Synthesis of bis(bora)calix[4]arenes bearing perfluoroaryl substituents†

Carl Redshaw*[a] and Mark R. J. Elsegood[b]

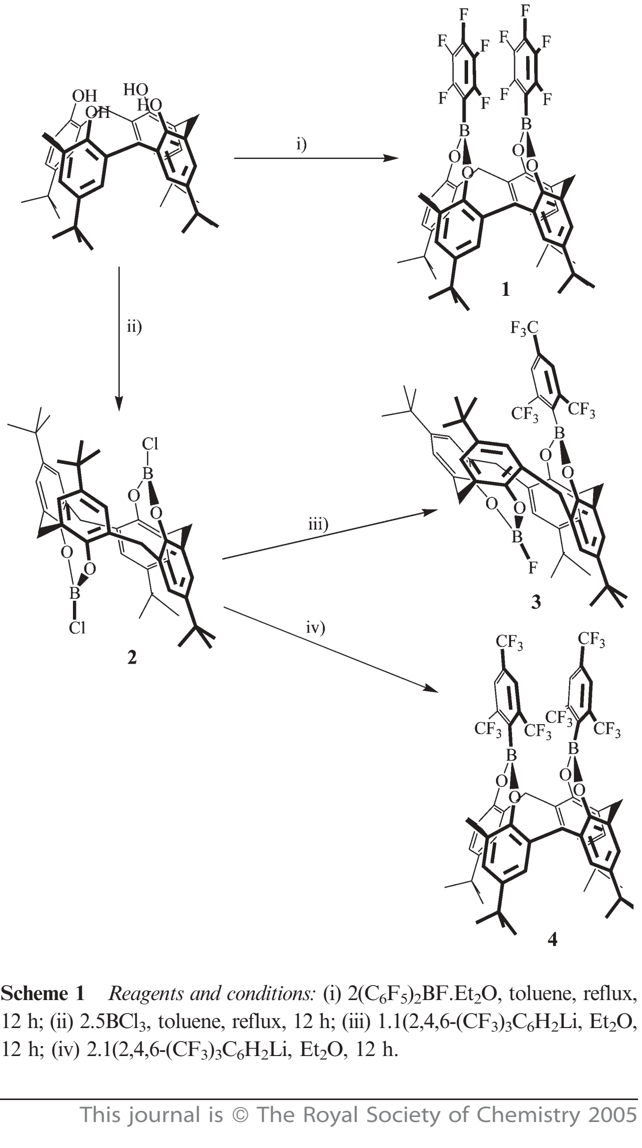
Received (in Cambridge, UK) 7th July 2005, Accepted 12th August 2005
First published as an Advance Article on the web 7th September 2005
DOI: 10.1039/b509556e

New routes to perfluoroaryl complexes of bis(bora)calix[4]-arenes are described; crystallographic and spectroscopic data are presented.

Calixarenes and their derivatives have been the focus of intense research in recent years due to their varied potential applications.[1] A significant focus of this research is their application as sensors,[2] of which a particularly attractive approach is the use of boracalixarenes as fluorescent sensors. Recent reports by Davidson *et al.*[3] and Mair *et al.*[4] have highlighted both the ease and difficulties associated with organoboron derivatisation at the lower-rim. In order to increase the scope of this field, alternative and more efficient routes to boracalixarenes are essential. In this context, we are currently investigating the coordination chemistry of bis(bora)calix[4]arenes containing bulky electron-withdrawing perfluoroaryl ligands. Here, we describe the facile synthesis and molecular structures of {[Ar^{f}B]$_2$*tert*-butylcalix[4]arene} (Ar^f = C_6F_5 **1**, 2,4,6-$(CF_3)_3C_6H_2$ **4**), together with the intermediate species {[ClB]$_2$*tert*-butylcalix[4]arene} **2** and {[2,4,6-$(CF_3)_3C_6H_2$ B]-[BF]*tert*-butylcalix[4]arene} **3**—see Scheme 1—all of which represent rare examples of boron-containing calixarene species.‡

We have prepared compound **1** by the direct reaction of *tert*-butylcalix[4]areneH$_4$ with [$(C_6F_5)_2BF\cdot Et_2O$]. Following work-up and recrystallization from acetonitrile, the complex {[(C_6F_5)B]$_2$*tert*-butylcalix[4]arene}·3MeCN (**1**·3MeCN) was obtained as colourless needles in *ca.* 60% yield. Complex **1** is presumed to form *via* loss of two molecules of both C_6F_5H and HF. In the ^{1}H NMR spectrum, the methylene groups appear as four doublets consistent with the approximate two-fold symmetry of the calixarene ligand. The ^{11}B NMR spectrum consists of a broad peak at *ca.* 27 ppm and is consistent with a three-coordinate centre bound to π-donor ligands. In the solid state (Fig. 1), **1**·3MeCN crystallises with 3 molecules of solvent (MeCN); one of these solvent molecules sits within the calix[4]arene cone with the methyl group protruding furthest into the cone.§ Each boron possesses a pseudo trigonal geometry and both are displaced from the O_4 mean plane by 0.58 Å. The boron centres are 3.448 Å apart (*cf.* 3.429 Å for phenyl derivative),[3] with the two C_6F_5 units close to being parallel [the deviation between mean planes C(45) → C(50) and C(51) → C(56) is 8.7°] with a graphitic separation [C(45)–C(51) 3.48 Å, C(54)–C(48) 3.628 Å] and are almost fully eclipsed [the torsional angle F(3)–B(1)–B(2)–F(8) is 6.8°]. However, both the C_6F_5 rings are tilted with respect to the lower-rim of the calix[4]arene molecule as defined by the O_4 mean plane [F(3)–B(1)–B(2) 81.4°; F(8)–B(2)–B(1) 99.8°]. The lack of intramolecular π–π interactions in organometallic chemistry has recently been noted.[5]

Given the tendency of reagents of the type [(Ar^f)$_2$BF.Et$_2$O] to decompose on heating,[6] an alternative approach *via* the new chloro complex {[ClB]$_2$*tert*-butylcalix[4]arene} **2** was explored. This intermediate can be easily prepared on a multi-gram scale by the addition of a slight excess of BCl_3 (2.5 equivalents) to the parent *tert*-butylcalix[4]areneH$_4$ in toluene and subsequent extraction into acetonitrile, from which it can readily be recrystallised (in *ca.* 40% yield). The solid-state structure of **2**·MeCN has been determined and reveals (Fig. 2) a rare example of a 1,2-alternate conformation



Scheme 1 *Reagents and conditions:* (i) 2$(C_6F_5)_2$BF.Et$_2$O, toluene, reflux, 12 h; (ii) 2.5BCl$_3$, toluene, reflux, 12 h; (iii) 1.1(2,4,6-$(CF_3)_3C_6H_2$Li, Et$_2$O, 12 h; (iv) 2.1(2,4,6-$(CF_3)_3C_6H_2$Li, Et$_2$O, 12 h.

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[a] *School of Chemical Sciences Pharmacy, The University of East Anglia, Norwich, UK. E-mail: carl.redshaw@uea.ac.uk; Fax: +44 (0)1603 592003; Tel: +44 (0)1603 593137*
[b] *Chemistry Department, Loughborough University, Loughborough, Leicestershire, UK LE11 3TU. E-mail: m.r.j.elsegood@lboro.ac.uk; Fax: +44 (0)1509 223925; Tel: +44 (0)1509 228751*

† Electronic supplementary information (ESI) available: Alternative views of **1–4**. See http://dx.doi.org/10.1039/b509556e

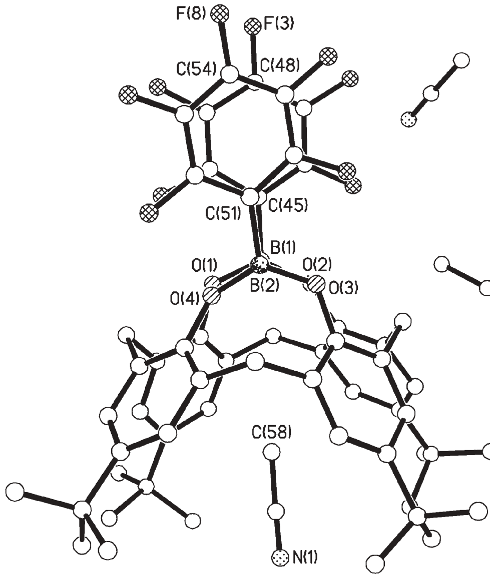

Fig. 1 Selected bond lengths (Å) and angles (°) for **1**: B(1)–O(1) 1.350(2), B(1)–O(2) 1.353(2), B(2)–O(3) 1.350(2), B(2)–O(4) 1.361(2), B(1)–B(2) 3.448; O(1)–B(1)–O(2) 129.10(16), O(1)–B(1)–C(45) 114.92(15), O(2)–B(1)–C(45) 115.87(15).

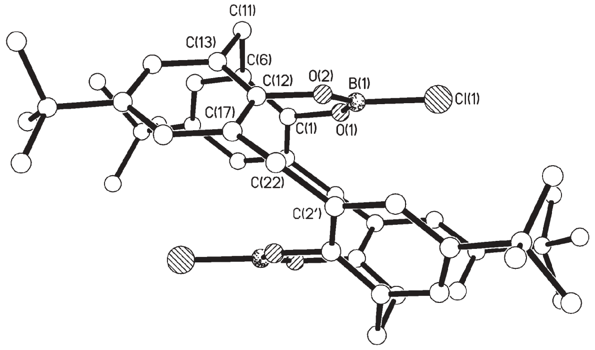

Fig. 2 Selected bond lengths (Å) and angles (°) for **2**: B(1)–O(1) 1.341(3), B(1)–O(2) 1.348(3), B(1)–Cl(1) 1.781(2); O(1)–B(1)–O(2) 133.68(18), O(1)–B(1)–Cl(1) 112.72(15), O(2)–B(1)–Cl(1) 113.58(15), B(1)–O(1)–C(1) 135.04(16), B(1)–O(2)–C(12) 131.10(15).

leading to a '*trans*' deposition of the B–Cl bonds.¶ The C_{ring}–CH_2–C_{ring} angles between *syn* [C(6)–C(11)–C(13) 106.55(15)°] and *anti* [C(17)–C(22)–C(2′) 121.45(16)°] units are at the extremes expected for calix[4]arenes.[7] The asymmetric unit contains half a molecule of **2** and a solvent (MeCN) molecule. The methylene groups appear as a singlet in the ^{1}H NMR spectrum, whilst the ^{11}B NMR is broad (*ca* 25 ppm).

The reaction of **2** with one equivalent of 2,4,6-$(CF_3)_3C_6H_2Li$ in diethylether at −78 °C gave, following work-up, rather complicated NMR spectra, for example the methylene region consisted of a multitude of overlapping signals. However, recrystallisation from toluene at 0 °C did afford a small amount of crystalline material, the structure of which was determined using synchrotron radiation,[8] and was found to be {[Ar^{f}B][FB]*tert*-butylcalix[4]arene}·C_7H_8 (**3**) (see Fig. 3).‖ The formation of **3** clearly indicates that F–Cl exchange is occurring at boron, a process that must involve a CF_3 group. Interestingly, Dillon and Fox *et al.* have also observed such an exchange on reaction of ArLi with BCl_3 to afford Ar_2BF (Ar = 2,4,6-$(CF_3)_3C_6H_2$), and this was partly ascribed to favourable bond energies.[9] The associated *syn* [107.6(3) & 108.5(3)°] and *anti* [119.6(3) & 121.3(3)°] C_{ring}–CH_2–C_{ring} angles in **3** are similar to those in **2**. The B–F bond length [1.359(4) Å] is typical and F(1) resides in the cleft under rings attached to O(3)/O(4). The CF_3 group containing C(53) also resides in a cleft (of rings attached to O(1)/O(3). The disparity in the size of the groups bound to B(1) and B(2) results in an unusual 'squashing' of the calix[4]arene conformation.

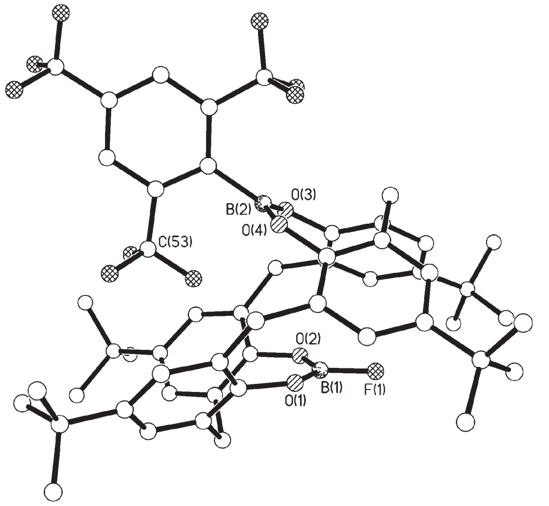

Fig. 3 Selected bond lengths (Å) and angles (°) for **3**: B(1)–F(1) 1.359(4), B(1)–O(1) 1.352(4), B(1)–O(2) 1.346(4), B(2)–O(3) 1.357(5), B(2)–O(4) 1.355(5); O(1)–B(1)–O(2) 131.8(3), O(3)–B(2)–O(4) 131.0(3).

Complex **3**, once its synthesis has been optimised, should allow access to mixed perfluoroaryl boron calix[4]arene species.[10]

Reaction of **2** with an excess of 2,4,6-$(CF_3)_3C_6H_2Li$ in diethylether at −78 °C led to the formation of {[(2,4,6-$(CF_3)_3C_6H_2$)B]$_2$*tert*-butylcalix[4]arene}·MeCN (**4**) in good yield (60%) as a white powder. Crystals of **4**·3MeCN suitable for X-ray diffraction were grown from a saturated acetonitrile solution at ambient temperature. The solid-state molecular structure of **4** is depicted in Fig. 4.** The two 2,4,6-$(CF_3)_3C_6H_2$ groups are far from parallel, bending back from each other: the B(1)–O(1)–O(2) plane is tilted by 26.0° with respect to the plane C(1)–C(12)–O(1)–O(2). Indeed, as shown in Fig. 4, the aryl rings are pushed so far apart that there is no overlap of the C6 cores. The B–B distance is 4.066 Å.

The geometrical parameters associated with the arylboron groups are collected in Table 1 and are compared with Ar = Ph.[3] It is evident that on increasing the bulk from Ar = Ph through to Ar = 2,4,6-$(CF_3)_3C_6H_2$, there is a marked deviation from an eclipsed/parallel conformation. There is also a concomintant increase in the B–B bond length on increasing size of Ar. It is worth emphasising here that the presence of two perfluoroaryl (BAr^f) groups in compounds such as **1** and **4** promotes the adoption of the cone conformation, whereas replacement of one (as in **3**) or both BAr^f groups (as in **2**) with B–halide favours adoption of the 1,2-alternate conformer. Furthermore, the presence of bulky *o*-CF_3 groups (as in **3** and **4**) leads to considerably strained and distorted calixarene fragments; **1** and **2**, for which there are no *o*-CF_3 groups are relatively unstrained.

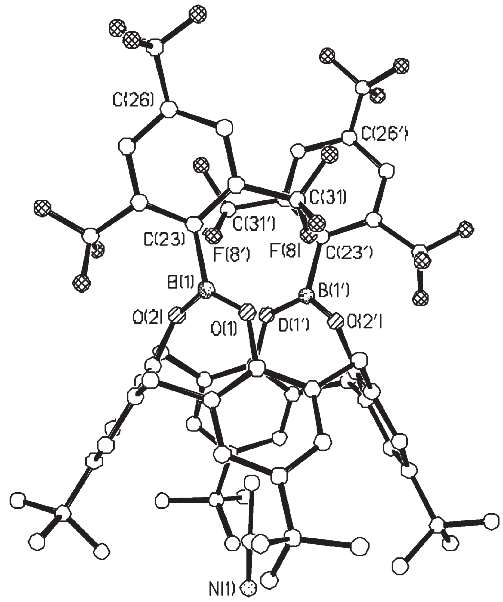

Fig. 4 Selected bond lengths (Å) and angles (°) for **4**: B(1)–O(1) 1.360(2), B(1)–O(2) 1.355(2), B(1)–B(2) 4.066; O(1)–B(1)–O(2) 126.68(15), B(1)–O(1)–C(1) 131.43(13), B(1)–O(2)–C(12) 134.37(13).

Table 1 Structural parameters associated with the arylboron groups

Derivative	B–B distance/Å	Ring 'off-set'/°
Ph	3.429	4.8
C_6F_5	3.448	8.7
2,4,6-$(CF_3)_3C_6H_2$	4.066	Rings not overlapping

In summary, new synthetic routes to boracalix[4]arenes have been developed, thereby increasing the scope for generating yet more highly functionalised boracalixarenes. The potential of perfluorinated aromatics as synthons to new materials has recently been noted.[11]

The University of East Anglia and The Royal Society are thanked for financial support. The EPSRC is thanked for beam-time at Daresbury Laboratory. We also thank the EPSRC Mass Spectrometry Service Centre, Swansea.

Notes and references

‡ Satisfactory microanalyses have been obtained for **1**,**2** and **4**. Selected spectroscopic data: For **1**: ^{1}H NMR (C_6D_6, 298 K, 300 MHz) δ: 7.36 (s, 4H, aryl*H*), 7.13 (s, 4H, aryl*H*), 5.43 (d, 2H, $^2J_{HH}$ 13.0 Hz, *endo*-C*H*$_2$), 4.16 (d, 2H, $^2J_{HH}$ 14.3 Hz, *endo*-C*H*$_2$), 3.66 (d, 2H, $^2J_{HH}$ 12.8 Hz, *exo*-C*H*$_2$), 3.51 (d, 2H, $^2J_{HH}$ 14.3 Hz, *exo*-C*H*$_2$), 1.27 (s, 36H, C(C*H*$_3$)$_3$), 0.72 (s, 1.5H, ½*Me*CN), 0.48 (s, 3H, *Me*CN). ^{19}F NMR (C_6D_6) δ: −128.8 (m, 4F, *o-F*), −149.06 (m, 2F, *p-F*), −162.54 (m, 4F, *m-F*). ^{11}B NMR (C_6D_6) δ: 26.71 (br). MS (EI): 1042 ($M^+ - 2$MeCN), 823 ($M^+ - 3$MeCN − C_6F_5B). For **2**: ^{1}H NMR (C_6D_6, 298 K, 300 MHz) δ: 7.03–6.94 (m, 8H, aryl*H*), 3.80 (s, 8H, C*H*$_2$), 1.22 (s, 36H, C(C*H*$_3$)$_3$), 1.15 (s, 3H, *Me*CN). ^{11}B NMR ($CDCl_3$) δ: 24.7 (br). MS (EI, high temp): 667 ($M^+ - 2$Cl − 2MeCN). For **3**: MS (EI): 903 ($M^+ - 2CF_3 - F$), 757 ($M^+ - 2,4,6\text{-}(CF_3)_3C_6H_2 - F$), 746 ($M^+ - 2,4,6\text{-}(CF_3)_3C_6H_2 - BF$). For **4**: ^{1}H NMR (C_6D_6, 298 K, 300 MHz) δ: 6.93 (s, 4H, aryl*H*), 6.61 (m, 4H, aryl*H*), 5.39 (d, 2H, $^2J_{HH}$ 12.6 Hz, *endo*-C*H*$_2$), 4.07 (d, 2H, $^2J_{HH}$ 14.1 Hz, *endo*-C*H*$_2$), 3.11 (d, 2H, $^2J_{HH}$ 12.8 Hz, *exo*-C*H*$_2$), 2.99 (d, 2H, $^2J_{HH}$ 14.4 Hz, *exo*-C*H*$_2$), 0.85 (s, 36H, C(C*H*$_3$)$_3$), 0.22 (s, 3H, *Me*CN). ^{19}F NMR (C_6D_6) δ: −59.78 (s, 6F, *o*-C*F*$_3$), −63.68 (s, 6F, *p*-C*F*$_3$), −63.71 (s, 6F, *p*-C*F*$_3$), −66.83 (s, 6F, *o*-C*F*$_3$), −67.05 (s, 6F, *o*-C*F*$_3$). ^{11}B NMR (C_6D_6) δ:22.54 (br). MS (EI): 1311 (M^+ − MeCN), 1228 (M^+ − 3MeCN).

§ *Crystal data* for **1**·3MeCN $C_{62}H_{61}B_2F_{10}N_3O_4$, M = 1123.76, orthorhombic, space group $Pna2_1$, a = 13.3771(4), b = 28.5640(9), c = 15.3254(5) Å, U = 5855.9(3) Å^3, T = 150(2) K, Z = 4, μ(Mo-Kα) = 0.100 mm^{-1}, λ = 0.71073 Å, 49143 reflections measured, 13756 unique (R_{int} = 0.019) which were used in all calculations. The final w$R2$ = 0.108 (all data) and $R1$ = 0.040 (for 11982 data with $F^2 > 2\sigma(F^2)$). CCDC 278174.

¶ *Crystal data* for **2**·2MeCN $C_{48}H_{58}B_2Cl_2N_2O_4$, M = 819.48, monoclinic, space group $I2/a$, a = 16.4659(12), b = 16.7508(12), c = 18.1131(13) Å, β = 115.137(2)°, U = 4522.8(6) Å^3, T = 150(2) K, Z = 4, μ(Mo-Kα) = 0.188 mm^{-1}, λ = 0.71073 Å, 18907 reflections measured, 5145 unique (R_{int} = 0.028) which were used in all calculations. The final w$R2$ = 0.144 (all data) and $R1$ = 0.051 (for 3919 data with $F^2 > 2\sigma(F^2)$). CCDC 278175.

|| *Crystal data* for **3**·C_7H_8 $C_{60}H_{62}B_2F_{10}O_4$, M = 1058.72, triclinic, space group $P\bar{1}$, a = 13.5632(12), b = 14.6088(13), c = 16.3167(14) Å, α = 112.636(2)°, β = 90.622(2)°, γ = 111.418(2)° U = 2734.4(4) Å^3, T = 150(2) K, Z = 2, μ = 0.101 mm^{-1}, λ = 0.8466 Å (silicon 111 monochromated synchrotron radiation, Daresbury SRS, Station 16.2SMX), 19437 reflections measured, 10452 unique (R_{int} = 0.041) which were used in all calculations. The final w$R2$ = 0.187 (all data) and $R1$ = 0.067 (for 7224 data with $F^2 > 2\sigma(F^2)$). CCDC 278176.

** *Crystal data* for **4**·3MeCN $C_{68}H_{65}B_2F_{18}N_3O_4$, M = 1351.85, monoclinic, space group $C2/c$, a = 23.8326(10), b = 15.2792(6), c = 19.0184(8) Å, β = 107.495(2)°, U = 6605.1(5) Å^3, T = 150(2) K, Z = 4, μ(Mo-Kα) = 0.118 mm^{-1}, λ = 0.71073 Å, 28545 reflections measured, 7939 unique (R_{int} = 0.024) which were used in all calculations. The final w$R2$ = 0.156 (all data) and $R1$ = 0.051 (for 6192 data with $F^2 > 2\sigma(F^2)$). CCDC 278177. See http://dx.doi.org/10.1039/b509556e for crystallographic data in CIF or other electronic format.

1 C. D. Gutsche, *Calixarenes Revisited*, Royal Society of Chemistry, London, 1998.
2 F. Cadogan, K. Nolan and D. Diamond, in *Calixarenes 2001*, ed. Z. Asfari, V. Böhmer, J. Harrowfield, J. Vicens, Kluwer, Dordrecht, 2001, vol. 34, p. 627.
3 S. Arimori, M. G. Davidson, T. M. Fyles, T. G. Hibbert, T. D. James and G. I. Kociok-Köhn, *Chem. Commun.*, 2004, 1640.
4 W. I. Cross, M. P. Lightfoot, F. S. Mair and R. G. Pritchard, *Inorg. Chem.*, 2000, **39**, 2690.
5 G. S. Hair, A. H. Cowley, J. D. Gordon, J. N. Jones, R. A. Jones and C. L. B. Macdonald, *Chem. Commun.*, 2003, 424.
6 R. Duchateau, S. J. Lancaster, M. Thornton-Pett and M. Bochmann, *Organometallics*, 1997, **16**, 4995.
7 J. C. Aime, J. de Mendoza, P. Prados, P. M. Nieto and C. Sanchez, *J. Org. Chem.*, 1991, **56**, 3372.
8 (*a*) W. Clegg, M. R. J. Elsegood, S. J. Teat, C. Redshaw and V. C. Gibson, *J. Chem. Soc., Dalton Trans.*, 1998, 3037; (*b*) W. Clegg, *J. Chem. Soc., Dalton Trans.*, 2000, 3223.
9 S. M. Cornet, K. B. Dillon, C. D. Entwistle, M. A. Fox, A. E. Goeta, H. P. Goodwin, T. B. Marder and A. L. Thomson, *Dalton Trans.*, 2003, 4395.
10 Such studies are currently in progress.
11 Y. Xie, H. F. Schaefer, III and F. A. Cotton, *Chem. Commun.*, 2003, 102.