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# Triple-decker main group cations†

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**The syntheses of the first main group triple-decker cations are described, namely, [(η⁵-C$_5$Me$_5$)Sn(μ-η⁵-C$_5$Me$_5$)Sn(η⁵-C$_5$Me$_5$)][Ga(C$_6$F$_5$)$_4$] and [(η⁶-C$_7$H$_8$)In(μ-η⁵-C$_5$Me$_5$)In(η⁶-C$_7$H$_8$)][(C$_6$F$_5$)$_3$BO(H)B(C$_6$F$_5$)$_3$], both of which have been characterized by X-ray crystallography; the former was prepared by the reaction of Sn(η⁵-C$_5$Me$_5$)$_2$ with Ga(C$_6$F$_5$)$_3$, while the latter was prepared by treatment of [In(η⁵-C$_5$Me$_5$)]$_6$ with an equimolar mixture of B(C$_6$F$_5$)$_3$ and H$_2$O·B(C$_6$F$_5$)$_3$.**

An elegant approach to the formation of multidecker, sandwich-type anions of the heavier main group elements consists of the addition of cyclopentadienide anions to neutral metallocenes in the presence of weakly coordinating cations.[1,2] However, to our knowledge, the inverse of this approach has not been reported, *viz.* the synthesis of homonuclear multidecker p-block cations by the addition of positively charged fragments to neutral metallocenes in the presence of appropriate anions. We report two different but complementary reactions that demonstrate the viability of the latter approach.

Since it is known[3] that the reaction of Sn(η$^5$-C$_5$Me$_5$)$_2$ with a variety of acidic reagents results in salts of [Sn(η$^5$-C$_5$Me$_5$)]$^+$, it was reasoned that, in principle, this cation should be able to add to Sn(η$^5$-C$_5$Me$_5$)$_2$ to afford the desired triple decker cation [(η$^5$-C$_5$Me$_5$)Sn(μ-η$^5$-C$_5$Me$_5$)Sn(η$^5$-C$_5$Me$_5$)]$^+$ **1**$^+$. Moreover, it was recognized that the choice of the gegenion would be important, bearing in mind that (a) the anion should be weakly coordinating, and (b) the chance of obtaining a crystalline product would be maximized if the anion and cation were of comparable size. Addition of a toluene solution of Sn(η$^5$-C$_5$Me$_5$)$_2$[4] (0.38 g, 0.98 mmol) to a solution of Ga(C$_6$F$_5$)$_3$[5] (0.60 g, 1.0 mmol) in the same solvent at 0 °C resulted in a yellow precipitate which was recrystallized from hot toluene solution to afford 0.51 g (74.5% yield) of [**1**][Ga(C$_6$F$_5$)$_4$]. The positive and negative CI mass spectra for [**1**][Ga(C$_6$F$_5$)$_4$] revealed the presence of **1**$^+$ and [Ga(C$_6$F$_5$)$_4$]$^-$ ions, respectively.[6] The $^1$H, $^{13}$C and $^{119}$Sn NMR spectra[6] evidenced only one type of C$_5$Me$_5$ group and a unique Sn center thus suggesting reversible dissociation of **1**$^+$ into Sn(η$^5$-C$_5$Me$_5$)$_2$ and [Sn(η$^5$-C$_5$Me$_5$)]$^+$. Definitive structural information was provided by a low-temperature X-ray crystal structure.[7] As shown in Fig. 1, the solid state consists of **1**$^+$ and [Ga(C$_6$F$_5$)$_4$]$^-$ ions[8,9] and there are no unusually short interionic contacts. The structure of **1**$^+$ is such that a pentahapto C$_5$Me$_5$ ring serves as a bridging group for two Sn(η$^5$-C$_5$Me$_5$) units. Within experimental error, the two Sn atoms are located equidistantly from the ring centroid [X(1C)] of the μ-(η$^5$-C$_5$Me$_5$) group [2.644(19) Å] and the Sn(1)–X(1C)–Sn(2) angle is close to 180° [174.9(4)°]. The average distance from the Sn atoms to the ring centroids of the two terminal (η$^5$-C$_5$Me$_5$) rings, X(1A) and X(1B), is shorter than that to the bridging (η$^5$-C$_5$Me$_5$) moiety [2.246(18) Å] and lies between the values reported for Sn(η$^5$-C$_5$Me$_5$)$_2$ (2.396 Å)[3c] and [Sn(η$^5$-C$_5$Me$_5$)]$^+$ (2.157 Å).[3c] The X(1A)–Sn–X(1C) and X(1B)–Sn–X(1C) angles of 154.6(7) and 151.8(7)°, respectively are very similar to the values reported for Sn(η$^5$-C$_5$Me$_5$)$_2$ (av. 154.9°).[3c] An intriguing feature of the overall structure is that **1**$^+$ adopts a cis-type geometry while the triple decker anions [(η$^5$-C$_5$H$_5$)$_3$Tl$_2$]$^-$ and [(η$^5$-C$_5$H$_5$)Cs$_2$]$^-$ possess transoid arrangements.[1b,2]

A second method of triple decker cation synthesis recognized the isolobal relationship of *e.g.* [Sn(η$^5$-C$_5$H$_5$)]$^+$ and [In(η$^6$-C$_6$H$_6$)]$^+$ thus suggesting that cations of the latter type should add to In(η$^5$-C$_5$Me$_5$) units.[10] Since protolytic cleavage of In(η$^5$-C$_5$Me$_5$) in the presence of an arene solvent represented a potential source of [In(arene)]$^+$ cations, we treated In(η$^5$-C$_5$Me$_5$) (0.1 g, 0.4 mmol) with equimolar quantities (0.195 mmol each) of B(C$_6$F$_5$)$_3$[11] and the Brønsted acid H$_2$O·B(C$_6$F$_5$)$_3$[12] in toluene solution at 0 °C. The reaction mixture afforded colorless crystals (0.25 g, 70.4% yield) upon storage at −30 °C for several days. Since the product could not be characterized unambiguously on the basis of spectroscopic data,[6] an X-ray crystallographic study was undertaken.[7] The solid state (Fig. 2) consists of [(η$^6$-C$_7$H$_8$)In(μ-η$^5$-C$_5$Me$_5$)In(η$^6$-C$_7$H$_8$)]$^+$ **2**$^+$ and [(C$_6$F$_5$)$_3$BO(H)B(C$_6$F$_5$)$_3$]$^-$ ions[8] with 1.5 additional toluene molecules per asymmetric unit. There are no unusually short interionic contacts. The central core of **2**$^+$ features an η$^5$-bonded In atom on each face of the (μ-C$_5$Me$_5$)

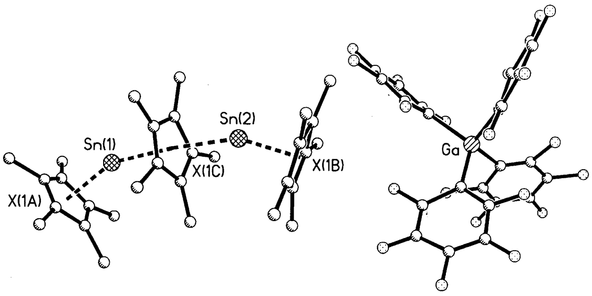

**Fig. 1** View of [**1**][Ga(C$_6$F$_5$)$_4$] with hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Sn(1)–C(1*n*) av. 2.556(18), Sn(1)–C(3*n*) av. 2.896(18), Sn(2)–C(2*n*) av. 2.540(14), Sn(2)–C(3*n*) av. 2.92(2), Sn(1)–X(1A) 2.259(18), Sn(1)–X(1C) 2.632(19), Sn(2)–X(1B) 2.232(18), Sn(2)–X(1C) 2.655(19), X(1A)–Sn(1)–X(1C) 154.6(4), Sn(1)–X(1C)–Sn(2) 174.9(4), X(1C)–Sn(2)–X(1B) 151.8(4).

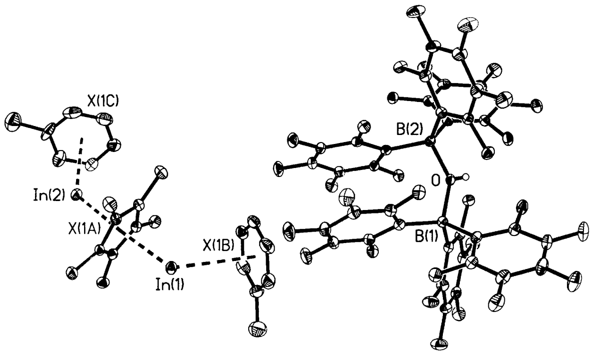

**Fig. 2** View of [**2**][(C$_6$F$_5$)$_3$BO(H)B(C$_6$F$_5$)$_3$]·1.5C$_7$H$_8$, with hydrogen atoms and non-coordinated toluene molecules omitted for clarity. Selected bond distances (Å) and angles (°): In(1)–C(1*n*) av. 2.807(3), In(1)–C(2*n*) av. 3.752(3), In(2)–C(1*n*) av. 2.722(3), In(2)–C(3*n*) av. 3.598(3), In(1)–X(1A) 2.528(4), In(1)–X(1B) 3.490(4), In(2)–X(1B) 2.435(4), In(2)–X(1C) 3.325(4), B–C av. 1.646(4), B–O av. 1.559(4); X(1A)–In(1)–X(1B) 124.4(4), In(1)–X(1A)–In(2) 176.0(4), X(1A)–In(2)–X(1C) 130.3(4).

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† Electronic supplementary information (ESI) available: summary of theoretical data. See http://www.rsc.org/suppdata/cc/b0/b005425i/

group. The In–ring centroid [X(1A)] distances of 2.528(4) and 2.435(4) Å for In(1) and In(2), respectively are longer than those reported[10] for monomeric [2.288(4) Å] and hexameric [2.302(4) Å] In(($\eta^5$-$C_5Me_5$). As in the case of $\mathbf{1}^+$, the metal–X–metal angle in $\mathbf{2}^+$ is close to linear [176.0(4)°]. The triple decker structure of $\mathbf{2}^+$ is completed by capping $\eta^6$-bonded toluene molecules. The In–ring centroid [X(1B) and X(1C)] distances of 3.490(4) and 3.325(4) Å for In(1) and In(2), respectively are considerably longer than those reported for [In(I)·2mesitylene]$^+$ (2.83 and 2.89 Å).[13] Nevertheless, it is interesting to note that, akin to $\mathbf{1}^+$, the toluene–(μ-$C_5Me_5$)–toluene moieties are distinctly bent [124.4(4) and 130.3(4)° for X(1A)–In(1)–X(1B) and X(1A)–In(2)–X(1C), respectively] and that the overall cationic geometry is cisoid.

Part of the reason for the long arene distances in $\mathbf{2}^+$ may relate to the fact that the net +1 charge is delocalized over two In centers. However, the bonding in $\mathbf{2}^+$ can be interpreted in two different ways, namely (a) as a triple-decker sandwich cation or (b) a base-stabilized inverse sandwich cation. Density functional theory (DFT) optimization[14] of the model system [In(μ-$\eta^5$-$C_5H_5$)In]$^+$ predicts a $D_{5h}$ symmetric structure with a computed In–X distance of 2.515 Å, close to the value observed experimentally for $\mathbf{2}^+$. Moreover, the $\eta^6$-coordination of two benzene molecules to the [In(μ-$C_5H_5$)In]$^+$ moiety causes only a slight perturbation of the core thus lending credence to model (b). Furthermore, the benzene–In bond dissociation energy (6.6 kcal mol$^{-1}$) suggests a very weak interaction. In sharp contrast, calculations on [($\eta^5$-$C_5H_5$)Sn(μ-$\eta^5$-$C_5H_5$)Sn($\eta^5$-$C_5H_5$)]$^+$ as a model for $\mathbf{1}^+$ predict a much more tightly bonded triple-decker sandwich environment—the weakest bond (36.6 kcal mol$^{-1}$) being that between [($\eta^5$-$C_5H_5$)Sn($\eta^5$-$C_5H_5$)] and [Sn($\eta^5$-$C_5H_5$)]$^+$ fragments. Thus the ($C_5Me_5$) acidolysis methodology may be used to prepare isolobally related compounds with very different properties. We are currently investigating the utility of this technique for the synthesis of larger sandwich, cluster and mixed-metal compounds.

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5 $Ga(C_6F_5)_3$ was prepared by a similar procedure to that described by K. Ludovici, W. Tyrra and D. Naumann, *J. Organomet. Chem.*, 1992, **441**, 363. We have determined the X-ray crystal structure of $Ga(C_6F_5)_3$·THF; pertinent data have been deposited at the Cambridge Crystallographic Data Centre (file no. CCDC-137250).

6 [**1**][$Ga(C_6F_5)_4$] (74.5% yield, mp >250 °C). HRMS: calc. for $C_{30}H_{45}Sn_2$, *m/z* 641.155; found, 641.155. NMR ($CD_2C1_2$): $^1$H, $\delta$ 2.07 [s, 45 H, $\eta^5$-$C_5Me_5$, $J$($^{119}$Sn–$^1$H) 27 Hz]. $^{13}$C, $\delta$ 10.2 [s, $\eta^5$-$C_5(CH_3)_5$] 121.0 [s, $\eta^5$-$C_5(CH_3)_5$]. $^{19}$F, $\delta$ −119.8 (s, *o*-$C_6F_5$), −155.4 (s, *p*-$C_6F_5$), −160.7 (s, *m*-$C_6F_5$). $^{119}$Sn, $\delta$ −2112. Anal. calc. for $C_{54}H_{45}F_{20}GaSn_2$: C, 46.95; H, 3.26. Found: C, 45.61; H, 3.25. [**2**][$(C_6F_5)_3BO(H)B(C_6F_5)_3$]·1.5$C_7H_8$ (70.4% yield, mp 87 °C). HRMS: calc. for $C_{10}H_{15}In$, *m/z* 364.925; found, 364.924. NMR ($C_6D_6$): $^1$H: $\delta$ 1.494 (s, 15H, $\eta^5$-$C_5Me_5$), 2.091 (s, 6H, Ph*Me*), 2.092 (s, 6H, Ph*Me*), 6.9–7.0 (m, 8H, free *o*- and *m*-Tol), 7.02–7.04 (m, 2H, free *p*-Tol), 7.09–7.12 (m, 8H, bound *o*- and *m*-Tol), 7.12–7.13 (m, 2H, bound *p*-Tol), $^{13}$C, δ 9.63 [s, $\eta^5$-$C_5(CH_3)_5$], 21.36 (s, Ph*Me*), 116.72 [s, $\eta^5$-$C_5(CH_3)_5$], 125.64 (s, *p*-Tol), 128.51 (s, *m*-Tol), 129.28 (s, *o*-Tol), 137.85 (s, *ipso*-Tol). $^{19}$F: $\delta$ −134.35 (d, $^2J_{FF}$ 17.4 Hz, *p*-$C_6F_5$), −158.16 (‘t’, $^2J_{FF}$ 20.9 Hz, *p*-$C_6F_5$), (m, *m*-$C_6F_5$). $^{11}$B: $\delta$ −9.95. Anal. Calc. for $C_{70.5}H_{44}B_2F_{30}In_2O_1$: C, 48.99; H, 2.57. Found: C, 49.66; H, 2.86%.

7 *Crystal data*: for [**1**][$Ga(C_6F_5)_4$]: $C_{54}H_{45}F_{20}GaSn_2$, monoclinic, space group *Cc*, yellow prisms, $a$ = 22.147(4), $b$ = 15.092(3), $c$ = 17.352(4) Å, $\beta$ = 115.11(3)°, $V$ = 5252(2) Å$^3$, $Z$ = 4, $D_c$ = 1.747 g cm$^{-3}$, $\mu$(Mo-Kα) = 1.561 mm$^{-1}$, $R_1$ = 0.063, $wR_1$ = 0.0823, GOF = 1.344. For [**2**][$(C_6F_5)_3BO(H)B(C_6F_5)_3$]·1.5$C_7H_8$: $C_{70.5}H_{44}B_2F_{30}In_2O_1$, monoclinic space group, $P2_1/c$, colorless blocks, $a$ = 16.042(3), $b$ = 20.771(4), $c$ = 21.165(4) Å, $\beta$ = 107.74(3)°, $V$ = 6717(2) Å$^3$, $Z$ = 4, $D_c$ = 1.693 g cm$^{-3}$, $\mu$ (Mo-Kα) = 0.814 mm$^{-1}$, $R_1$ = 0.0411, $wR_1$ = 0.1138, GOF = 1.383. Both data sets were collected at 153 K on a Nonius-Kappa CCD diffractometer. CCDC 182/1871. See http://www.rsc.org/suppdata/cc/b0/b005425i/ for crystallographic files in .cif format.

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