Molecular structure of the unusual tris(tribromoindate)methane anion, $[HC(InBr_3)_3]^{3-}$

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The title molecule, which is obtained as the tetraphenylphosphonium salt following the reaction of InBr and $HCBr_3$, is shown to involve pseudo-tetrahedral carbon and indium(III) sites; it is a member of a series of related $[H_{4-n}C(InBr_3)_n]^{n-}$ anions.

There is increasing interest in the synthesis and structural investigation of complexes in which metal atoms cluster around a centre which may be metallic or non-metallic. Schmidbaur[1] has reviewed his extensive work on molecules in which $[(R_3P)Au]^+$ and similar gold(I) cations are bonded to a large variety of such centres, and has emphasized the important isolobal relationship between LAu^+ and the H^+ and R^+ cations.[2]

In earlier papers, the reactions of indium(I) halides (InX, X = Cl, Br, I) with halogenomethanes were shown to proceed *via* oxidative addition to give neutral derivatives of X_2InCH_2X and $X_2InCH_2InX_2$ and the anionic complexes $[X_3InCH_2X]^-$ and $[H_2C(InX_3)_2]^{2-}$ have also been reported, although not for all X.[3,4] We have now prepared the salt $[PPh_4]_3[HC(InBr_3)_3]$, and established its structure. The room temperature reaction between InBr and $CHBr_3$ (1 : 3 mole ratio, mmol quantities) in 1,4-dioxane (diox) gave, on work-up, a colourless solid, shown to be the 1 : 1 adduct $Br_2InCHBr_2$·diox. (Calc. for $C_5H_9O_2$-Br_4In, In 21.4. Found: In 21.2%) ^1H NMR $[(CD_3)_2SO]$ δ 5.36 (s, 1 H, CH), 3.60 (m, 8 H, diox). ^{13}C NMR $[(CD_3)_2SO]$ δ 37.31 (CH), 67.77 (diox). This was redissolved in dioxane and treated with 2 equiv. of InBr, to give an oil, which was dissolved in acetonitrile; addition of PPh_4Br, concentration and crystallization from MeCN–ethanol gave $[PPh_4]_3[HC(InBr_3)_3]$ **1** in 84% yield.† It seems very probable that the reaction proceeds by successive oxidative additions, with the related $Br_2InCHBr_2$ and $(Br_2In)_2CHBr$ species as intermediates.

The structure of the anion of **1** is shown in Fig. 1.‡ The In–Br bond distances are similar to those for other inorganic and organometallic compounds of indium(III) [*e.g.* $InBr_4^-$, r = 2.479(2);[5] $Br_3InCH_2PPh_3$, r = 2.512(2);[3] Br_3InCH_2(tmtu), r = 2.517(6) Å (tmtu = 1,1,3,3-tetramethyl-2-thiourea)[6]], as are the In–C distances; the lengthening of the In–Br bonds relative to those in the neutral ylide adducts is ascribed to the repulsive effect of the triple negative charge on this molecule. The sum of the angles in a tetrahedral MX_4 molecule is 657°, and in the present case the corresponding sums at the three indium atoms are 655.1, 655.5 and 654.4°, respectively, so that these are pseudo-tetrahedral sites, as in the molecules previously noted. The In–C–In angles lead to a similar conclusion for the carbon atom of this molecule.

This anion can be regarded as a member of the series $[H_{4-n}C(InBr_3)_n]^{n-}$. The salts of $H_3CInX_3^-$ have been known for some time,[7] and crystallographic studies of $[H_3CInCl_3]^-$ and $[C_2H_5InI_3]^-$ have confirmed the pseudo-tetrahedral symmetry at metal and carbon atoms in such anions.[8,9] As noted above, the anions $[H_2C(InX_3)_2]^{2-}$ have also been prepared; the structure of the neutral adducts such as (tmen)$Cl_2InCH_2InCl_2$-(tmen) (tmen = N,N,N',N'-tetramethylethanediamine) demonstrates the presence of the central $H_2C(InX_2)_2$ group.[10] The
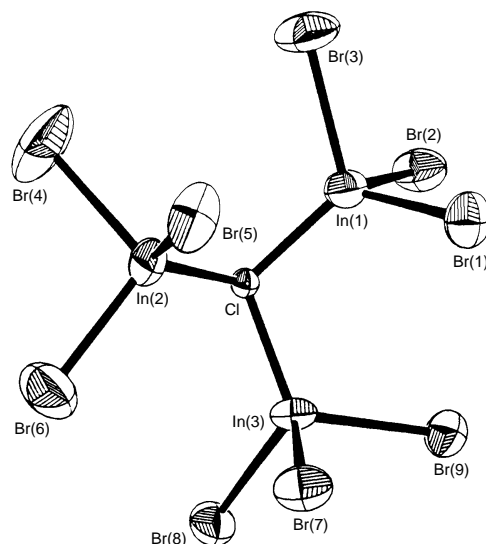
Fig. 1 Molecular structure of the $[HC(InBr_3)_3]^{3-}$ anion, showing 30% probability ellipsoids. Selected bond distances (Å) and bond angles (°): In(1)–Br (av.) 2.545, In(2)–Br (av.) 2.526, In(3)–Br(av.) 2.546, overall In–Br range 2.518(6)–2.560(5), In–C 2.11(3), 2.13(3), 2.17(3); Br–In(1)–Br (av.) 103.0, Br–In(2)–Br (av.) 104.0, Br–In(3)–Br 102.1, overall range 98.9 (2)–106.92(2), In–C–In 115(2), 112(1), 113(1).

series is therefore complete except for n = 4; work on this is proceeding.

It seems probable that similar series can be prepared with other metallo-ligands of main group elements. In particular, some members of the series of tin compounds $H_{4-n}C(SnMe_3)_n$ are already known, and analogous sets of related compounds are easily formulated, at least on paper. We also note the existence of complexes such as $[Pt(SnCl_3)_5]^{3-}$, in which the tri-chlorostannate group acts as an anionic ligand, and it could well be that analogous species with InX_3^- ligands will be accessible.

Notes and References

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† *Elemental analysis.* Calc. for $C_{73}H_{61}Br_9In_3P_3$: C 41.9; H, 2.93; Br, 34.3; In, 16.4. Found C, 41.8; H, 3.07; Br, 34.0; In, 16.0%. ^1H NMR $[(CD_3)_2SO]$ δ 8.01–7.71 (m, 60 H, C_6H_5), 0.20 (s, 1 H, In_3CH). ^{13}C NMR (CD$_3$CN) δ 135.27 [d, J(PC$_p$) 2.68 Hz], 134.41 [d, J(PC$_o$) 10.56 Hz], 130.38 [d, J(PC$_m$) 12.82 Hz], 117.57 [d, J(PC$_i$) 88.90 Hz]. No ^{13}C resonance was detected for the In_3CH atom, and this is ascribed to the immediate presence of high-spin indium atoms (^{115}In, I = 9/2); similar problems have been reported for related organoindium compounds.[3,6]

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