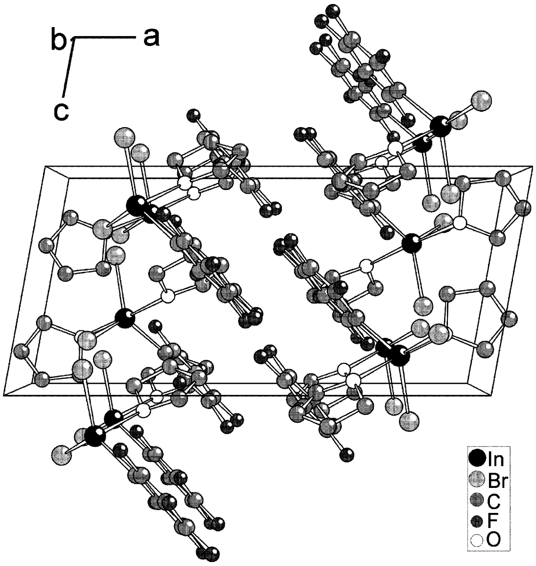


Fig. 2. Perspective view of the crystal structure of In(C_6F_5)Br_2·2THF along [0 1 0].

The indium oxygen bond lengths of 229.5 and 233.0 pm are slightly longer than those measured in $InBr_3$·2THF [16] and shorter than those measured in $(CH_3)_2$CHInBr_2·2THF and $C_6H_5CH_2$InBr_2·2THF [17]. As in $InBr_3$·2THF, the angle O2–In–O3 is found to be 177°. The distances to the bromide ions are also slightly but not remarkably longer than in $InBr_3$·2THF and in good agreement with values reported for $(CH_3)_2$CHInBr_2·2THF and $C_6H_5CH_2$InBr_2·2THF [17]. The angles within the equatorial plane vary from 118° to 121° and are close to the ideal value of 120°. The equatorial plane and the plane formed by the atoms of the C_6F_5 ligand are tilted with respect to each other by 34° (Fig. 1). It should be noted that the shortest distances of In to the fluoride atoms of the C_6F_5 group are 327 and 330 pm and, hence, are slightly shorter than the calculated van der Waals contact (350 pm [18]).

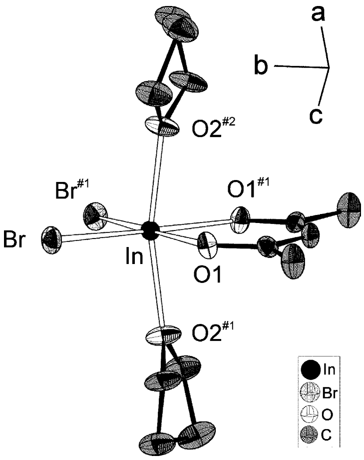


Fig. 3. Molecular structure of In(acac)Br_2·2THF.

In the crystal structure (Fig. 2), $In(C_6F_5)Br_2 \cdot 2THF$ molecules are arranged in a manner that layers are formed parallel to [1 0 0]. The C_6F_5 groups of one layer are located opposite to the THF molecules of adjacent layers. The shortest distances of the C atoms of the THF groups to the F atoms of the C_6F_5 group (for example C33–F14: 316 pm) probably might be interpreted in terms of a weak hydrogen bonding.

2.3.2. Single crystal structure of $In(acac)Br_2 \cdot 2THF$

The substitution of the monodentate pentafluorophenyl group in $In(C_6F_5)Br_2 \cdot 2THF$ by the bi-dentate chelating acetylacetonate ligand gives a distorted octahedral co-ordination around the indium centre in $In(acac)Br_2 \cdot 2THF$ (Fig. 3). In comparison with $In(C_6F_5)Br_2 \cdot 2THF$, the distances of indium to the oxygen atoms of the THF ligands standing *trans* to each other (224.5 pm, Table 3) are significantly shorter. On the other hand, In–Br bond lengths are elongated by about 6 pm (Table 3). These changes are in good agreement with observations for other octahedral indium complexes with bromine and oxygen ligands such as $InBr_3 \cdot 3DMSO$ [19] or $InBr_3 \cdot 3DMF$ [16] compared with the trigonal bipyramidal complex $InBr_3 \cdot 2THF$ [16]. Bromine and oxygen atoms of the acetylacetonate group form a nearly ideal square plane. The angles Br–In–$Br^{\#1}$, O1–In–$O1^{\#1}$, O1–In–Br (84°–99°) as well as $Br^{\#1}$–In–O1 (172.56°) deviate from the 90° angle and the 180° angle, respectively, in the expected range. The O atoms of the THF molecules are shifted away from the bromide ions. Therefore, the angle O2–In–$O2^{\#2}$ of 166.2° significantly deviates from linearity.

The molecular structure is best compared with that of (2,2′-bipyridine)(2,4-pentanedionato)indium dichloride, $In(acac)Cl_2 \cdot 2,2'\text{-}(C_5H_4N)_2$ [20]. Both derivatives $In(acac)Cl_2 \cdot 2,2'\text{-}(C_5H_4N)_2$ [20] and $In(acac)Br_2 \cdot 2THF$ exhibit octahedrally co-ordinated indium centres. Bond lengths to the oxygen atom of the chelating pentanedionato ligands are of comparable size (212.4 and 216.4 pm [20] and 215.6 pm). In contrast to the structure described in this paper, the 'equatorial' plane in $In(acac)Cl_2 \cdot 2,2'\text{-}(C_5H_4N)_2$ [20] is not built up by the two oxygen atoms of the acetylacetonate and two halogen atoms but by one halogen and one nitrogen atom of the donor molecule with one chlorine atom *trans* to oxygen and one *trans* to nitrogen. With respect to the angles, the structure of $In(acac)Cl_2 \cdot 2,2'\text{-}(C_5H_4N)_2$ deviates more from a 'regular octahedron' than that of $In(acac)Br_2 \cdot 2THF$.

Molecules in the crystal structure are orientated in a manner that in direction [0 1 0] bromine atoms and acetylacetonate ligands are opposite to each other (Fig. 4).

3. Experimental

Schlenk techniques were used throughout most of the manipulations. Indium wire or pellets were purchased from Strem, InBr from Aldrich, C_6F_5Br from ABCR. THF, pyridine, and dichloromethane were purified and dried by common methods. NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.1 MHz (^1H). External standards were used in all cases (^1H, ^{13}C: $(CH_3)_4Si$; ^{19}F: CCl_3F). Acetone-d_6 was used as an external lock (5 mm tube) in reaction control measurements, while an original sample of the reaction mixture was measured in a 4-mm insert. Mass spectra were run on a Finnigan MAT 95 spectrometer using the electron impact method (20 eV). Intensities are referenced to the most intensive peak. Decomposition points were determined using the apparatus HWS Mainz 2000.

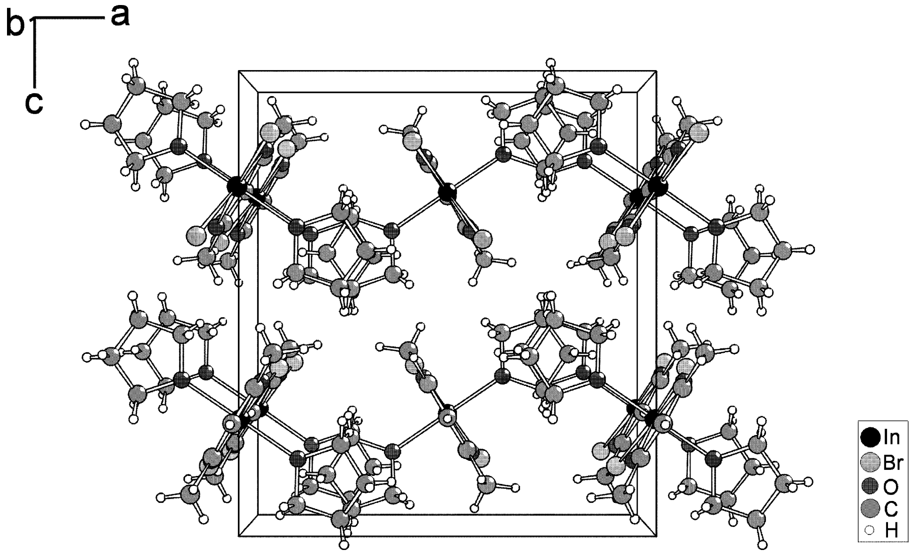


Fig. 4. Perspective view of the crystal structure of $In(acac)Br_2 \cdot 2THF$ along [0 1 0].

Table 1
Crystallographic data and their determination

Compound	$In(acac)Br_2 \cdot 2THF$	$In(C_6F_5)Br_2 \cdot 2THF$
Lattice parameter		
a (pm)	1314.9(2)	1694.3(2)
b (pm)	928.5(1)	1421.5(2)
c (pm)	1468.4(2)	813.42(9)
β (°)		100.3(1)
Molar volume ($cm^3 mol^{-1}$)	269.9	290.3
No. of formula units	4	4
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbcn* (Nr. 61)	$P2_1/c$ (Nr. 14)
Measure device	Stoe IPDS	
Radiation	Mo–K_α (graphite monochrom., $\lambda = 71.07$ pm)	
Measuring temperature (K)	293	170
Theta range (°)	$3 < 2\theta < 48$	$5 < 2\theta < 48$
Index range	$-15 \le h \le 17$, $-12 \le k \le 12$, $-19 \le l \le 18$	$-19 \le h \le 19$, $-16 \le k \le 16$, $-8 \le l \le 8$
Rotation angle (°); φ increment (°)	$0 < \varphi < 260$; 2.0	$0 < \varphi < 200$; 2.0
No. of images	130	100
Exposure time (min)	6	5
Detector distance (mm)	60	60
Data corrections	Polarisation and Lorentz factors	
Absorption correction	Numerical after crystal shape optimisation [24]	
μ (cm^{-1})	57.8	54.2
Measured reflections	7877	12 095
Unique reflections	1405	2934
Unique reflections with $I > 2\sigma(I)$	1058	1705
R_{int}	0.0458	0.1587
Structure solution and refinement	SHELXS-86 and SHELXL-93 [25,26]	
Scattering factors	Intern. Tables, Vol. C	
Goodness of fit	0.917	0.928
R_1; wR_2 [$I > 2\sigma(I)$]	0.0209; 0.0415	0.0637; 0.1386
R_1; wR_2 (all data)	0.0347; 0.0435	0.1072; 0.1528

Table 2
Selected distances (pm) and angles (°) for $In(C_6F_5)Br_2 \cdot 2THF$

In–Br1	250.0(2)	C11–In–Br1	121.0(3)
In–Br2	250.2(2)	C11–In–Br2	120.8(3)
In–O2	229.5(7)	C11–In–O2	91.9(3)
In–O3	233.0(8)	C11–In–O3	91.4(3)
In–C11	218.7(11)	O2–In–Br1	89.3(2)
		O2–In–Br2	89.9(2)
C11–C12	138(2)	O2–In–O3	176.7(3)
C11–C16	139(2)	O3–In–Br1	88.8(2)
C12–C13	136(2)	O3–In–Br2	88.6(2)
C13–C14	139(2)	Br1–In–Br2	118.2(1)
C14–C15	134(2)	O2–In–O3	176.6(2)
C15–C16	136(2)	O2–C21	147(2)
C12–F12	136(1)	O2–C24	150(1)
C13–F13	138(1)	C21–C22	149(2)
C14–F14	137(1)	C22–C23	137(2)
C15–F15	135(1)	C23–C24	150(2)
C16–F16	136(1)		
		O3–C31	149(1)
		O3–C34	143(1)
		C31–C32	148(2)
		C32–C33	144(2)
		C33–C34	146(2)

Table 3
Selected distances (pm) and angles (°) for $In(acac)Br_2 \cdot 2THF$

In–Br	(2*x*)	255.9(1)	O1–In–Br	(2*x*)	172.56(7)
In–O1	(2*x*)	215.6(2)	O1–In–Br$^{\#1}$	(2*x*)	88.02(7)
In–O2	(2*x*)	224.5(3)	O1–In–O2	(2*x*)	86.26(10)
			O1–In–O2$^{\#2}$	(2*x*)	83.56(10)
C11–C12	(2*x*)	139.2(4)	O1–In–O$^{\#1}$		84.9(1)
C12–C13		150.5(6)	O2–In–Br	(2*x*)	93.61(7)
C12–O1		127.0(4)	O2–In–Br$^{\#1}$	(2*x*)	95.33(7)
C11–H111		92(5)	O2–In–O$^{\#2}$		166.2(1)
C13–H131		93(4)	Br–In–Br$^{\#1}$		99.11(2)
C13–H132		90(5)			
C13–H133		97(5)	C21–H211		74(4)
			C21–H212		118(5)
O2–C21		145.9(5)	C22–H221		98(5)
O2–C22		145.7(6)	C22–H222		99(6)
C21–C23		147.8(8)	C23–H231		92(5)
C22–C24		150.1(7)	C23–H232		97(6)
C23–C24		151.0(8)	C24–H241		85(6)
			C24–H242		101(6)

#1: $-x, y, -z+\frac{1}{2}$; #2: $x, -y, z+\frac{1}{2}$.

CHN analyses were carried out with a Heraeus CHN Rapid apparatus. Elemental analyses were performed by literature procedures: In [21], F [22], Br [23].

3.1. Crystal structure analyses

Both compounds easily form colourless to pale yellow single crystals which were sealed in glass capillaries and the suitability checked with the help of an IP-diffractometer (STOE IPDS) [24]. The same device was used to collect the reflection data of the respective best specimen. The positions of the heavy atoms were extracted from these data using the direct methods provided by the program SHELXS-86 [25]. The light atoms were localised during the refinement (SHELXL-93) by difference Fourier syntheses [26]. For $In(acac)Br_2 \cdot 2THF$ the hydrogen atom positions were found in the difference Fourier map and refined without constraints [27]. The hydrogen atoms in the crystal structure of $In(C_6F_5)Br_2 \cdot 2THF$ could not be detected although the measurement was carried out at low temperature. Details of data aquisition and the crystallographic data are summarised in Tables 1–3 [28].

3.2. Syntheses of (pentafluorophenyl)indium dibromide adducts

3.2.1. bis(tetraHydrofuran)(pentafluorophenyl)indium dibromide, $In(C_6F_5)Br_2 \cdot 2THF$

Two gram (10.27 mmol) of InBr was suspended and partly dissolved in 15 ml of THF. 1.50 ml (12.03 mmol) of C_6F_5Br was added. The reaction mixture was stirred for 16 h at ambient temperature. During this period red InBr completely vanished giving a nearly colourless solution. ^{19}F-NMR control revealed that the mixture contained $In(C_6F_5)Br_2 \cdot 2THF$, excess C_6F_5Br besides minor amounts of C_6F_5H. All volatile compounds were distilled off in vacuo at ambient temperature giving $In(C_6F_5)Br_2 \cdot 2THF$ in nearly quantitative yield (5.91 g, 98%). The product is a pale yellow solid with an intensive characteristic smell ('honey melon like') being insensitive to air and water-soluble.

Instead of InBr, elemental indium and bromine (Br_2) in a molar ratio of 2:1 may alternatively be used in a similar procedure as described above. Reactions were terminated after all indium had been consumed. Isolated yields were nearly quantitative in all cases.

Pale yellow solid; m.p. 68–69 °C.

^{19}F-NMR (188.3 MHz, CD_3CN): $\delta = -119.1$ (m, 2F, F-2,6); -154.0 (tt, 1F, F-4); -161.1 (m, 2F, F-3,5); (D_2O) -121.3 (m, 2F, F-2,6); -154.1 (tt, 1F, F-4); -161.5 (m, 2F, F-3,5).

^1H-NMR (200.1 MHz, CD_3CN): $\delta = 3.74$ (m, 4H, CH_2O); 1.82 (m, 4H, CH_2).

^{13}C-NMR (50.3 MHz, CD_3CN): $\delta = 149.2$ (dm, $^1J_{F,C} = 241$ Hz, C-2,6); 142.7 (dm, $^1J_{F,C} = 250$ Hz, C-4); 137.9 (dm, $^1J_{F,C} = 246$ Hz, C-3,5); 119.8 (br, C-1); 69.3 (t, $^1J_{C,H} = 148$ Hz, CH_2O); 26.0 (t, $^1J_{C,H} = 133$ Hz, CH_2); ($CH_3NO_2/C_6D_6 = 3:1$): $\delta = 148.4$ (dm, $^1J_{F,C} = 237$ Hz, C-2,6); 142.4 (dm, $^1J_{F,C} = 251$ Hz, C-4); 137.3 (dm, $^1J_{F,\ C} = 256$ Hz, C-3,5); 115.8 (br, C-1); 69.2 (t, $^1J_{C,H} = 150$ Hz, CH_2O); 25.2 (t, $^1J_{C,H} = 133$ Hz, CH_2); (D_2O): $\delta = 148.2$ (dm, $^1J_{F,C} = 231$ Hz, C-2,6); 140.6 (dm, $^1J_{F,C} = 267$ Hz, C-4); 136.5 (dm, $^1J_{F,C} = 246$ Hz, C-3,5); 119.3 (t, $^2J_{F,C} = 54.6$ Hz, C-1); 68.0 (t, $^1J_{C,H} = 146$ Hz, CH_2O); 25.1 (t, $^1J_{C,\ H} = 135$ Hz, CH_2).

EIMS 20 eV (150 °C), *m/z* (rel. int.): 975 $[C_{24}Br_3F_{20}In_2]^+$ (3); 890 $[C_{18}Br_2F_{15}In_2]^+$ (8); 803 $[C_{12}Br_3F_{15}In_2]^+$ (6); 616 $[C_{18}F_{15}In]^+$ (4); 528 $[C_{12}BrF_{10}In]^+$ (9); 449 $[C_{12}F_{10}In]^+$ (100); 361 $[C_6BrF_5In]^+$ (58); 168 $[C_6HF_5]^+$ (55); 115 $[In]^+$ (85); 71 $[C_4H_7O]^+$.

Anal. Calc. for $C_{14}H_{16}Br_2F_5InO_2$: C, 28.7; H, 2.8; Br, 27.3; F, 16.2; In, 19.6%. Found: C, 28.2; H, 2.9; Br, 27.1; F, 16.0; In, 19.8%.

The results of the crystal structure analysis are summarised in Tables 1 and 2.

3.2.2. bis(Pyridine)(pentafluorophenyl)indium dibromide, $In(C_6F_5)Br_2 \cdot 2C_5H_5N$

In a similar manner as described for the THF complex, the pyridine adduct was obtained using 1:4 mixtures of CH_2Cl_2 and pyridine. $In(C_6F_5)Br_2 \cdot 2C_5H_5N$ was obtained in approximately quantitative yield as a colourless solid. NMR data of the C_6F_5 group matched well with those reported for the THF complex. ^1H- and ^{13}C-NMR data of the ligand did not significantly differ from those of neat pyridine.

Colourless solid; m.p. 240 °C (dec.).

EIMS 20 eV (125 °C), *m/z* (rel. int.): $[C_{18}F_{15}In]^+$ (1); 528 $[C_{12}BrF_{10}In]^+$ and $[C_{17}H_5F_{10}BrInN]^+$ (10); 449 $[C_{12}F_{10}In]^+$ (51); 442 $[C_{11}H_5BrF_5InN]^+$ (40); 361 $[C_6BrF_5In]^+$ (69); 354 $[Br_3In]^+$ (24); 275 $[Br_2In]^+$ (19); 194 $[BrIn]^+$ (14); 168 $[C_6HF_5]^+$ (9); 115 $[In]^+$ (72); 79 $[C_5H_5N]^+$ and $[Br]^+$ (100).

Anal. Calc. for $C_{16}H_{10}Br_2F_5InN_2$: Br, 26.6; F, 15.8; In, 19.1%. Found: Br, 26.5; F, 14.9; In, 18.7%. Sufficient results of a CHN analysis cannot be provided due to incomplete combustion of the samples.

3.3. Reactions of $In(C_6F_5)Br_2 \cdot 2THF$

3.3.1. Synthesis of (4-dimethylaminopyridine)tris-(pentafluorophenyl)indium, $In(C_6F_5)_3 \cdot DMAP$

Four gram (6.82 mmol) of $In(C_6F_5)Br_2 \cdot 2THF$ was added to a freshly prepared solution of 17.00 mmol of $Mg(C_6F_5)Br$ (0.43 g Mg, 2.12 ml C_6F_5Br) in diethylether. The reaction mixture was stirred for 24 h at 30 °C. 0.82 g (6.71 mmol) of DMAP was added and the mixture stirred for additional 24 h at ambient temperature. After filtration of the solid residue, all volatile compounds were removed in vacuo leaving an ochre residue from which $In(C_6F_5)_3 \cdot DMAP$ was extracted with CH_2Cl_2 in a Soxhlet-apparatus in 74% yield (3.72 g). Analytic and spectroscopic data agreed well with those reported earlier [1].

3.3.2. Synthesis of indium tris(diethyldithiocarbamate), $In[SC(S)N(C_2H_5)_2]_3$

Two gram (3.41 mmol) of $In(C_6F_5)Br_2 \cdot 2THF$ and 0.60 g (2.66 mmol) of $NaSC(S)N(C_2H_5)_2 \cdot 3H_2O$ were dissolved in a mixture of 15 ml of THF and 5 ml of H_2O. The reaction was terminated when C_6F_5H was detected as the only fluorine-containing component in the ^{19}F-NMR spectra of the reaction mixture. All volatile compounds were distilled off in vacuo. The remaining residue was extracted with toluene. Evaporation of toluene under a ventilated hood for several days yielded colourless crystals of $In[SC(S)N(C_2H_5)_2]_3$ which were identified by a single crystal structure analysis [12] and an elemental analysis.

3.3.3. Reaction of $In(C_6F_5)Br_2 \cdot 2THF$ with aqueous HBr

Two gram (3.41 mmol) of $In(C_6F_5)Br_2 \cdot 2THF$ was dissolved in 20 ml of THF at ambient temperature. One milliliter of aqueous HBr (48%) was added. The mixture was diluted with 2 ml water. After a total reaction time of 2 d, exclusive formation of C_6F_5H was detected in the ^{19}F-NMR spectra. After vacuum-drying, an extremely hygroscopic colourless solid was obtained (1.67 g) which was identified as $InBr_3 \cdot nH_2O$.

3.3.4. *Synthesis of bis(tetrahydrofuran)(2,4-pentanedionato)indium dibromide, In(acac)Br_2·2THF*

Four gram (6.82 mmol) of In(C_6F_5)Br_2·2THF were suspended and partly dissolved in 15 ml of THF. 1.20 ml (11.39 mmol) of Hacac and 1 ml of water were added. The reaction mixture was stirred for 5 d at ambient temperature. Crystals were grown from the mother liquor at room temperature over a period of several weeks. After decanting the covering liquid phase, In(acac)Br_2·2THF was isolated in 80% yield (2.82 g) as a colourless crystalline solid which was dried in vacuo. Results of the single crystal analysis are summarised in Tables 1 and 3.

Colourless crystalline solid; m.p. 81–82 °C.

^{1}H-NMR (200.1 MHz, CD_3CN): $\delta = 5.58$ (s, 1H, CCHC(acac)); 3.78 (m, 8H, CH_2O (THF)); 2.00 (s, 6H, CCH_3 (acac)); 1.82 (m, 8H, CH_2 (THF)).

$^{13}C\{^1H\}$-NMR (50.3 MHz, CD_3CN): $\delta = 196.7$ (s, C = O); 101.8 (s, C = OCHC = O); 69.6 (s, CH_2O(THF)); 28.5 (s, CH_3C); 25.9 (s, CH_2(THF)).

EIMS 20 eV (110 °C), *m/z* (rel. int.): 374 $[C_5H_7Br_2InO_2]^+$ (38); 359 $[C_4H_4Br_2InO_2]^+$ (20); 313 $[C_{10}H_{14}InO_4]^+$ (6); 293 $[C_5H_7BrInO_2]^+$ (100); 275 $[Br_2In]^+$ (9); 214 $[C_5H_7InO_2]^+$ (7); 199 $[C_4H_4InO_2]^+$ (6); 115 $[In]^+$ (42); 72 $[C_4H_8O]^+$ (46).

Anal. Calc. for $C_{13}H_{23}Br_2InO_4$: C, 30.2; H, 4.5; Br, 30.9; In, 22.2%. Found: C, 29.8; H, 4.6; Br, 30.6; In, 22.1%.

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[28] Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 196920 for In(C_6F_5)Br_2·2THF and CCDC 196919 for In(acac)Br_2·2THF. Copies of the data can be obtained, free of charge, on application to CCDC, 13 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1323-336033 or e-mail: deposit@ccdc.cam.ac.uk).