

This article was downloaded by:

On: 29 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

### Anion inclusion within the cavity of $\pi$ -metalated *p-t*-butylcalix[5]arene

Jonathan W. Steed<sup>a</sup>; Carl P. Johnson<sup>a</sup>; Ravindra K. Juneja<sup>b</sup>; Jerry L. Atwood<sup>a</sup>; Robert S. Burkhater<sup>b</sup>

<sup>a</sup> Department of Chemistry, University of Missouri-Columbia, Columbia, MO, USA <sup>b</sup> Department of Chemistry, University of Alabama, Tuscaloosa, AL, USA

**To cite this Article** Steed, Jonathan W. , Johnson, Carl P. , Juneja, Ravindra K. , Atwood, Jerry L. and Burkhater, Robert S.(1996) 'Anion inclusion within the cavity of  $\pi$ -metalated *p-t*-butylcalix[5]arene', *Supramolecular Chemistry*, 6: 3, 235 – 238

**To link to this Article:** DOI: 10.1080/10610279608032540

**URL:** <http://dx.doi.org/10.1080/10610279608032540>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

COMMUNICATION

# Anion inclusion within the cavity of $\pi$ -metalated *p-t*-butylcalix[5]arene

JONATHAN W. STEED<sup>1</sup>, CARL P. JOHNSON<sup>1</sup>, RAVINDRA K. JUNEJA<sup>2</sup>, JERRY L. ATWOOD<sup>1\*</sup> and ROBERT S. BURKHALTER<sup>2</sup>

<sup>1</sup>Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211 (USA) and <sup>2</sup>Department of Chemistry, University of Alabama, Tuscaloosa, AL 35487 (USA)

(Received February 1, 1995)

The X-ray crystal structure of the triridium *p-t*-butylcalix[5]arene host molecule  $[\{\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\}_3(p\text{-}t\text{-butylcalix[5]arene-H)}][\text{BF}_4]_5$  5 reveals the deep inclusion of one of the  $\text{BF}_4$  anions within the bowl shaped cavity of the macrocycle.

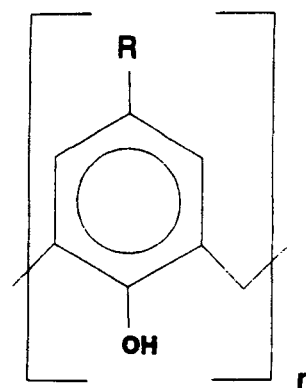
## INTRODUCTION

The complexation of anions by non-covalent interactions is a relatively unexplored field of endeavor in comparison with the extensive range of cation binding hosts such as crown ethers,<sup>1,2</sup> cryptands,<sup>3</sup> calixarenes<sup>4-7</sup> etc. Recently however, anion binding,<sup>8-12</sup> especially by polyammonium based receptors,<sup>8,13,14</sup> has received considerable attention and a number of practical applications such as waste water treatment to remove phosphate contaminants<sup>15,16</sup> or inhibition of the energy producing ATP to ADP conversion<sup>17</sup> by binding the triphosphate residues of ATP can be envisaged.

Recently<sup>18,19</sup> we have reported the synthesis and complexation behavior of a new range of organometallic calix[4]arene (1a) based host molecules designed to bring about the complexation of anionic guests within the bowl shaped calixarene cavity by electrostatic interactions with the partial positive charge associated with  $\pi$ -metalated phenolic residues of the macrocycle. In the case of the water-soluble tetrairidium host  $[\{\text{Ru}(p\text{-cymene)}\}_4(\text{calix[4]arene-2H})]^{6+}$  2 we have isolated a number of anion inclusion species with small anions such as  $\text{BF}_4$ ,  $\text{I}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  etc. of which the X-ray crystal structure of the  $\text{BF}_4$  salt reveals the deep penetration of the anion within the host cavity.<sup>18</sup> The analogous structure of the iodide salt reveals a more shallow penetration of an iodide ion within the calixarene cavity as a result of

the larger size of  $\text{I}^-$ .<sup>20</sup> Clearly, in order to obtain selective anion recognition, a range of host bowl shapes and sizes are necessary and we now report an extension of these studies to host molecules with larger cavities based on *p-t*-butylcalix[5]arene 1c.

Previously we have demonstrated that either two or four " $\text{Cp}^*\text{Ir}^{2+}$ " ( $\text{Cp}^*$  = pentamethylcyclopentadienyl) moieties may be appended to the carbocyclic rings of calix[4]arene 1a to give respectively the di- and tetrairidium species  $[\{\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\}_2(\text{C}_{28}\text{H}_{20+n}\text{O}_4)]^{n+}$  ( $n = 2$ , 3a,  $n = 3$ , 3b,  $n = 4$ , 3c) and  $[\{\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\}_4(\text{C}_{28}\text{H}_{22}\text{O}_4)]^{6+}$  4. Similarly the *p-t*-butylcalix[4]arene (1b) analogues of complexes 3 may readily be prepared in excellent yield, although the *p-t*-butylcalix[4]arene

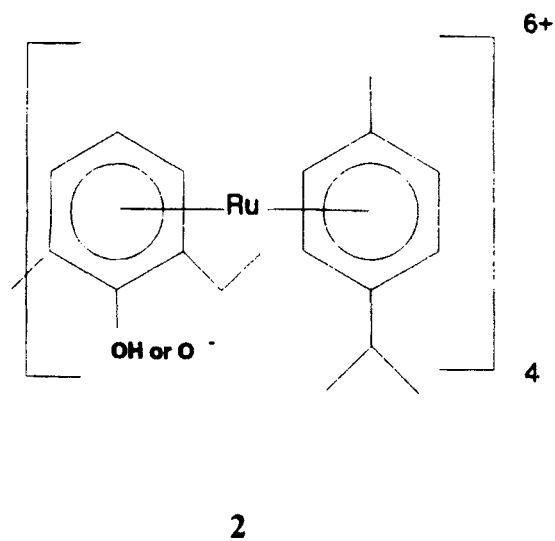


$n = 4$ ,  $\text{R} = \text{H}$  1a

$n = 4$ ,  $\text{R} = t\text{-butyl}$  1b

$n = 5$ ,  $\text{R} = t\text{-butyl}$  1c

\*To whom correspondence should be addressed.



analogue of **4** could not be synthesized possibly due to a steric crowding effect. The X-ray crystal structure of **3b**·NO<sub>2</sub>Me·Et<sub>2</sub>O (as the tetrafluoroborate salt) reveals that the complex exists in the cone conformation but the narrow entrance to the bowl shaped molecular cavity does not permit the ingress of any BF<sub>4</sub> anion. Instead the host is occupied by a diethyl ether guest molecule.

Treatment of excess  $\{[\text{Ir}(\text{Cp}^*)\text{Cl}(\mu\text{-Cl})]_2\}^{21}$  with Ag[BF<sub>4</sub>] in acetone followed by refluxing for 24 h. with **1c** resulted (after recrystallisation from CH<sub>3</sub>NO<sub>2</sub>/Et<sub>2</sub>O) in the isolation of the triiridium species  $\{[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)\}_3(\text{C}_{55}\text{H}_{69}\text{O}_5)[\text{BF}_4]_5 \cdot 0.5\text{CH}_3\text{NO}_2 \cdot n\text{Et}_2\text{O}$  **5** ( $n \approx 2$ ) in 71% yield, resulting from the metalation of three of the five carbocyclic rings and loss of one of the phenolic protons from the lower rim of the calixarene. This enhanced acidity upon metalation has been noted previously for complexes **2-4** and various organometallic phenol species.<sup>19,22</sup> The nuclearity of the complex was confirmed by a FAB mass spectrum which showed a clear molecular ion peak at  $m/z$  1964 (the cation in **5** in association with two BF<sub>4</sub> anions) along with major fragmentation peaks associated with the loss of one and two BF<sub>4</sub> ions and also loss of one Cp\*Ir unit. The <sup>1</sup>H NMR spectrum of this material was consistent with the proposed formulation exhibiting two resonances arising from the Cp\* protons in the ratio of 2:1. In the high field region fourteen singlet signals were observed, arising from the aromatic ring protons and the phenolic hydroxyl functionalities suggesting that the two halves of the molecule are magnetically unique in solution, possibly as a consequence of the deprotonation of only one of the hydroxyl functionalities. Addition of a small quantity of D<sub>2</sub>O to the NMR tube resulted in a reduction in intensity of four of these signals to give a pattern consistent with that expected for the ring protons alone. The NMR data are insufficient to distinguish between the two possible

isomers of **5** (either rings A, C and D or rings A, B and C may be metalated) but it seems likely that the cationic metal centers will be as widely separated as possible (as in the case of complexes **3**) which would favor the ACD isomer.

The supramolecular chemistry of **5** was investigated by X-ray crystallography.<sup>23</sup> The structure of **5** is shown in Fig. 1 along with the atom numbering scheme adopted. The structure consists of a *p-t*-butylcalix[5]arene monoanion with two adjacent rings (C and D) bound to Cp\*Ir moieties as well as the distal ring, A. There are three types of supramolecular interactions in the structure: i) inclusion of nitromethane in a disordered fashion along the crystallographic twofold rotation axis, ii) inclusion of a large amount of disordered diethyl ether in the pocket formed at the base of the molecule by the protrusion of the Cp\* methyl groups below the lower rim of the calixarene and, most importantly, iii) the incorporation of one of the BF<sub>4</sub> anions within the large bowl shaped cavity of the metalated host. The anionic guest is situated in proximity to the metalated pair of phenolic residues (C and D) with shortest F...C contacts F(2A)-C(3C) 2.93 Å and F(3A)-C(1D) 3.09 Å, based on the rigid group refinement adopted for the BF<sub>4</sub> anion. These distances are consistent with those observed for **2** (2.85, 2.86, 3.06 and 3.11 Å<sup>18</sup>) in which the guest anion refined freely. The fluorine atom F(1A) penetrates most deeply into the cavity although there are no short F...C contacts; F(1A)...centroid distances for rings B and E 3.88 and 3.66 Å respectively. The rather disordered nature of the included anion contrasts with that observed for the structure of **2**<sup>18</sup> in which the guest is extremely rigidly held, and probably results from the size mismatch between the small BF<sub>4</sub> anion and the large cavity and the flat potential energy surface represented by the pair of metalated rings. This suggests that metathesis experiments may prove fruitful in which BF<sub>4</sub> is replaced by larger anions such as polyphosphates.

As observed for **3b**, the atom C(1) in each of the metalated rings is notably above the plane formed by C(2)-C(6) with a long Ir-C(1) distance of 2.52(2) Å av. compared to 2.22(2) Å av. for Ir-C(2-6), consistent with the proposed oxocyclohexadienyl nature of the coordinated phenolic fragment.<sup>22</sup> Also interestingly, the conformation of the calixarene itself is quite regular with the phenolic residues forming angles of 40.9°-81.7° with the plane containing O(1A)-O(1E). This contrasts with the structure of the parent ligand **1c** and a range of structures of *p*-sulfonatocalix[5]arene in which two rings invariably lay flatter (at an angle of *ca.* 25-35° to the plane of the phenolic oxygen atoms) while the other three are more upright (60-80°).<sup>25-27</sup> This almost certainly arises from the presence of the bulky Cp\* rings which would cause unfavorable steric interactions in a more irregular conformation.

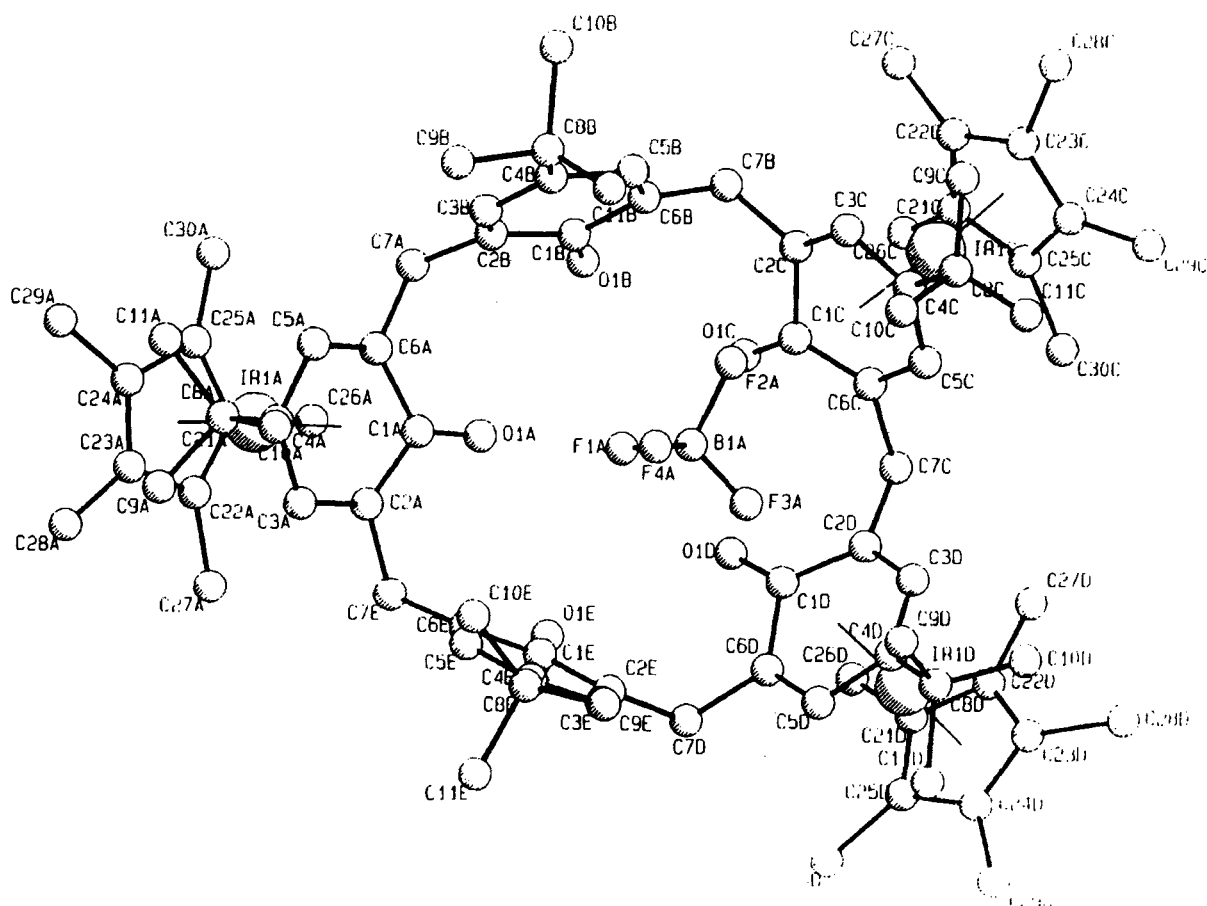


Figure 1a.

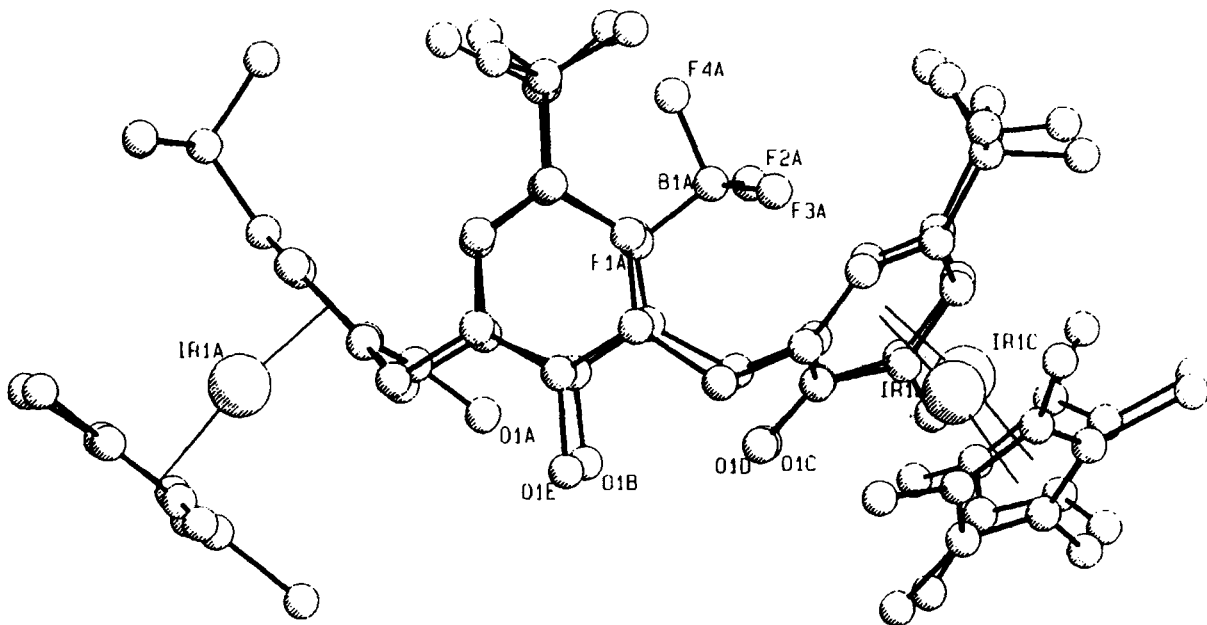


Figure 1b.

**Figure 1.** X-ray crystal structure of  $\{(\text{Ir}(\eta^5\text{-C}_5\text{Me}_5))_3(\text{C}_{55}\text{H}_{69}\text{O}_5)\}[\text{BF}_4]_5 \cdot 0.5\text{NO}_2\text{Me} \cdot n\text{Et}_2\text{O}$  ( $n = \text{ca. } 2$ ) along with the included tetrafluoroborate anion a) top view, b) side view. Selected bond lengths: Ir(A)-C(1A) 2.53(2), Ir(A)-C(2-6A) 2.22(2) av., Ir(C)-C(1C) 2.54(2), Ir(C)-C(2-6C) 2.22(2) av., Ir(D)-C(1D) 2.48(2), Ir(D)-C(2-6D) 2.23(2) Å av.

## CONCLUSION

While the poor size complementarity between  $\text{BF}_4^-$  and the calix[5]arene cavity results in less tight anion binding than that observed for calix[4]arene complexes such as **2**, this work establishes i) that anionic guests may be included in organometallic hosts in which not all the rings are metalated and ii) that anion selectivity based upon shape and size considerations may be introduced in the next generation of organometallic host molecules. It is also noteworthy that the crowding of the upper rim of the calixarene with bulky *t*-butyl groups does not prevent entry of the anion.

## ACKNOWLEDGEMENTS

We thank the US National Science Foundation for support of this work and EPSRC/NATO for the award of a research fellowship (to J.W.S.).

## REFERENCES

- Pedersen, C.J. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1021.
- Mertes, K.B.; Lehn, J.-M. "Multidentate Macrocyclic and Macropolycyclic Ligands" in *Comprehensive Coordination Chemistry*, (Eds: Wilkinson, G.; Gillard, R.; McCleverty, J.A.) Pergamon, Oxford, 1987, vol. 2, pp 915–957.
- (a) Lehn, J.-M. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 89. (b) Dietrich, B. in *Inclusion Compounds*, (Eds: Atwood, J. L.; Davies, J.E.D.; MacNicol, D.D.) Oxford University Press, Oxford, 1984, vol. 2, ch. 10.
- Atwood, J.L. in *Cation Binding by Macrocycles*, (Eds: Inoue, Y.; Gokel, G.W.) Dekker, 1991.
- Shinkai, S.; Koreshi, H.; Ueda, K.; Arimura, T.; Manabe, O. *J. Am. Chem. Soc.* **1987**, *109*, 6371.
- Bott, S.G.; Coleman, A.W.; Atwood, J.L. *J. Am. Chem. Soc.* **1986**, *108*, 1709.
- Gutsche, C.D.; Nam, K.C. *J. Am. Chem. Soc.* **1988**, *110*, 6153.
- Katz, H.E. in *Inclusion Chemistry* (Eds: Atwood, J.L.; Davies, J.E.D.; MacNicol, D.D.) Oxford University Press, Oxford, 1991, vol. 4, ch. 9, p 391. (b) Kaufmann, D.E.; Otten, A. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1832. (c) Dietrich, B. *Pure Appl. Chem.* **1993**, *65*, 1457. (d) Pierre, J.-L.; Baret, P. *Bull. Soc. Chim. Fr.* **1983**, 367.
- Brown, S.E.; Coates, J.H.; Easton, C.J.; van Eyk, S.J.; Lincoln, S.F.; May, B.L.; Stile, M.A.; Whalland, C.B.; Williams, M.L. *J. Chem. Soc., Chem. Commun.* **1994**, 47.
- Worm, K.; Schmidtchen, F.P.; Schier, A.; Schafer, A.; Hesse, M. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 327.
- Bott, S.G.; Coleman, A.W.; Atwood, J.L. *J. Am. Chem. Soc.* **1988**, *110*, 610.
- Muller, A.; Hovemeier, K.; Rohlfing, R. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1192.
- (a) Bencini, A.; Bianchi, A.; Dapporto, P.; Garcia-Espana, E.; Micheloni, M.; Paoletti, P.; Paoli, P. *J. Chem. Soc., Chem. Commun.* **1990**, 753. (b) Bencini, A.; Bianchi, A.; Dapporto, P.; Garcia-Espana, E.; Micheloni, M.; Ramirez, J.A.; Paoletti, P.; Paoli, P. *Inorg. Chem.* **1992**, *31*, 1902.
- Dietrich, B.; Lehn, J.-M.; Guilhem, J.; Pascard, C. *Tetrahedron Lett.* **1989**, *30*, 4125. (b) Boudon, S.; Decian, A.; Fischer, J.; Hosseini, M.W.; Lehn, J.-M.; Wipff, G. *J. Coord. Chem.* **1991**, *23*, 113. (c) Kimura, E.; Sakonaka, A.; Yatsunami, T.; Kodama, M. *J. Am. Chem. Soc.* **1981**, *103*, 3041. (d) Dietrich, B.; Guilhem, J.; Lehn, J.-M.; Pascard, C.; Sonveaux, E. *Helv. Chim. Acta* **1984**, *67*, 91.
- Beer, P.D.; Chen, Z.; Goulden, A.J.; Graydon, A.; Stokes, S.E.; Wear, T. *J. Chem. Soc., Chem. Commun.* **1993**, 1834.
- Rudkevich, D.M.; Brzozka, Z.; Palys, M.; Visser, H.C.; Verboom, W.; Reinhoudt, D.N. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 467.
- Knowles, J.R. *Annu. Rev. Biochem.* **1980**, *49*, 877.
- Steed, J.W.; Juneja, R.K.; Atwood, J.L. *Angew. Chem.*, in press.
- Steed, J.W.; Juneja, R.K.; Burkhalter, R.S.; Atwood, J.L. *J. Chem. Soc., Chem. Commun.* **1994**, 2205.
- Steed, J.W.; Juneja, R.K.; Atwood, J.L. unpublished work.
- Kang, J.W.; Moseley, K.; Maitlis, P.M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.
- White, C.; Thompson, S.J.; Maitlis, P.M. *J. Organomet. Chem.* **1977**, *127*, 415.
- Crystal data*: monoclinic space group C2/c,  $a = 46.388(8)$ ,  $b = 15.532(6)$ ,  $c = 31.816(6)$  Å.  $\beta = 118.380(7)^\circ$ ,  $Z = 8$ ,  $U = 20168(9)$  Å<sup>3</sup>,  $\mu(\text{Mo-K}\alpha) = 40.34$  cm<sup>-1</sup>. A total of 13096 data were collected on an Enraf-Nonius CAD4 diffractometer (2 range 4–44°, Mo-K $\alpha$ ) of which 12360 unique reflections were used in structure solution (SHELXS-86<sup>24a</sup>) and refinement according to the SHELXL-93 method.<sup>24b</sup> Full matrix least squares refinement on F<sup>2</sup> based on 843 parameters led to convergence at a  $wR_2$  value of 0.2282, corresponding to a conventional  $R$  factor of 0.067 based on 5353 reflections with  $I > 2\sigma(I)$  ( $wR_2 = 0.167$  for observed data). Heavy atoms and  $sp^3$  hybridised carbon atoms as well as the included tetrafluoroborate anion were treated anisotropically whilst an isotropic model was adopted for the remaining atoms due to the paucity of data. Hydrogen atoms were included in calculated positions for ordered carbon atoms and allowed to ride on the atoms to which they were attached. The  $\text{BF}_4^-$  anions were refined as rigid tetrahedra, in some cases disordered. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See notice to authors, issue no. 1.
- (a) Sheldrick, G.M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (b) Sheldrick, G.M. *SHELXL-93*, University of Gottingen, 1993.
- Gallagher, J.F.; Ferguson, G.; Bohmer, V.; Kraft, D. *Acta Crystallogr., Sect. C* **1994**, *50*, 73.
- Johnson, C.P.; Juneja, R.K.; Steed, J.W.; Atwood, J.L.; Clark, D.L.; Reilly, S. submitted for publication.
- Atwood, J.L.; Juneja, R.K.; Junk, P.C.; Robinson, K.D. *J. Chem. Crystallogr.* **1994**, *24*, 573.