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Note

Use of a smaller counterion results in an ‘inverse sandwich’ diindium cation

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Dedicated to Professor Jerry Atwood in recognition of his many seminal contributions to main group and supramolecular chemistry

Abstract

Treatment of In(C_5Me_5) with [(toluene)H[[B(C_6F_5)$_4$] affords the salt [In(η^5-C_5Me_5)In][B(C_6F_5)$_4$]. X-ray analysis indicates that the cation possesses an inverse sandwich structure, one indium atom of which experiences a close contact with a *meta*-fluorine of a C_6F_5 group of a $[B(C_6F_5)_4]^-$ counterion. The other indium atom exhibits a weak η^6-interaction with a C_6F_5 group of a different $[B(C_6F_5)_4]^-$ anion.

Keywords: Indium; Cation; Pentamethylcyclopentadienyl; Tetrakis(pentafluorophenyl)borate

1. Introduction

In principle, the sandwiching of main group elements between multihapto-bonding carbocyclic rings represents a viable means of supramolecular construction. As an initial step in this direction, we recently reported the synthesis and structural assay of the first examples of triple decker main group cations, namely $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^5\text{-}C_5Me_5)Sn(\eta^5\text{-}C_5Me_5)]^+$ ($\mathbf{1}^+$) and $[(\eta^6\text{-}C_7H_8)In(\mu\text{-}\eta^5\text{-}C_5Me_5)In(\eta^6\text{-}C_7H_8)]^+$ ($\mathbf{2}^+$) [1]. Cations $\mathbf{1}^+$ and $\mathbf{2}^+$ were isolated as their $[Ga(C_6F_5)_4]^-$ and $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ salts, respectively. At the time, we pointed out that although $\mathbf{2}^+$ could be construed as a triple decker system, it could equally well be thought of as an ‘inverse sandwich’ cation. The distinction between these possibilities, of course, depends on whether the capping η^6-interacting toluene molecules are considered to be bonded or not. Given the substantial indium–ring centroid distances of 3.490(4) and 3.325(4) Å for the toluene molecules in $\mathbf{2}^+$, coupled with MO calculations on a model system that indicated only very weak (ca. 7 kcal mol^{-1}) indium–arene interactions [1], we were inclined to the opinion that $\mathbf{2}^+$ is probably best viewed as an inverse sandwich cation. However, in order to gain further insight into this question, we decided to attempt replacement of the voluminous $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ anion by a counterion of more modest size.

2. Results and discussion

Treatment of two equivalents of In(η^5-C_5Me_5) [2] with one equivalent of [(toluene)H[B(C_6F_5)$_4$] in toluene solution at −78 °C resulted, after solvent removal, in a thick brown oil that contained colorless, prismatic crystals. The HRMS of the crystalline material was consistent with the cation $[In(\mu\text{-}C_5Me_5)In]^+$ and there was no indication of the presence of toluene on the basis of ^{1}H-NMR spectroscopy. Confirmation of the proposed cation structure was provided by an X-ray crystallographic study. The compound $[In(\mu\text{-}\eta^5\text{-}C_5Me_5)In][B(C_6F_5)_4]$ (**3**) crystallizes in the monoclinic

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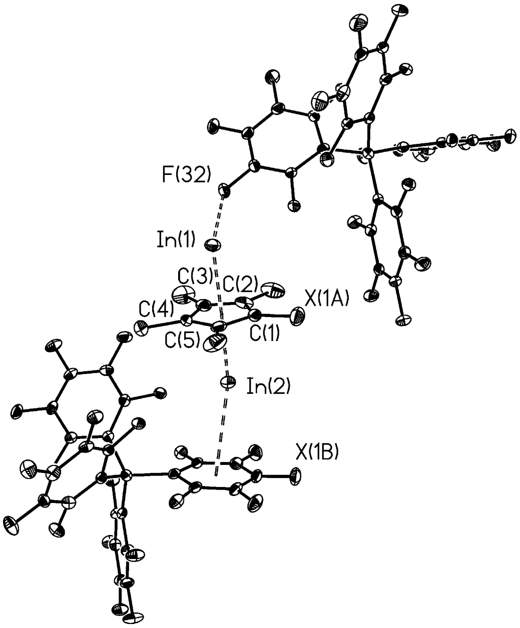

Fig. 1. View of the structure of $[In(\eta^5\text{-}C_5Me_5)In]^+$ showing the close contacts with $[B(C_6F_5)_4]^-$ anions. Important distances (Å) and angles (°): C(1)–C(2) 1.406(7), C(2)–C(3) 1.388(8), C(3)–C(4) 1.411(8), C(4)–C(5) 1.459(8), C(5)–C(1) 1.414(7), In(1)–C(1) 2.728(5), In(1)–C(2) 2.765(5), In(1)–C(3) 2.772(5), In(1)–C(4) 2.730(6), In(1)–C(5) 2.701(4), In(2)–C(1) 2.722(5), In(2)–C(2) 2.748(5), In(2)–C(3) 2.749(5), In(2)–C(4) 2.675(5), In(2)–C(5) 2.687(6); C(1)–C(2)–C(3) 110.4(5), C(2)–C(3)–C(4) 107.1(5), C(3)–C(4)–C(5) 108.5(4), C(4)–C(5)–C(1) 105.9(4), C(5)–C(1)–C(2) 108.1(5).

space group $P2_1/c$ with $Z = 8$. The structure of the cation features two In atoms that are η^5-bonded to either side of a C_5Me_5 group (Fig. 1). The In(1)–ring centroid–In(2) angle is 175.25(2)° and the In(1)–ring centroid distance (2.4603(7) Å) is slightly longer than that for In(2) (2.4350(7) Å). In turn, each of these distances is comparable to those in $\mathbf{2}^+$ which average 2.486(4) Å. All the foregoing distances are longer than those reported [2] for monomeric (2.288(4) Å) and hexameric (2.302(4) Å) $In(\eta^5\text{-}C_5Me_5)$.

The replacement of $[(C_6F_5)_3BO(H)B(C_6F_5)_3]^-$ by the smaller anion $[B(C_6F_5)_4]^-$ has the effect of 'squeezing' the toluene molecules out of $\mathbf{2}^+$ and forming $\mathbf{3}^+$. However, this leaves $\mathbf{3}^+$ in a somewhat electrophilic condition, a consequence of which is the existence of some close cation–anion contacts. Thus, a *meta*-fluorine atom [F(32)] of one C_6F_5 group of a $[B(C_6F_5)_4]^-$ anion is located 3.150(3) Å from In(1 A). Although this distance is less than the sum of van der Waals radii for In and F (3.90 Å), shorter In···F contacts have, in fact, been reported for $In(2,4,6\text{-}(CF_3)_3C_6H_2)_3$ (average 2.762(7) Å) and $In_2(2,4,6\text{-}(CF_3)_3C_6H_2)_4$ (range 2.801(10)–2.957(13) Å) [3]. Interestingly, the other indium atom of $\mathbf{3}^+$ undergoes a weak η^6-interaction with one of the C_6F_5 groups of a second $[B(C_6F_5)_4]^-$ anion; the In(2 A) to ring centroid distance is 3.588(4) Å. To our knowledge, this represents an unprecedented mode of interaction for the $[B(C_6F_5)_4]^-$ anion.

3. Experimental

All reactions were performed under a dry, oxygen-free Ar atmosphere utilizing Schlenk manifold techniques or a drybox. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded on a General Electric QE 300 spectrometer at 295 K (^{1}H 300.16 MHz) and chemical shifts are reported relative to $SiMe_4$ ($\delta = 0.00$). High-resolution mass spectra were obtained using a VG Analytical ZABZ-E mass spectrometer operating in the chemical ionization mode with methane as the ionizing gas.

3.1. Preparation of $[In(\eta^5\text{-}C_5Me_5)In][B(C_6F_5)_4]$

Two equivalents of $In(\eta^5\text{-}C_5Me_5)$ (0.648 g, 2.59 mmol) in 50 ml of $C_6H_5CH_3$ were treated with $[H(C_7H_8)][B(C_6F_5)_4]$ (1.0 g, 1.30 mmol) in 50 ml of $C_6H_5CH_3$ at −78 °C. The resulting solution was stirred at −78 °C for 2 h, after which the solvent and volatiles were removed in vacuo from the cooled (ca. −20 °C) solution leaving a dark brown, thick oil that contained a crop of colorless crystals. The product was then warmed to ambient temperature to remove any additional traces of $C_6H_5CH_3$. The yield was 39%.

3.1.1. Spectroscopic data

HRMS (CI, CH_4): Calc. for $C_{10}H_{15}In_2$, *m/z* 364.925. Found: 364.926. ^{1}H-NMR (C_6D_6): δ 1.49 (ring Me).

3.1.2. Crystal data

$C_{10}H_{15}BF_{20}In_2$, $M = 755.67$, monoclinic, space group $P2_1/c$, $a = 10.065(2)$, $b = 23.157(5)$, $c = 16.451(3)$ Å, $\beta = 103.48(3)°$, $V = 3728.7(13)$ Å^3, $D_{calc} = 2.692$ g cm^{-3}, $Z = 8$, $\lambda(\text{Mo-K}_\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}_\alpha) = 2.665$ mm^{-1}. A total of 8444 reflections was collected on a Nonius Kappa diffractometer at 153(2) K with 2θ between 7.3 and 55.0°. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to R_1 and wR_2 values of 0.0897 and 0.2281, respectively.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 192393 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033;

e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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