APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2005; **19**: 578–582
Published online in Wiley InterScience (www.interscience.wiley.com). DOI:10.1002/aoc.827

Triple-decker tin and lead cations[†]

Alan H. Cowley[1]*, Jamie N. Jones[1] and Charles L. B. Macdonald[2]

[1]Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, TX 78712, USA
[2]Department of Chemistry and Biochemistry, The University of Windsor, 401 Sunset Ave., Windsor, Ontario N9B 3P4, Canada

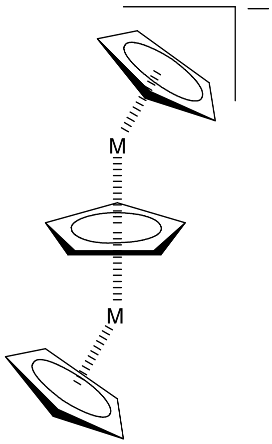
Received 2 August 2004; Revised 6 September 2004; Accepted 21 September 2004

The triple-decker cation salts [(η^5-C_5Me_5)M(μ-η^5-C_5Me_5)M(η^5-C_5Me_5)][$B(C_6F_5)_4$] (M = Sn, Pb) have been prepared by treatment of [(η^5-C_5Me_5)M][$B(C_6F_5)_4$] with the corresponding metallocenes, [M(η^5-C_5Me_5)$_2$] (M = Sn, Pb). Investigation of the structures of these triple-decker systems by X-ray crystallography revealed an overall cis-type cationic geometry. In solution, NMR studies indicate that the triple-decker cations undergo rapid, reversible dissociation. The reaction of [In(η^5-C_5Me_5)] with an equimolar quantity of $H_2O \cdot B(C_6F_5)_3$ and $B(C_6F_5)_3$] afforded [(η^6-toluene)In(μ-η^5-C_5Me_5)In(η^6-toluene)][$(C_6F_5)_3B(OH)B(C_6F_5)_3$]. Density functional theory calculations on a model system indicate that the capping toluene molecules in this di-indium cation are weakly bonded. Use of the smaller counter-ion [$B(C_6F_5)_4$]$^-$ results in isolation of the inverse sandwich cation [In(μ-η^5-C_5Me_5)In]$^+$.

KEYWORDS: germanium; tin; lead; indium; cations; structures

INTRODUCTION

This overview is a brief account of our efforts that are directed toward the assembly of new materials in which main group elements are interposed between stacks of aromatic ligands. The first step in this direction is to learn how two main group elements can be inserted between three aromatic ring systems. Interestingly, only two such triple-decker systems have been reported, namely the dithallium (**1**)[1] and dicesium (**2**)[2] anions. Each anion is stabilized by the presence of an appropriate weakly coordinating cation. Moreover, in contrast to the triple-decker cations described below, both triple-decker anions possess a trans-type geometry.



1 (M = Tl)
2 (M = Cs)

Our entry into this field was somewhat serendipitous. For some time we have been interested in the preparation and structural assay of compounds that feature donor–acceptor bonds between Group 13 elements. The possibility of forming such bonds arises because univalent Group 13 molecules of the type RM (M = B, Al, Ga, In, Tl) exist in a singlet ground state that possesses considerable lone pair character.[3] The donor behavior of such univalent entities is evident from the observation that donor–acceptor complex formation takes place in the presence of appropriately strong Group 13 Lewis acids, such as $B(C_6F_5)_3$ and heavier congeners.[4–6] Since decamethylstannocene, Sn(η^5-C_5Me_5)$_2$ (**3**),[7] is a low-valent species that also possesses a singlet ground state, it seemed logical to explore the reactivity of this compound toward strong Lewis acids in anticipation of the formation of compounds with Group 14–Group

---

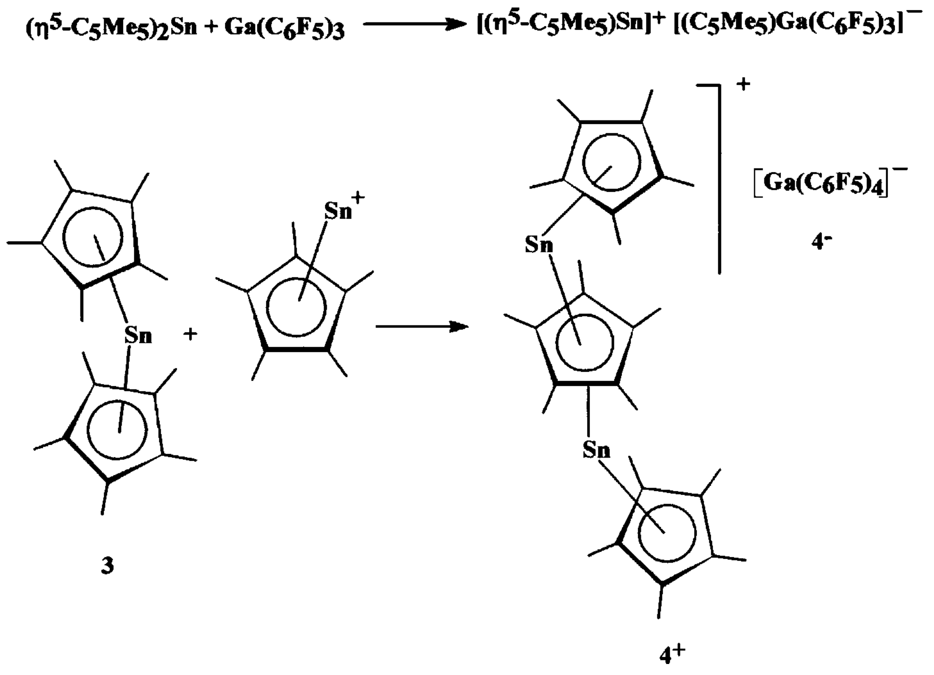
*Correspondence to: Alan H. Cowley, Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station A5300, Austin, TX 78712, USA.
E-mail: cowley@mail.utexas.edu

[†]Dedicated to the memory of Professor Colin Eaborn who made numerous important contributions to the main group chemistry.

Contract/grant sponsor: National Science Foundation; Contract/grant number: CHE-0240008.
Contract/grant sponsor: Robert A. Welch Foundation; Contract/grant number: F-135.

13 donor–acceptor bonds. However, this was not the case, and the reaction of **3** with $Ga(C_6F_5)_3$ afforded the first example of a triple-decker sandwich cation salt, $[(\eta^5\text{-}C_5Me_5)Sn(\mu\text{-}\eta^5\text{-}C_5Me_5)Sn(\eta^5\text{-}C_5Me_5)][Ga(C_6F_5)_4]$ (**4**).[8] It was hypothesized that the formation of **4** arose via initial abstraction of a $[C_5Me_5]^-$ anion to form the $[Sn(C_5Me_5)]^+$ cation, which, in turn, attacked some remaining decamethylstannocene to form $\mathbf{4}^+$, as summarized in Scheme 1. Note that the counter-anion, $[Ga(C_6F_5)_4]^-$ ($\mathbf{4}^-$), is not the one that is presumed to be formed initially, namely $[(C_5Me_5)Ga(C_6F_5)_3]^-$. Evidently, the latter anion undergoes dismutation to $\mathbf{4}^-$. Such exchange reactions are known for borate anions.[9] The X-ray structure of the triple-decker cation $\mathbf{4}^+$ is illustrated in Fig. 1. One significant feature is that the overall conformation of $\mathbf{4}^+$ is cis, as opposed to the triple-decker anions cited earlier that possess trans geometries. Another noteworthy structural aspect is that the average distance from the tin atoms to the centroid of the bridging $\pi\text{-}C_5Me_5$ ring (2.643(19) Å) is longer than that to the terminal $\pi\text{-}C_5Me_5$ ring centroids (2.245(18) Å). The implication of stronger bonding of the tin atoms to the terminal C_5Me_5 rings than to the central ring is relevant to the interpretation of the ^1H and ^{13}C NMR spectra of $\mathbf{4}^+$ (see later). The average (ring centroid) C_5Me_5 (terminal)–Sn–C_5Me_5(bridging) angle in $\mathbf{4}^+$ is 153.2(4)°.

At this point, it is worth recalling that the reaction of stannocene, $[Sn(\eta^5\text{-}C_5H_5)_2]$ (**5**), with BF_3 does not result in a triple-decker cation analogous to $\mathbf{4}^+$, but to a solid-state structure that comprises a loosely associated array of $[Sn(\eta^5\text{-}C_5H_5)_2]$, $[Sn(\eta^5\text{-}C_5H_5)]^+$, $[BF_4]^-$



Scheme 1.

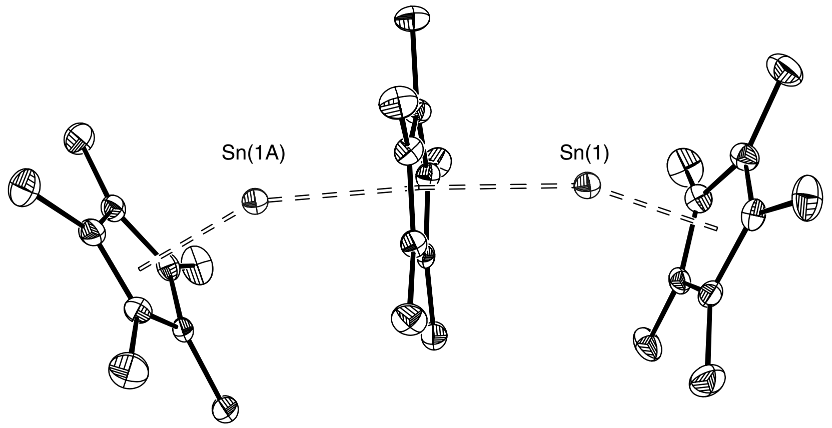
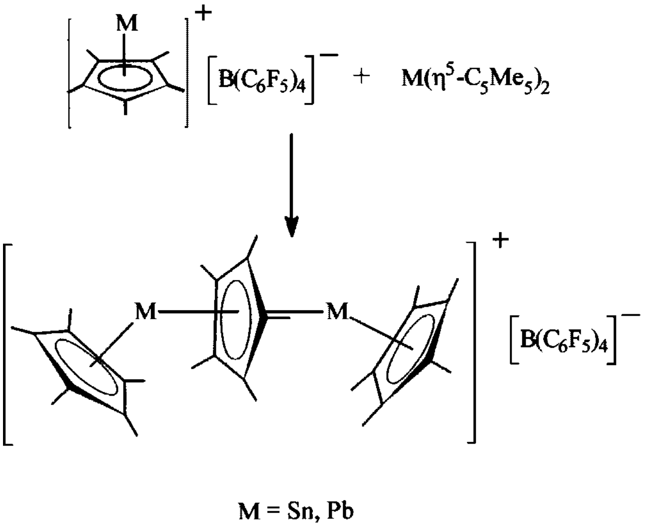


Figure 1. Overall geometry of the triple-decker cation $\mathbf{4}^+$ showing the cis-type geometry.



Scheme 2.

and tetrahydrofuran.[10] In an earlier infrared spectroscopic study, it had been concluded that the reaction of **5** with BF_3 results in the formation of a Lewis acid–base complex.[11]

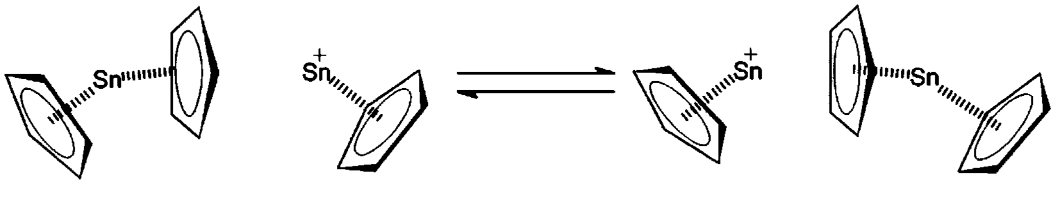
Based on the proposed reactions outlined in Scheme 1, it was clear that the development of a rational approach to the synthesis of triple-decker cations would depend on the following factors: (i) addition of appropriate positively charged fragments to neutral metallocenes; (ii) maximization of the lattice energy of the resulting triple-decker salts by matching the sizes of the cation and the anion. Another factor, albeit much more difficult to control, would be the nature and magnitudes of the various packing interactions. As shown in Scheme 2, suitable positively charged fragments are cations of the type $[M(C_5Me_5)]^+$ ($M = Ge$, Sn, Pb). Some of these cations have been reported previously as their $[BF_4]^-$ salts;[7] however, with an eye to optimizing lattice energies, it was necessary to employ the bulkier anion, $[B(C_6F_5)_4]^-$. The requisite salts $[M(\eta^5\text{-}C_5Me_5)][B(C_6F_5)_4]$ (**6** ($M = Ge$); **7** ($M = Sn$); **8** ($M = Pb$)) were easily prepared via the metathetical reactions of the chlorides $M(C_5Me_5)Cl$ with $Li[B(C_6F_5)_4]$.[12] The tin salt **7** has been prepared previously,[13] but no structural data are available. All three salts were characterized by X-ray crystallography.[12] In each case, the Group 14 element is bonded to the C_5Me_5 ring in a pentahapto fashion. However, there are close contacts between some of the fluorine atoms of the C_6F_5 groups and the Group 14 element.

Treatment of the tin and lead salts, $[M(\eta^5\text{-}C_5Me_5)][B(C_6F_5)_4]$, with decamethylstannocene (**3**)[7] and decamethylplumbocene (**9**)[14] respectively, resulted in good yields of the triple-decker cation salts $[\mathbf{4}^+][B(C_6F_5)_4]$[12] and $[Pb(\eta^5\text{-}C_5Me_5)(\mu\text{-}\eta^5\text{-}C_5Me_5)Pb(\eta^5\text{-}C_5Me_5)][B(C_6F_5)_4]$ (**10**).[12] Interestingly, we have not been able to prepare the triple-decker germanium cation so far using this method. The structure of $\mathbf{10}^+$ is very similar to that of $\mathbf{4}^+$, with respect to conformation and the trend in bond distances. Thus, there is an ~0.3 Å difference between the average $Pb\text{–}C_5Me_5$ terminal ring centroid distance (2.339 Å) and the average $Pb\text{–}C_5Me_5$ (bridging) ring centroid distance (2.672 Å). The average C_5Me_5(terminal)–Pb–C_5Me_5 (bridging) angle of 152.6° is virtually identical to that in the tin analogue $\mathbf{4}^+$.

The ^1H and ^{13}C NMR spectra of $\mathbf{4}^+$ and $\mathbf{10}^+$ both exhibit single peaks down to $-80\,°C$, thus implying a facile exchange process that renders the terminal and bridging C_5Me_5 groups equivalent. As pointed out earlier, for both triple-decker cations the metal–C_5Me_5 ring centroid distances are shorter for the terminal rings than for the bridging ring, thus suggesting that the bridging Me_5C_5–metal bonds are weaker than those to the terminal rings. This view was confirmed by density functional theory (DFT) calculations on the model triple-decker cation $[(\eta^5\text{-}C_5H_5)Sn(\mu\text{-}\eta^5\text{-}C_5H_5)Sn(\eta^5\text{-}C_5H_5)]^+$, which revealed that the tin to bridging C_5H_5 group bond energy is modest (36.6 kcal mol^{-1}).[8] Accordingly, it is suggested that the exchange process takes place as represented in Scheme 3, recognizing, of course, that the $[Sn(\eta^5\text{-}C_5H_5)]^+$ cation can become attached to either of the C_5H_5 rings of the neutral stannocene. The facile exchange process postulated in Scheme 3 also explains our inability to isolate triple-decker systems in which the two metals differ. Some of the attempts to prepare such cations are summarized in Equations (1)–(3), along with the outcomes of these experiments.[12] Note that the equations are unbalanced because, at this stage, all of the products have not been identified.

$$\underset{\mathbf{7}}{[\mathrm{Sn}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{B(C_6F_5)_4}]} + \mathrm{Ge}(\eta^5\text{-}\mathrm{C_5Me_5})_2 \longrightarrow \underset{\mathbf{6}}{[\mathrm{Ge}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{B(C_6F_5)_4}]} \quad (1)$$

$$\underset{\mathbf{7}}{[\mathrm{Sn}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{B(C_6F_5)_4}]} + \underset{\mathbf{9}}{\mathrm{Pb}(\eta^5\text{-}\mathrm{C_5Me_5})_2}$$

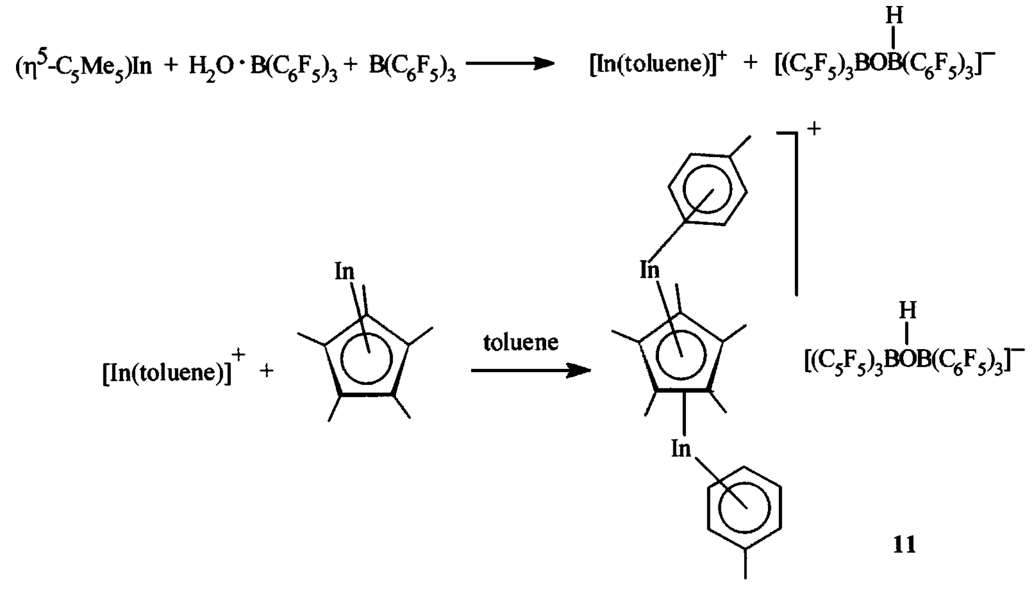


Scheme 3.

$$\longrightarrow [(\eta^5\text{-C}_5\text{Me}_5)\text{Pb}(\mu\text{-}\eta^5\text{-C}_5\text{Me}_5)\text{Pb}(\eta^5\text{-C}_5\text{Me}_5)][\text{B}(\text{C}_6\text{F}_5)_4] \quad \underset{\mathbf{10}}{} \qquad (2)$$

$$[\text{Sn}(\eta^5\text{-C}_5\text{Me}_5)][\text{B}(\text{C}_6\text{F}_5)_4] + \text{Mg}(\eta^5\text{-C}_5\text{Me}_5)_2$$
$$\mathbf{7}$$
$$\longrightarrow [(\eta^5\text{-C}_5\text{Me}_5)\text{Sn}(\mu\text{-}\eta^5\text{-C}_5\text{Me}_5)\text{Sn}(\eta^5\text{-C}_5\text{Me}_5)][\text{B}(\text{C}_6\text{F}_5)_4] \quad [\mathbf{4}^+][\text{B}(\text{C}_6\text{F}_5)_4] \qquad (3)$$

Although strictly outside the purview of a conference on germanium, tin and lead chemistry, it is worth exploring the consequences of extending the investigation of Group 14 triple-decker cations to include analogous Group 13 systems. In order to do this, it is necessary, first, to recognize the isoelectronic relationships between the cations $[\text{M}(\text{C}_5\text{R}_5)]^+$ (M = Ge, Sn, Pb) and $[\text{M}(\text{C}_6\text{R}_6)]^+$ (M = Ga, In, Tl). Stated differently, the requisite capping groups for Group 13 triple-decker cations need to be arenes. Accordingly, the strategy for synthesizing a Group 13 triple-decker cation was to generate a solvated In^+ cation for electrophilic attack of the $[\text{In}(\eta^5\text{-C}_5\text{Me}_5)]$ monomer, the process being completed by η^6-coordination of capping toluene molecules. The overall process is outlined in Scheme 4. Evident from this scheme is the necessity of treating $\text{In}(\eta^5\text{-C}_5\text{Me}_5)$ (which exists as a weakly bound hexamer in the solid state)[15] with an equimolar mixture of the Brønsted acid $\text{H}_2\text{O}\cdot\text{B}(\text{C}_6\text{F}_5)_3$[16] and the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene solution. The Brønsted acid is necessary for the generation of $[\text{In(toluene)}]^+$ by protolytic cleavage of $[\text{In}(\eta^5\text{-C}_5\text{Me}_5)]$. In order to have a counter-anion of sufficient size, it was thought necessary to complex $[(\text{HO})\text{B}(\text{C}_6\text{F}_5)_3]^-$, the resulting conjugate base, with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ to form the bulky anion $[(\text{C}_6\text{F}_5)_3\text{B(OH)B}(\text{C}_6\text{F}_5)_3]^-$. The crystalline material isolated from this reaction corresponded to the composition $[(\eta^6\text{-toluene})\text{In}(\mu\text{-}\eta^5\text{-C}_5\text{Me}_5)\text{In}(\eta^6\text{-toluene})][(\text{C}_6\text{F}_5)_3\text{B(OH)B}(\text{C}_6\text{F}_5)_3]$ (**11**).[8] As shown in Fig. 2, the central core of $\mathbf{11}^+$ consists of two η^5-bonded indium atoms on either side of a bridging C_5Me_5 group at an average In–ring centroid distance of 2.481(4) Å. The In–ring centroid–In angle is essentially linear (176.0(4)°). In turn, each indium atom is capped by an η^6-bonded toluene molecule. In the sense that the overall geometry of $\mathbf{11}^+$ is cis, there is clearly a resemblance between the indium triple-decker sandwich cation and the tin and lead triple-decker cations, $\mathbf{4}^+$ and $\mathbf{10}^+$. However, the trend in metal–ring distances is opposite, because for $\mathbf{11}^+$ the indium–ring centroid distances are considerably shorter for the bridging C_5Me_5 ring (av. 2.481(4) Å) than for the terminal toluene rings (av. 3.407(4) Å). Moreover, these arene–indium distances for $\mathbf{11}^+$ are much longer than those reported for $[\text{In}(1)\cdot 2 \text{ mesitylene}]^+$ (av. 2.86 Å),[17,18] indicating that the toluene molecules are very weakly bound. This view is supported by DFT calculations on the model system $[(\eta^6\text{-C}_6\text{H}_6)\text{In}(\mu\text{-}\eta^5\text{-C}_5\text{H}_5)\text{In}(\eta^6\text{-C}_6\text{H}_6)]^+$, which indicate that the binding energy of the benzene molecules to the $[\text{In}(\mu\text{-}\eta^5\text{-C}_5\text{H}_5)]^+$ core is only 6.6 kcal mol^{-1}. Thus, an alternative way of thinking about $\mathbf{11}^+$ is to view it as the first example of a weakly solvated inverse sandwich cation rather than as a triple-decker cation. Examination of Fig. 3 shows that the anion $\mathbf{11}^-$ is considerably larger than cation $\mathbf{11}^+$. Accordingly, it was thought that replacement of the voluminous anion $\mathbf{11}^-$ by the smaller anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ might have the effect of 'squeezing out' the weakly coordinated η^6-toluene molecules from $\mathbf{11}^+$, thereby forming the inverse sandwich salt $[\text{In}(\eta^5\text{-C}_5\text{Me}_5)\text{In}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**12**). Indeed, this is the case (Fig. 3).[19] The In–C_5Me_5 ring centroid–In angle in $\mathbf{12}^+$ (175.25(2)°) is similar to that in $\mathbf{11}^+$ (176.0(4)°), as are the average indium–ring centroid angles (2.4976(7) Å and



Scheme 4.

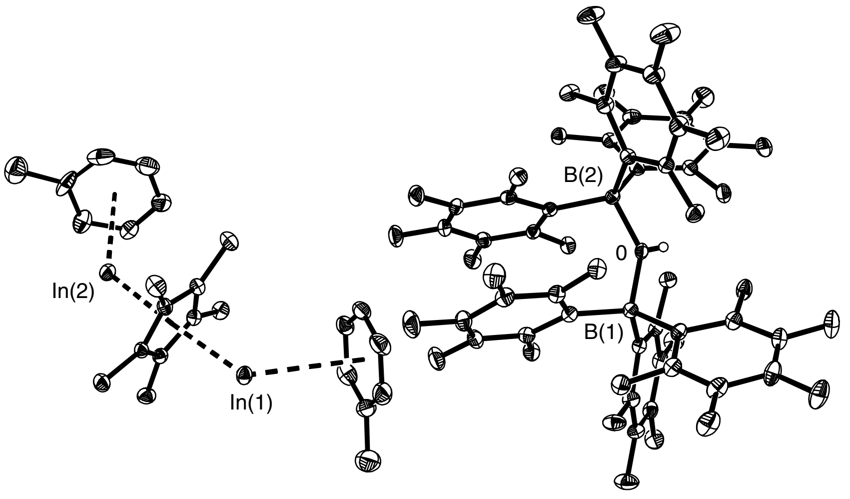


Figure 2. View of the structure of [(η^6-toluene)In(μ-η^5-C_5Me_5)In(η^6-toluene)][$(C_6F_5)_3B(OH)B(C_6F_5)_3$] (**11**) with hydrogen atoms omitted for clarity.

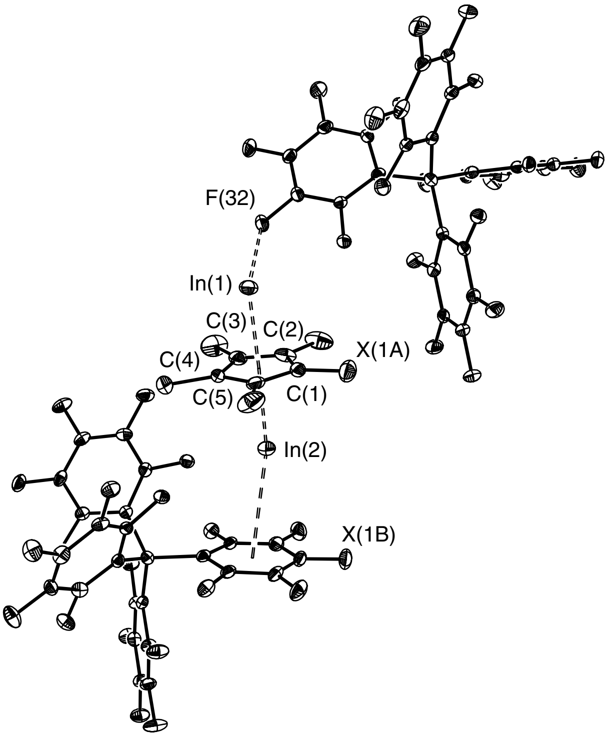


Figure 3. View of the structure of [In(η^5-C_5Me_5)In]$^+$ showing the close contacts with [$B(C_6F_5)_4$]$^-$ anions.

2.486(4) Å in **12**$^+$ and **11**$^+$ respectively). Thus, the presence or absence of the capping toluene molecules has very little effect on the metrical parameters of the inverse sandwich cation, **11**$^+$. However, note that when the toluene molecules are removed there is a short contact with a meta fluorine of one C_6F_5 group of a [$B(C_6F_5)_4$]$^-$ anion and a weak η^6-interaction with one of the C_6F_5 groups of a second [$B(C_6F_5)_4$]$^-$ anion.

Acknowledgements

We are grateful to the National Science Foundation (grant CHE-0240008) and the Robert A. Welch Foundation (grant F-135) for financial support.

REFERENCES

1. Armstrong DR, Edwards AJ, Moncrieff D, Paver MA, Raithby PA, Rennie MA, Russell CA, Wright DS. *J. Chem. Soc. Chem. Commun.* 1995; 927.
2. Harder S, Prosenc MH. *Angew. Chem. Int. Ed. Engl.* 1996; **35**: 97.
3. Macdonald CLB, Cowley AH. *J. Am. Chem. Soc.* 1999; **121**: 12 113.
4. Gorden JD, Voigt A, Macdonald CLB, Silverman JS, Cowley AH. *J. Am. Chem. Soc.* 2000; **122**: 950.
5. Gorden JD, Macdonald CLB, Cowley AH. *Chem. Commun.* 2001; 75.
6. Hardman NJ, Power PP, Gorden JD, Macdonald CLB, Cowley AH. *Chem. Commun.* 2001; 1866.
7. Jutzi P, Kohl F, Hofmann P, Krüger C, Tsay Y-H. *Chem. Ber.* 1980; **113**: 757.
8. Cowley AH, Macdonald CLB, Silverman JS, Gorden JD, Voigt A. *Chem. Commun.* 2001; 175.
9. Dioumaev VK, Harrod JF. *Organometallics* 1997; **16**: 2798.
10. Dory TS, Zuckerman JJ, Barnes CL. *J. Organometal. Chem.* 1985; **281**: C1.
11. Harrison PG, Zuckerman JJ. *J. Am. Chem. Soc.* 1970; **92**: 2577.
12. Jones JN. PhD dissertation, The University of Texas at Austin, 2004.
13. Rhodes B, Chien JCW, Rausch MD. *Organometallics* 1998; **17**: 1931.
14. Atwood JL, Hunter WE, Cowley AH, Jones RA, Stewart CA. *J. Chem. Soc. Chem. Commun.* 1981; 925.
15. Beachley Jr OT, Blom R, Churchill MR, Faegri K, Fettinger JC, Pazik JC, Victoriano L. *Organometallics* 1989; **8**: 346.
16. Doerrer LH, Green MLH. *J. Chem. Soc. Dalton Trans.* 1999; 4325.
17. Ebenhöch J, Müller G, Riede J, Schmidbaur H. *Angew. Chem. Int. Ed. Engl.* 1984; **23**: 386.
18. Schmidbaur H. *Angew. Chem. Int. Ed. Engl.* 1985; **24**: 893.
19. Jones JN, Macdonald CLB, Gorden JD, Cowley AH. *J. Organometal. Chem.* 2003; **666**: 3.