The synthesis, structure and reactivity of 4-nonafluorobiphenyl complexes[†]

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The Grignard reagent $Ar_F'MgBr$ ($Ar_F' = 4$ -(C_6F_5) C_6F_4) reacts with Me₃SiCl, Me₂SiCl₂ and Me₃SnCl to give the 4-nonafluorobiphenyl group 14 complexes $Ar_F'Me_3Si$, (Ar_F')₂Me₂Si and $Ar_F'Me_3Sn$ respectively. $Ar_F'Me_3Sn$ undergoes only methyl group exchange when treated with BBr₃, yielding $Ar_F'Me_2SnBr$. The solid state structures of $Ar_F'Me_3Sn$ and $Ar_F'Me_2SnBr$ have been determined and exhibit the expected distorted tetrahedral geometries at tin. The reaction between three equivalents of $Ar_F'MgBr$ and BF_3 was not selective, while one equivalent of $Ar_F'MgBr$ and (Ar_F)₂BF ($Ar_F = C_6F_5$) reacted cleanly to give (Ar_F)₂ $Ar_F'B$. Treatment of BCl₃ with three equivalents of $Ar_F'Li$, prepared at low temperature from the reaction between $Ar_F'Br$ and *n*-BuLi, yielded (Ar_F')₃B. The molecular structures of the acetonitrile adducts of (Ar_F)₂ $Ar_F'B$ and (Ar_F')₃B closely resemble that of (Ar_F)₃B·NCMe. During the course of the boron investigations, reaction with adventitious water led to the structural characterization of (Ar_F')₂BOH·OH₂ as a hydrogen-bonded dimer. The Grignard reagent reacts selectively with ZnCl₂ in diethyl ether giving first [(Ar_F')Zn(μ -Cl)(OEt₂)]₂ then (Ar_F')₂Zn(OEt₂)₂, both of which have been characterised by X-ray diffraction. The corresponding reaction with HgCl₂ requires the use of tetrahydrofuran as the solvent and yields (Ar_F')₂Hg(THF)₂.

Introduction

The pentafluorophenyl group has been widely employed to prepare metal complexes because it combines the highly electronwithdrawing character of a halide with the steric requirements of an arene ligand.^{1,2} Main group complexes of the pentafluorophenyl ligand were subject to a first flourish of interest in the 1960s with the publication of the homoleptic zinc and boron compounds.^{3,4} Following a period of dormancy, they are currently enjoying considerable attention across a remarkably broad range of applications.

The majority of reports on bis(pentafluorophenyl)zinc have been concerned with its utility as a C_6F_5 -transfer reagent.⁵ Recently it has found direct application as an initiator component for the carbocationic polymerisation of isobutene.⁶ We have focused upon the supramolecular assembly of Lewis adducts of the form (C_6F_5)₂ZnL₂ (where L is an amine, pyridine or benzonitrile donor) through N–H····F–C, face-to-face $C_6F_5 \cdots C_6H_5$ and offset $C_6F_5 \cdots C_6F_5$ interactions.⁷⁻⁹

The importance of $(Ar_F)_3B$ $(Ar_F = C_6F_5)$ as a Lewis acidic activator, or as the basis for poorly coordinating anions, in 1alkene polymerisation catalysis has led to a number of studies directed towards elaborating the perfluoroaryl group;¹⁰ the most significant example being $(2-(C_6F_5)C_6F_4)_3B$.¹¹ $(Ar_F')_3B$ $(Ar_F' = 4-(C_6F_5)C_6F_4)$ appears in the patent literature, but few synthetic and characterisation details are presented.¹² In contrast to boron, reports of further-substituted derivatives of bis(pentafluorophenyl)zinc are scarce. Bochmann *et al.* have reported the elegant, but somewhat unconventional, synthesis of $(2-(C_6F_5)C_6F_4)_2Zn$ from EtZnCl and $2-(C_6F_5)C_6F_4Li$.¹³ The only other example of the preparation of a relevant derivative of $(C_6F_5)_2Zn$ of which we are aware is that of $(4-(CF_3)C_6F_4)_2Zn$.¹⁴ A number of synthetic routes to the parent compound, $(C_6F_5)_2Zn$, have been reported, including the thermal decomposition of the carboxylate¹⁵ and the salt metathesis reactions between magnesium, lithium and silver reagents with zinc halides.^{3,5,16} The ligand exchange reaction between R₂Zn and $(C_6F_5)_3B^{17}$ is the most convenient, since the preparation and purification of $(C_6F_5)_3B$ is facile.¹⁸

This report describes an exploration of the main group chemistry of the 4-nonafluorobiphenyl group utilizing lithium, magnesium and tin reagents for the preparation of novel zinc complexes and includes the attempted isolation of a base-free borane as a potential intermediate.

Results and discussion

The Grignard reagent, $Ar_F'MgBr$ (1), was prepared at room temperature in diethyl ether solution and has not been isolated. The reaction is accompanied by a darkening of the solution, similar to that seen for Ar_FMgBr , but the reagent is indefinitely stable if stored in solution under nitrogen at 5 °C. Reactions involving 1 can be conveniently followed by ¹⁹F NMR. The chemical shift of the fluorine in the 2-position (*F2*) (1: $\delta = -114.1$ ppm) is sensitive to the (metal) substituent in the 1-position and is characteristic for these compounds.¹⁹⁻²¹ Not surprisingly, this sensitivity drops off dramatically with the distance from the metal, such that the remaining ¹⁹F chemical shifts are similar for all the complexes reported herein.

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The success of the Grignard reagent preparation was confirmed by quenching with either one equivalent of trimethylsilylchloride or 0.5 equivalents of dimethylsilyldichloride giving 49 and 84% isolated yields of $Ar_F'Me_3Si(2)$ and $(Ar_F')_2Me_2Si(3)$, respectively (Scheme 1). The ¹⁹F NMR spectra of 2 and 3 are very similar and in both cases the *F2* resonances are found at considerably lower frequency than those of the Grignard reagent, 1.²¹ Compounds 2 and 3 gave elemental analyses in very good agreement with the expected values.



While perfluoroaryl silane reagents undergo defluorosilylation reactions with silver fluoride,²² there is little precedent for their application in the preparation of boron compounds and no reaction occurs between **2** or **3** and BF₃·OEt₂, BCl₃ or BBr₃.²³ In contrast, stannane reagents have been widely used for the selective introduction of perfluoroaryl substituents to boron.^{10b,f}

Treatment of 1 with one equivalent of trimethyltin chloride in diethyl ether gave the tin reagent $Me_3Ar_F'Sn$ (4) in 71% yield (Scheme 1). The F2 chemical shift of **4** is found at $\delta = -121.4$ ppm and is therefore intermediate between those of 1 and the silicon homologue 2. The structure of 4 was confirmed by single-crystal X-ray diffraction. Compound 4 and BCl₃ do not react under a range of experimental conditions, including refluxing toluene. When 4 was heated to 60 °C in neat BBr₃ a new crystalline compound, 4a, was isolated from the reaction mixture. The ¹H NMR spectrum was sufficient to determine that a reaction had taken place but the signal for F2 at $\delta = -121.9$ ppm was rather similar to that of 4 and not in the range expected for a boron compound. Unequivocal identification was achieved through Xray diffraction, whereby 4a was determined to be Ar_F'Me₂SnBr. Rather than $Ar_{\rm F}'/Br$ exchange, the reaction between 4 and BBr₃ proceeds through Me/Br exchange (Scheme 2). This reaction resembles that observed by Piers et al. when attempting the synthesis of related binapthyl derivatives.²⁴



The molecular structures of **4** (Fig. 1) and **4a** (Fig. 2) are rather similar, with essentially tetrahedral geometries at tin. Replacement of a methyl group with a bromine substituent results in more



Fig. 1 Molecular structure of 4. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: Sn(1)-C(21) 2.131(4); Sn(1)-C(22) 2.133(4); Sn(1)-C(23) 2.137(4); Sn(1)-C(11) 2.196(4); C(22)-Sn(1)-C(21) 113.76(18); C(21)-Sn(1)-C(23) 112.76(19); C(22)-Sn(1)-C(23) 110.36(18); C(21)-Sn(1)-C(11) 106.95(17); C(22)-Sn(1)-C(11) 109.25(16); C(23)-Sn(1)-C(11) 103.11(18).



Fig. 2 Molecular structure of 4a. Displacement ellipsoids are drawn at the 50% probability level. The acetonitrile molecule has been omitted for clarity. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: Sn(1)-C(11) 2.166(3); Sn(1)-C(21) 2.128(3); Sn(1)-C(22) 2.119(3); Sn(1)-Br(2) 2.5587(3); C(22)-Sn(1)-C(21) 123.04(12); C(22)-Sn(1)-C(11) 113.71(11); C(21)-Sn(1)-C(11) 117.33(11); C(11)-Sn(1)-Br(2) 93.87(7); C(21)-Sn(1)-Br(2) 99.52(8); C(22)-Sn(1)-Br(2) 100.64(8).

substantial distortion from ideal tetrahedral geometry in **4a**. At 2.196(4) and 2.166(3) Å in **4** and **4a** respectively the Sn(1)–C(11) bonds are slightly longer than the 2.126(8) Å found for the homoleptic tetrakis(pentafluorophenyl)tin.²⁵

The preferred procedure for the preparation of $(C_6F_5)_3B$ sees BF_3 treated with three equivalents of Ar_FMgBr in diethyl ethertoluene solution and warmed to 100 °C to ensure complete conversion.¹⁸ The analogous reaction between BF_3 and three equivalents of 1 proceeds to completion with respect to the Grignard reagent. However, the plethora of signals in the ¹¹B and ¹⁹F NMR spectra suggest that the crude product consists of a mixture of $[XMg(OEt_2)_n][B(Ar_F')_{4-y}X_y]$ and $B(Ar_F')_{3-2}X_z$ compounds (where X = F or Br). Whereas extraction of the Ar_F system with hexane gives the borane in typically 60% yield,¹⁸ the analogous procedure did not yield pure $(Ar_F')_3$; however, it remains probable that it is present in the product mixture.

A small quantity of crystalline material was isolated during an attempted preparation of $(Ar_F')_3B$. Attempted NMR spectroscopy was frustrated by the very small quantity of material present and provided signals for more than one compound. Despite this and difficulties caused by the low melting point of the crystals, an X-ray diffraction data set was ultimately collected. The structure was determined to be that of the deuterated benzene solvate $(Ar_F')_2B(OH)(OH_2).(C_6D_6)_3$ (5), which was presumably formed through reaction between adventitious water and $(Ar_F')_3B$ or $(Ar_F')_2BF^{26}$ This compound is noteworthy since bis(pentafluorophenyl)borinic acid has received considerable attention as a promoter in synthetic chemistry because of the unusual combination of Lewis acidic, Lewis basic and Brønsted acidic sites.^{27–29}

The molecular structure of **5** is presented in Fig. 3. Bond length B(1)–O(2) is significantly shorter than that for B(1)–O(1), which is consistent with B(1)–O(1) having dative character. In addition, the hydrogen atoms were located in the difference map and have been freely refined, further supporting the assertion that **5** is a Lewis adduct between bis(4-nonafluorophenyl)borinic acid and water. Molecules of **5** are strongly hydrogen bonded in pairs (Fig. 4), resembling the pattern in [(C₆F₅)₂(HO)BO(Me)H]₂.²⁸ As well as the hydrogen bond, there are a number of O–H \cdots F–C close contacts (Table 1).



Fig. 3 Molecular structure of $(Ar_F)_2B(OH)(OH_2)$ (5). Displacement ellipsoids are drawn at the 50% probability level. Solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: B(1)–O(1), 1.542(5); B(1)–O(2), 1.462(5); B(1)–C(11), 1.637(6); B(1)–C(21), 1.630(5); O(2)–B(1)–O(1), 102.9(3); O(2)–B(1)–C(21), 114.7(3); O(1)–B(1)–C(21), 107.9(3); O(1)–B(1)–C(11), 110.8(3); O(2)–B(1)–C(11), 109.7(3); C(21)–B(1)–C(11), 110.6(3).

In contrast to the rather poor selectivity observed for the reaction between three equivalents of 1 and boron trifluoride, treating bis(pentafluorophenyl)boron fluoride³⁰ with one equivalent of 1 gave $(Ar_F')(Ar_F)_2B$ (6) in near quantitative yield (Scheme 3). The ether adduct of 6 proved not to share the high crystallinity of $(Ar_F)_3B$ ·OEt₂ and isolation of a crystalline solid was only achieved after addition of acetonitrile, giving $(Ar_F')(Ar_F)_2B$ ·NCMe (6·NCMe), the identity of which was confirmed through diffraction methods.

The initial reluctance to employ the 4-nonafluorobiphenyl lithium reagent stems from the thermal sensitivity of related lithium salts and the associated explosion hazard.^{11,31} However, 2-



Fig. 4 Illustrating the hydrogen-bond driven dimerisation of 5. Nonafluorobiphenyl ligands are represented by the first carbon atom for clarity. The two halves of the molecule are related by the symmetry operator 2 - x, 1 - y, 1 - z.

nonafluorobiphenyl lithium can be handled without incident if the correct solvent and temperature conditions are employed.¹¹ Following the procedure of Marks and co-workers for the preparation of tris(2-nonafluorobiphenvl)borane, the lithiation of $Ar_{\rm F}$ 'Br at -78 °C was performed in a 1:1 solvent mixture of diethyl ether and light petroleum (Scheme 3).¹¹ Three equivalents of the lithium salt were treated with boron trichloride to give a mixture of $(Ar_{F})_{3}B(7)$ (Scheme 3) and a second unidentified by-product. Solvent removal from the light petroleum fraction yielded only a crude brown oil. The isolation of a crystalline solid was again facilitated by the addition of acetonitrile, giving rise to the adduct, 7.NCMe, the structure of which was elucidated by X-ray crystallography. The ¹¹B NMR signals for the neutral four-coordinate adducts 6 NCMe and 7-NCMe are similar at δ -10.8 and -9.1 ppm respectively. Both 6 NCMe and 7 NCMe gave elemental analyses in good agreement with the calculated values.

The mixed-aryl boron compound 6·NCMe crystallises from acetonitrile with one molecule of solvent coordinated to the boron and a second of crystallisation (Fig. 5). Compound 7·NCMe (Fig. 6) was recrystallised from dichloromethane and there are two disordered solvent molecules in the lattice. The molecular structures of both of the acetonitrile adducts reported here and also the known $(Ar_F)_3 B$ ·NCMe³² exhibit distorted tetrahedral environments about boron. The angles at boron between the nitrogen and the perfluoroaryl groups are generally more acute than those between perfluoroaryl groups, reflecting the steric demands of the substituents. The B–N distances for 6·NCMe,

Table 1 Hydrogen bonds and close O-H · · · F contacts in compound 5

$D-H\cdots A^{a}$	Symmetry operation for interactions	Distance $(H \cdots A)/Å$	Distance $(D \cdots A)/Å$	Angle (DHA)/°
$O(1) - H(1b) \cdots O(2)$	2-x, 1-y, 1-z	1.64(2)	2.464(4)	173(6)
$O(1) - H(1a) \cdots F(12)$	x, y, z	2.36(4)	2.710(4)	108(4)
$O(1) - H(1a) \cdots F(26)$	x, y, z	2.10(3)	2.724(4)	134(4)
$O(2) - H(2) \cdots F(22)$	x, y, z	2.27(5)	2.772(3)	122(5)
$O(2) - H(2) \cdots F(16)$	1 - x, 1 - y, 1 - z	2.40(4)	3.075(3)	146(5)

^a A is the hydrogen bond acceptor and D the hydrogen bond donor.



Scheme 3 The synthesis of boron complexes of the $Ar_{F'}$ ligand.

7·NCMe and $(Ar_F)_3$ B·NCMe at 1.583(3), 1.600(5) and 1.610(5) Å are essentially identical.



Fig. 5 Molecular structure of 6·NCMe. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms and the acetonitrile solvate molecule have been omitted for clarity. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: B(1)-N(4), 1.583(3); B(1)-C(11), 1.624(3); B(1)-C(21), 1.640(3); B(1)-C(31), 1.624(3); N(4)-B(1)-C(11), 103.38(18); N(4)-B(1)-C(21), 104.63(17); N(4)-B(1)-C(31), 109.50(19); C(11)-B(1)-C(21), 115.70(19); C(11)-B(1)-C(31), 115.91(18); C(31)-B(1)-C(21), 106.99(18).

Refining the synthesis of 7, to yield the pure, base-free precursor required for the ligand exchange reaction with R_2Zn , was considered unlikely to provide the most expedient route to $(Ar_F')_2Zn$. In order to gauge the effectiveness of a more direct salt metathesis route to the $(Ar_F')_2M$ complexes of group 12, the reaction between mercury dichloride and the Grignard reagent



Fig. 6 Molecular structure of 7·NCMe. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms and the CH_2Cl_2 molecules of crystallisation have been omitted for clarity. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: B(1)–N(41), 1.600(5); B(1)–C(11), 1.621(5); B(1)–C(21), 1.627(6); B(1)–C(31), 1.632(5); N(41)–B(1)–C(11), 103.6(3); N(41)–B(1)–C(21), 104.8(3); N(41)–B(1)–C(31), 105.8(3); C(11)–B(1)–C(21), 115.1(3); C(11)–B(1)–C(31), 114.0(3); C(21)–B(1)–C(31), 112.2(3).

was examined. Treatment of $HgCl_2$ with two equivalents of **1** in tetrahydrofuran gave complex **8** as a beige solid in modest yield (Scheme 4). The formulation of **8** as the expected product, $(Ar_F)_2Hg(THF)_2$, was based upon the NMR and elemental analysis results. The ¹H NMR spectrum simply indicated the presence of coordinated tetrahydrofuran. No reaction takes place if, instead of tetrahydrofuran, a mercury dichloride suspension in diethyl ether is treated with the Grignard reagent, presumably due to the mercury reagent's poor solubility.



Scheme 4

The good solubility of $ZnCl_2$ meant that not only does it react readily with 1 in diethyl ether, but the product stoichiometry can easily be controlled by the reactant ratio. Thus, when $ZnCl_2$ was treated with one equivalent of 1 in diethyl ether, a monosubstituted compound was obtained $[(Ar_F')Zn(\mu-Cl)(OEt_2)]_2$ (9) (Scheme 5). If two equivalents of Grignard reagent are employed the final product is $(Ar_F')_2Zn(OEt_2)_2$ 10. Following these reactions spectroscopically indicated that they proceed essentially quantitatively. However, compounds **9** and **10** were both isolated in only moderate yields of 51 and 54%, respectively, because of their poor solubility and difficulties associated with their separation from the magnesium halide by-products. The spectroscopic data are similar and the two compounds were ultimately distinguished through elemental analysis and X-ray crystallography. The deviation between the calculated and observed elemental analysis results for compound **9** is believed to reflect the facile loss of coordinated diethyl ether.

Compound 9 crystallises as a chloride bridged dimer, in which zinc has an essentially tetrahedral coordination environment (Fig. 7). The dative Zn–Cl bond in 9 is distinguished by a slightly greater interatomic separation. Both the Zn–C and Zn–Cl bond lengths in compound 9 are similar to those observed for the closely related and recently reported dimer $[(C_6Me_6)(Ar_F)Zn(\mu-Cl)]_2$.³³ Predictably, the Cl(1)–Zn(1)–Cl(1') and C(11)–Zn(1)–Cl(1) angles are greater in 9 than in Bochmann's arene adduct, since the η^3 -hexamethylbenzene ligand is sterically more demanding than diethyl ether.



Fig. 7 Molecular structure of **9**. Displacement ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity. The two monomers are related by an inversion centre lying at the centre of the Zn_2Cl_2 core. The two halves of the molecule are related by the symmetry operator 1 - x, 1 - y, 1 - z. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: Zn(1)-C(11), 1.984(4); Zn(1)-O(1), 2.050(3); Zn(1)-Cl(1), 2.3470(12); Zn(1)-Cl(1'), 2.3746(12); C(11)-Zn(1)-O(1), 116.97(16); C(11)-Zn(1)-Cl(1), 121.92(13); O(1)-Zn(1)-Cl(1), 99.73(10); C(11)-Zn(1)-Cl(1'), 119.03(13); O(1)-Zn(1)-Cl(1'), 101.46(10); Cl(1)-Zn(1)-Cl(1'), 93.13(4).

The zinc-bonded ligands in **10** adopt a somewhat distorted tetrahedral arrangement (Fig. 8). The origin of this distortion is the steric mismatch between the perfluoroaryl and ether ligands. So, while the C–Zn–O angle is close to the tetrahedral ideal, that of C–Zn–C is more obtuse and that of O–Zn–O is much more acute. As one would expect, the Zn–O bond length is similar to that found for $(Ar_F)_2Zn(THF)_2^{34}$ but is slightly longer than that found for **9**, which enjoys significantly less steric hindrance. The Zn–C bond lengths are unremarkable and within the range observed in studies of bis(pentafluorophenyl) zinc adducts.^{3,5,7–9,34}



Fig. 8 Molecular structure of **10**. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms have been omitted for clarity. The two pairs of ligands are related by a two-fold symmetry axis passing through the zinc atom. The two halves of the molecule are related by the symmetry operator 1 - x, y, 1/2 - z. Selected bond lengths (Å) and angles (°), Esd's are in parentheses: Zn(1)–C(11), 2.013(6); Zn(1)–O(2), 2.084(3); C(11)–Zn(1)–C(11'), 124.2(3); C(11)–Zn(1)–O(2), 108.6(2); O(2)–Zn(1)–O(2'), 85.98(19); C(11)–Zn(1)–O(2'), 111.43(19).

In each of the seven crystal structures reported here the two phenyl groups of each 4-nonafluorobiphenyl ligand are twisted, in order to minimise steric repulsion between the fluorine atoms.³⁵

Isolation of compound 9 facilitated the preparation of the mixed perfluoroaryl compound $(Ar_F')(Ar_F)Zn(THF)_2$ (11) through treatment of 9 with one equivalent of Ar_FMgBr (Scheme 5). The 1 : 1 ratio of Ar_F to Ar_F' groups was confirmed by ¹⁹F NMR and the identity of the sample was affirmed by the elemental analysis.

Conclusion

A broad range of 4-nonafluorobiphenyl complexes is accessible through reaction of the nucleophilic lithium and, preferably, magnesium reagents with main group electrophiles. The Grignard reagent $Ar_F'MgBr$ (1) reacts selectively with Me_3SiCl , Me_2SiCl_2 , Me_3SnCl and $(Ar_F)_2BF$. However, the reaction of BF_3 with three equivalents of 1 gives an intractable mixture of products. In one such reaction, adventitious hydrolysis lead to crystals of $(Ar_F')_2B(OH)(OH_2)$ (5) being obtained. In light of the elegant studies on bis(pentafluorophenyl)borinic acids and their synthetic importance, the borinic acid precursor to compound 5 and the structurally characterised aqua adduct merit further study. The borane $(Ar_{\rm F}')_3 B$ was isolated and crystallographically characterised as the acetonitrile adduct (7·NCMe) after synthetic recourse to the lithium reagent. In contrast to the lack of selectivity of the reaction between the Grignard reagent and boron trifluoride, treatment of zinc dichloride with one or two equivalents of 1 gave $[(Ar_{\rm F}')Zn(\mu Cl)(OEt_2)]_2$ (9) or $(Ar_{\rm F}')_2Zn(OEt_2)_2$ (10) respectively.

Our observations during the preparation and isolation of the boron and zinc complexes suggest that, while the 4nonafluorobiphenyl ligand may well be regarded as both sterically and electronically very similar to the pentafluorophenyl ligand there are subtle differences in both reactivity and solubility. From a molecular structure standpoint, at the metal(loid) centre, complexes of the 4-nonafluorobiphenyl ligand resemble their pentafluorophenyl analogues.

Experimental

Syntheses were performed under anhydrous oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled over sodium-benzophenone (diethyl ether, tetrahydrofuran), sodium (toluene), sodium-potassium alloy (light petroleum, bp 40-60 °C), or CaH₂ (dichloromethane, 1,2-difluorobenzene). NMR solvents (CDCl₃, C_6D_6 , C_7D_8) were dried over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NMR spectra were recorded using a Bruker DPX300 spectrometer at 293 K. Chemical shifts are reported in ppm and referenced to residual solvent resonances (1H, 13C); 19F is relative to CFCl₃; 11B is relative to BF₃·OEt₂. The atom numbering scheme is given in Chart 1. All coupling constants are given in Hz. The ¹⁹F NMR spectra of reaction mixtures, including the ethereal solution of 1, were obtained by adding 0.1 cm³ of the reaction medium to 0.5 cm^3 benzene- d_6 . Elemental analyses were performed at the Department of Health and Human Sciences, London Metropolitan University. 4-Bromo-2,3,5,6,2',3',4',5',6'-nonafluoro-biphenyl (Ar_F'Br) was prepared according to the literature procedure.³⁶ The remaining reagents were purchased from Aldrich or Alfa Aesar and used without further purification.



Chart 1 The fluorine atom numbering scheme in Ar_F' groups.

Compound **5** was obtained serendipitously in small quantity as described in the results and discussion above.

Preparation of Ar_F'MgBr (1) solution

A solution of $4-(C_6F_5)C_6F_4Br$ (4 g, 10 mmol) in 30 cm³ diethyl ether was added dropwise to a suspension of iodine-activated Mg turnings (0.5 g, 21 mmol) in 10 cm³ of diethyl ether. The resulting brown solution was stirred for a further 2 h at room temperature

to ensure complete reaction and the excess magnesium separated by filtration. (For a 0.1 cm³ aliquot of diethyl ether solution) $\delta_{\rm F}$ (282 MHz, C₆D₆) –114.1 (2F, m, F2), –139.7 (4F, m, F3 and F2'), –153.0 (1F, t, ³J_{EF} 22, F4'), –162.4 (2F, m, F3').

Ar_F'Me₃Si (2)

A solution of 12.7 mmol of **1** in diethyl ether (20 cm³) at room temperature was treated with chlorotrimethylsilane (1.79 cm³, 14 mmol) and stirred overnight. The soluble part was separated by filtration and the volatile materials removed under vacuum. After extraction with light petroleum, and distillation of the solvent under vacuum, the residue was crystallised from light petroleum to give Ar_F'SiMe₃ as colourless needles (2.43 g, 49%). $\delta_{\rm H}$ (300 MHz, CDCl₃) 0.46 (9H, s, Si(CH₃)₃). $\delta_{\rm F}$ (282 MHz, CDCl₃) –127.4 (2F, m, *F2*), –137.9 (2F, m, *F3* or *F2'*), –139.2 (2F, m, *F3* or *F2'*), –151.1 (1F, t, ³*J*_{EF} 21, *F4'*), –161.2 (2F, m, *F3'*). Elemental analysis found: C, 46.51; H, 2.20. Calculated for C₁₅H₉F₉Si: C, 46.40; H, 2.34.

(Ar_F')₂Me₂Si (3)

Dichlorodimethylsilane (1.9 mmol, 0.24 cm³) was added to a solution of **1** (3.8 mmol) in diethyl ether (15 cm³). The mixture was stirred for 36 h before filtration and removal of the volatile materials under vacuum afforded **3** as a brown solid (1.1 g, 84%), which did not require further purification. $\delta_{\rm H}$ (300 MHz, CDCl₃) 0.93 (6H, s, Si(CH₃)₂). $\delta_{\rm F}$ (282 MHz, CDCl₃): δ –127.2 (4F, m, *F2*), –137.7 (4F, m, *F3* or *F2'*), –138.1 (4F, m, *F3* or *F2'*), –150.7 (2F, t, ${}^{3}J_{\rm EF}$ 21, *F4'*), –161.1 (4F, m, *F3'*). Elemental analysis found: C, 45.44; H, 0.94. Calculated for C₂₆H₆F₁₈Si: C, 45.37; H, 0.88.

$Ar_{F}'Me_{3}Sn(4)$

A solution of chlorotrimethyltin (0.64 g, 3.2 mmol) in diethyl ether (10 cm³) was treated with 3.8 mmol of 1 dissolved in diethyl ether (15 cm^3) and the resulting reaction mixture was stirred overnight. The solvents were distilled off under reduced pressure and the product extracted with warm (40 °C) light petroleum (3×15 cm³). The light petroleum solution was concentrated until the point of crystallisation and cooled to -27 °C yielding crystals of compound 4 (1.2 g, 71%) suitable for X-ray crystallography. $\delta_{\rm H}$ (300 MHz, C_6D_6) 0.26 (s, 9H, Sn(CH₃)). δ_F (282 MHz, C_6D_6) -121.4 (m, 2F, F2), -138.3 (m, 2F, F3 or F2'), -139.2 (m, 2F, F3 or F2'), -150.0 (t, 1F, ${}^{3}J_{F,F} = 22$ Hz, F4'), -161.2 (m, 2F, F3'). In order to provide a comparison and to illustrate the independence of ¹⁹F NMR spectra upon the solvent, the data for chloroform- d_1 are also presented here.¹⁶ $\delta_{\rm H}$ (300 MHz, CDCl₃) 0.56 (s, 9H, Sn(CH₃)). $\delta_{\rm F}$ (282 MHz, CDCl₃) -121.3 (m, 2F, F2), -137.6 (m, 2F, F3 or F2'), -138.6 (m, 2F, F3 or F2'), -151.0 (t, 1F, ³J_{F,F} 21, F4'), -161.0 (2F, m, F3'). Elemental analysis found: C, 37.68; H, 1.81. Calculated for C₁₅H₉F₉Sn: C, 37.62; H, 1.89.

Ar_F'Me₂SnBr (4a)

A sample of compound **4** (0.24 g, 0.5 mmol) was dissolved in BBr₃ (2 cm³) and heated at 60 °C overnight. The volatile materials were removed under vacuum. The residue was extracted with light petroleum and crystallised from acetonitrile to afford crystals of **4a**·MeCN as colourless plates suitable for X-ray diffraction (0.13 g, 42%). $\delta_{\rm H}$ (300 MHz, C₆D₆) 0.66 (6H, s, Sn(CH₃)), 0.57 (3H, s,

CH₃CN). $\delta_{\rm F}$ (282 MHz, C₆D₆) –122.0 (2F, m, F2), –137.0 (2F, m, F3 or F2'), –139.0 (2F, m, F3 or F2'), –150.2 (1F, t, ${}^{3}J_{\rm FF}$ 21, F4'), –160.9 (2F, m, F3'). Elemental analysis found: C, 32.75; H, 1.52; N, 2.38. Calculated for C₁₆H₉F₉NBrSn: C, 32.86; H, 1.55; N, 2.40.

(Ar_F)₂(Ar_F')B(NCMe) (6·NCMe)

 C_6F_5Br (0.95 cm³, 7.6 mmol) was added dropwise to a suspension of Mg turnings (0.20 g, 8.4 mmol) in diethyl ether (10 cm³) and the mixture was stirred for 1 h. The resulting Grignard reagent solution was filtered and added to a solution of BF₃·Et₂O (0.47 cm³, 3.8 mmol) in diethyl ether (10 cm³) at 0 °C. The solution was warmed slowly to room temperature and stirred for 2 h, before all the volatile materials were removed under vacuum. A solution of 1 (20 cm³, 0.19 M in Et₂O, 3.8 mmol) was added directly to the solid residue and the resulting mixture stirred overnight at room temperature. After removing the solvent under vacuum the residue was extracted with warm (40 °C) light petroleum. Distilling off the light petroleum gave a crude pale brown solid. Compound 6-NCMe MeCN was obtained as colourless crystals following crystallisation from a mixture of acetonitrile and light petroleum at -27 °C (1.31 g, 48%). $\delta_{\rm H}$ (300 MHz, $C_6 D_6$) 0.61 (3H, s, free *MeCN*), 0.34 (3H, s, *bound MeCN*). δ_B (96.3 MHz, C₆D₆) –10.8 (br). $\delta_{\rm F}$ (282 MHz, C₆D₆) –133.5 (2F, d, ${}^{3}J_{\rm F,F}$ 23, F2), –134.6 (4F, d, ³*J*_{EF} 23, *o*-*F C*₆*F*₅), -138.9 (2F, m, *F3* or *F2'*), -139.8 (2F, m, *F3* or F2'), -150.8 (1F, t, ³J_{EF} 22, F4'), -155.3 (2F, t, ³J_{EF} 21, p-F C₆F₅), -161.2 (2F, m, F3'), -163.1 (4F, m, m-F C₆F₅). Elemental analysis found: C, 45.26; H, 0.74; N, 3.86. Calculated for C₂₈H₆BF₁₉N₂: C, 45.32; H, 0.81; N, 3.77.

(Ar_F')₃B(NCMe) (7·NCMe)

4-(C₆F₅)C₆F₄Br (1.16 g, 2.9 mmol) was dissolved in a mixed solvent of diethyl ether (16 cm³) and light petroleum (16 cm³) and the solution was cooled to -78 °C. A solution of *n*-butyl lithium (1.4 cm³, 2.1 M in hexane) was added dropwise and the mixture was stirred for 2 h. A solution of BCl₃ (1 cm³, 1.0 M in heptane, 1 mmol) was then introduced and the reaction mixture was allowed to warm slowly to room temperature. The LiCl was separated by filtration and acetonitrile (1 cm³) was added to the filtrate. The solvents were distilled off under vacuum to give a crude brown oil. Crystallisation by layering light petroleum over a dichloromethane solution at -27 °C gave colourless crystals of 7-NCMe·2(CH₂Cl₂) (0.53 g, 55%). $\delta_{\rm H}$ (300 MHz, C₆D₆) 0.23 (s, 3H, *MeCN*). δ_F (282 MHz, C₆D₆)-132.7 (6F, m, F2), -138.4 (6F, m, F3 or F2'), -138.8 (6F, m, F3 or F2'), -150.2 (3F, t, ³J_{F,F} 22, F4'), -160.7 (6F, m, F3'). $\delta_{\rm B}$ (96.3 MHz, C₆D₆) –9.1 (br). Elemental analysis found: C, 45.74; H, 0.15; N, 1.45. Calculated for C₃₈H₃BF₂₇N: C, 45.77; H, 0.30; N, 1.40.

(Ar_F')₂Hg(THF)₂ (8)

To a suspension of HgCl₂ (0.52 g, 1.9 mmol) in tetrahydrofuran (15 cm³) 3.8 mmol of **1** dissolved in THF (15 cm³) was added and the resulting reaction mixture stirred overnight. The solvent was then removed under vacuum and the residue extracted with toluene (3×15 cm³). The toluene was concentrated under reduced pressure to 10 cm³, 0.5 cm³ of tetrahydrofuran was added and the solution cooled to -27 °C precipitating a pale brown solid. Separation by filtration and drying under vacuum gave **8** as a beige

solid (0.57 g, 32%). $\delta_{\rm H}$ (300 MHz, C₆D₆) 3.57 (8H, m, 2,5-THF), 1.40 (8H, m, 3,4-THF). $\delta_{\rm F}$ (282 MHz, C₆D₆) –119.6 (4F, m, F2), -136.9 (4F, m, F3 or F2'), –138.0 (4F, m, F3 or F2'), –150.5 (2F, t, ${}^{3}J_{\rm FF}$ 21, F4'), –160.7 (4F, m, F3'). Elemental analysis found: C, 39.14; H, 1.55. Calculated for C₃₂H₁₆F₁₈HgO₂: C, 39.42; H, 1.65.

$[(Ar_{F}')Zn(\mu-Cl)(OEt_{2})]_{2}$ (9)

This compound was prepared using essentially the same procedure as outlined below for **10**, using only one equivalent of the Grignard reagent **1** (1.5 mmol in 10 cm³ of diethyl ether) to one equivalent of ZnCl₂ (1.5 mmol, 0.20 g). [(Ar_F')Zn(µ-Cl)(OEt₂)]₂ was crystallised by slow diffusion of light petroleum into diethyl ether at -27 °C, leading to colourless crystals suitable for a single crystal X-ray diffraction study (0.25 g, 51%). $\delta_{\rm H}$ (300 MHz, C₆D₆) 3.45 (4H, q, *J* 7.1, OCH₂CH₃), 0.85 (6H, t, *J* 7.1, OCH₂CH₃). $\delta_{\rm F}$ (282 MHz, C₆D₆) -117.8 (4F, m, *F2*), -138.9 (4F, m, *F3* or *F2'*), -139.4 (4F, m, *F3* or *F2'*), -151.7 (2F, t, ³*J*_{EF} 22, *F4'*), -161.7 (4F, t, ³*J*_{EF} 22, *F3'*). Elemental analysis found: C, 37.80; H, 1.78. Calculated for C₃₂H₂₀Cl₂F₁₈O₂Zn₂: C, 39.21; H, 2.06.

$(Ar_{F}')_{2}Zn(OEt_{2})_{2}$ (10)

A solution of ZnCl_2 (2.5 mmol, 0.34 g) in room temperature diethyl ether (10 cm³) was treated with a solution of **1**, (20 cm³, 0.25 M, 5 mmol). The reaction was appreciably exothermic and some white solid precipitated within a few minutes. After 2 h the ¹⁹F NMR spectrum confirmed complete consumption of the Grignard

Table 2 Crystal data and refinement results for all samples

reagent. The solvent was then removed under vacuum and the resulting crude solid washed with light petroleum and extracted with a 1:4 mixture of dichloromethane–light petroleum (3 × 20 cm³). The solvent was then distilled off under reduced pressure affording a white solid. The product was purified by crystallisation from a diethyl ether–light petroleum solvent mixture (0.93 g, 54%). Slow diffusion of light petroleum into a diethyl ether solution held at -27 °C afforded crystals suitable for a single crystal X-ray diffraction study. $\delta_{\rm H}$ (300 MHz, C₆D₆) 3.62 (4H, q, J 7.1, OCH₂CH₃), 1.22 (6H, t, J 7.1, OCH₂CH₃). $\delta_{\rm F}$ (282 MHz, C₆D₆) –118.4 (4F, m, *F2*), –138.0 (4F, m, *F3* or *F2'*), –138.7 (4F, m, *F3* or *F2'*), –151.8 (2F, t, ³J_{EF} 21, *F4'*), –161.6 (4F, t, ³J_{EF} 21, *F3'*). Elemental analysis found: C, 45.24; H, 2.32. Calculated for C₃₂H₂₀ $\Gamma_{\rm I8}O_2$ Zn: C, 45.55; H, 2.39.

$(Ar_F)(Ar_F')Zn(THF)_2$ (11)

To a solution of **9** (0.1 g, 0.2 mmol) in tetrahydrofuran (10 cm³) C_6F_5MgBr (0.64 cm³ of a 0.625 M solution, 0.4 mmol) was added. The reaction mixture was then stirred for 2 h before all the volatile materials were removed under vacuum. The residue was washed with light petroleum (20 cm³) and extracted with toluene (3 × 20 cm³). After the toluene was distilled off under reduced pressure, the residue was purified by precipitation from a tetrahydrofuran solution following addition of light petroleum to give compound **11** as a colourless solid (0.12 g, 0.18 mmol, 45%). $\delta_{\rm H}$ (300 MHz, CDCl₃) 3.94 (8H, br, 2,5-THF), 1.92 (8H, m,

Crystal	4	4a MeCN	$5.3(C_6D_6)$	6- NCMe∙MeCN	7-NCMe·2(CH ₂ Cl ₂)	9	10
Empirical formula	CHESp	CUEPrSn		C H DE N	C H PE N		С Ц Е О 7m
Empiricariorniula	C151191'9511	$C_{14}\Pi_6\Pi_9$ DI SII	$C_{24}\Pi_3 B\Gamma_{18}O_2$.	$C_{26}\Pi_{3}D\Gamma_{19}\Pi_{7}$	2(CH, CL)	$O_{32}\Pi_{20}O_{12}\Pi_{18}$	$C_{32}\Pi_{20}\Pi_{18}O_2Z\Pi_$
Formula wt/g mol ⁻¹	478.9	584.8	928.5	742.2	1167.1	980.1	843.8
Crystal system, space	Triclinic, P1	Monoclinic.	Triclinic, P1	Monoclinic.	Triclinic, P1	Triclinic, P1	Monoclinic.
group	7	$P2_1/n$,	$P2_1/c$,		C2/c
a/Å	6.7641(4)	9.8151(2)	7.0808(2)	10.1502(4)	9.2820(4)	7.9926(12)	19.078(4)
b/Å	11.2250(8)	10.5666(3)	14.5619(7)	9.9420(3)	13.8838(5)	10.3081(15)	8.1176(8)
c/Å	11 2842(8)	18 0686(4)	18 4705(8)	27 4704(11)	17 4899(7)	11 1367(13)	20.494(3)
$\alpha/^{\circ}$	66.841(7)	90	92.210(2)	90	104.808(3)	78.391(11)	90
$\beta/^{\circ}$	83.121(6)	96.468(2)	95.502(3)	99.069(4)	89.136(3)	88.745(11)	91.363(14)
$\gamma/^{\circ}$	81.090(6)	90	99.797(2)	90	105.715(3)	76.934(13)	90
$V/Å^3$	776.59(9)	1862.01(8)	1865.15(13)	2737.47(17)	2094.05(14)	875.2(2)	3172.9(9)
Z	2	4	2	4	2	1	4
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	2.048	2.086	1.653	1.801	1.851	1.860	1.767
Abs. coeff. μ/mm^{-1}	1.739	3.605	0.160	0.197	0.439	1.651	0.912
Colour, habit	Colourless	Colourless	Colourless	Colourless	Colourless plates	Colourless	Colourless
	blocks	blocks	plates	plates	•	blocks	needles
Crystal dimensions/mm ³	$0.46 \times 0.16 \times$	$0.29 \times 0.15 \times$	$0.18 \times 0.04 \times$	$0.29 \times 0.19 \times$	$0.52 \times 0.16 \times 0.09$	$0.38 \times 0.20 \times$	$0.59 \times 0.09 \times$
	0.13	0.07	0.005	0.11		0.11	0.06
θ range/°	3.5 to 27.5	3.2 to 30.0	2.9 to 22.5	3.5 to 25.0	3.1 to 25.0	3.9 to 27.5	4.0 to 20.0
Reflections collected/	10427/3543/	28886/5427/	24007/4873/	28704/4798/	23775/7309/	11781/3976/	8721/1460/
unique/observed	3192	3624	3638	3031	3380	2532	997
R _{int}	0.022	0.057	0.062	0.087	0.078	0.052	0.104
Absorption T_{\min}/T_{\max}	0.84/1.24	0.86/1.17	0.82/1.00	0.84/1.16	0.89/1.09	0.88/1.08	0.91/1.13
No. of	3543/0/229	5427/0/254	4873/3/580	4798/0/476	7309/18/694	3976/0/272	1460/0/240
data/restraints/parameters							
Final R indices $[F^2 >$	0.038, 0.097	0.028, 0.049	0.052, 0.094	0.038, 0.058	0.047, 0.074	0.054, 0.133	0.044, 0.051
$2\sigma(F^2)$]: R_1, wR_2	0.042.0.000	0.061.0.055	0.004.0.104	0.000 0.000	0 1 4 2 0 00 1	0.002 0.145	0.000 0.050
<i>R</i> indices (all data):	0.043, 0.099	0.061, 0.055	0.084, 0.104	0.088, 0.066	0.143, 0.091	0.093, 0.145	0.089, 0.058
K_1, WK_2	4.50 1 0.00	0.70 and 0.96	0.24 and 0.26	0.00 and 0.00	0.45 and 0.41	1 24 1 0 01	0.22 and 0.22
hole/e Å ⁻³	4.39 and -0.90	0.70 and -0.86	0.24 and -0.26	0.22 and -0.20	0.43 and -0.41	1.24 and -0.81	0.55 and -0.33

3,4-THF). $\delta_{\rm F}$ (282 MHz, CDCl₃) –117.7 (4F, br, *F2* and *o*-*F* C_6F_5), -137.8 (2F, br, *F3* or *F2'*), –140.0 (2F, br, *F3* or *F2'*), –152.5 (1F, t, ³ $J_{\rm FF}$ 20, *p*-*F* C_6F_5), –157.0 (1F, br, *F4'*), –161.7 (2F, m, *m*-*F* C_6F_5), -162.1 (br, 2F, *F'3*). Elemental analysis found: C, 44.99; H, 2.37. Calculated for C₂₆H₁₆F₁₄O₂Zn: C, 45.14; H, 2.33.

Crystal structure analyses†

A suitable crystal was selected and data for **5** were measured at 120 K at the National Crystallography Service on a Bruker Nonius APEX II CCD Area Detector equipped with a Bruker Nonius FR591 rotating anode ($\lambda_{Mo-K\alpha} = 0.71073$ Å) driven by COLLECT³⁷ and processed by DENZO³⁸ software. For **4**, **4a**, **6**, **7**, **9** and **10**, data were collected at 140 K at UEA on an Oxford Diffraction Xcalibur-3 CCD diffractometer equipped with Mo-K α radiation and graphite monochromator, the data were processed using the CrysAlis-CCD and -RED³⁹ programs. The structures were determined in SHELXS-97 and refined using SHELXL-97.⁴⁰ Crystal data and refinement results for all samples are collated in Table 2.

The large difference peak in compound 4 was thought to be of a minor, disordered tin atom (the rest of this molecule was not identified); refinement including this partially occupied atom gave better *R*-indices and coordinate Esd's but the results presented here are for the complete major component only.

References

- 1 M. A. Garcia-Monforte, P. J. Alonso, J. Fornies and B. Menjon, *Dalton Trans.*, 2007, 3347–3359.
- 2 G. B. Deacon, C. M. Forsyth and S. Nickel, *J. Organomet. Chem.*, 2002, 647, 50–60.
- 3 J. G. Noltes and J. W. G. van den Hurk, *J. Organomet. Chem.*, 1963, **1**, 377–383.
- 4 A. G. Massey, F. G. A. Stone and A. J. Park, *Proc. Chem. Soc.*, 1963, 212.
- 5 (a) Y. Sun, W. E. Piers and M. Parvez, *Can. J. Chem.*, 1998, **76**, 513–517;
 (b) W. E. Piers, G. J. Irvine and V. C. Williams, *Eur. J. Inorg. Chem.*, 2000, 2131–2142;
 (c) S. Aboulkacem, W. Tyrra and I. Pantenburg, *Z. Anorg. Allg. Chem.*, 2003, **629**, 1569–1574;
 (d) W. E. Piers, *Adv. Organomet. Chem.*, 2005, **52**, 1–76.
- 6 S. Garratt, A. Guerrero, D. L. Hughes and M. Bochmann, *Angew. Chem.*, *Int. Ed.*, 2004, **43**, 2166–2169.
- 7 A. J. Mountford, S. J. Lancaster, S. J. Coles, P. N. Horton, D. L. Hughes, M. B. Hursthouse and M. E. Light, *Organometallics*, 2006, 25, 3837– 3847.
- 8 E. Martin, D. L. Hughes and S. J. Lancaster, *Eur. J. Inorg. Chem.*, 2006, 4037–4041.
- 9 E. Martin, C. Spendley, A. J. Mountford, S. J. Coles, P. N. Horton, D. L. Hughes, M. B. Hursthouse and S. J. Lancaster, *Organometallics*, 2008, **27**, 1436–1446.
- 10 (a) W. E. Piers and T. Chivers, *Chem. Soc. Rev.*, 1997, 26, 345–354;
 (b) E. Y.-X. Chen and T. J. Marks, *Chem. Rev.*, 2000, 100, 1391–1434;
 (c) M. Bochmann, S. J. Lancaster, M. D. Hannant, A. Rodriguez, M. Schormann, D. A. Walker and T. J. Woodman, *Pure Appl. Chem.*, 2003, 75, 1183–1195; (d) M. Bochmann, *J. Organomet. Chem.*, 2004, 689, 3982–3998; (e) G. Erker, *Dalton Trans.*, 2005, 1883–1890; (f) W. E. Piers, *Adv. Organomet. Chem.*, 2005, 52, 1–76.
- 11 E. Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern and T. J. Marks, J. Am. Chem. Soc., 1998, 120, 6287–6305.
- 12 (a) Northwestern University, T. J. Marks, L. Lubin and Y. S. Cheol, *Int. Pat.* Appl., WO0102445, 2001; (b) Univation Tech LLC, M. W. Holtcamp, *Int. Pat.* Appl., WO9964476, 1999; There are a number

of patent examples of the application of salts of the tetrakis(4nonafluorobiphenyl)borate anion in alkene polymerisation, see for example: ExxonMobil, L. S. Baugh, A. O. Patil, C. P. Mehnert, K. R. Squire, K. A. Cook, C. Gong, E. Berluche, K. S. Colle, A. J. Oshinski, S. Zushma and B. J. Poole, *Int. Pat.* Appl., WO2008008112, 2008.

- 13 A. Guerrero, E. Martin, D. L. Hughes, N. Kaltsoyannis and M. Bochmann, Organometallics, 2006, 25, 3311–3313.
- 14 V. I. Krasnov, A. S. Vinogradov and V. E. Platonov, Mendeleev Commun., 2006, 16, 168–170.
- 15 P. Sartori and M. Weidenbruch, Chem. Ber., 1967, 100, 3016.
- 16 W. T. Miller and K. K. Sun, J. Am. Chem. Soc., 1970, 92, 6985–6987.
- 17 D. A. Walker, T. J. Woodman, D. L. Hughes and M. Bochmann, Organometallics, 2001, 20, 3772–3776.
- 18 S. J. Lancaster, http://www.syntheticpages.org/pages/215; J. L. W. Pohlmann and F. E. Brinckman, Z. Naturforsch., 1965, 20b, 5–11.
- 19 For 4-bromo-2,3,5,6,2',3',4',5',6'-nonafluoro-biphenyl: $\delta_{\rm F}$ (282 MHz, 293 K, C₆D₆) –131.7 (m, 2F), –137.3 (m, 2F), –138.3 (m, 2F), –149.4 (t, 1F, ${}^{3}J_{\rm EF}$ = 22 Hz), –160.3 (m, 2F).
- 20 We note that the ¹⁹F NMR spectra show little sensitivity to solvent, as is illustrated by comparison of the benzene- d_6 and chloroform- d_1 spectra of compound **4**, both of which are given in the experimental section.
- 21 The respective ¹⁹F NMR chemical shifts for the *F2* position are: -118 ppm in C₆D₆ for Zn (9–11), -120 ppm for Hg (8), -121 ppm for Sn (4, 4a), -127 ppm for Si (2 and 3) and -133 ppm for B (6·NCMe and 7·NCMe).
- 22 W. Tyrra and M. S. Wickleder, Z. Anorg. Allg. Chem., 2002, 628, 1841– 1847.
- 23 M. V. Metz, D. J. Schwartz, C. L. Stern, T. J. Marks and P. N. Nickias, Organometallics, 2002, 21, 4159–4168.
- 24 D. J. Morrison, S. D. Riegel, W. E. Piers, M. Parvez and R. McDonald, *Chem. Commun.*, 2006, 2875–2877.
- 25 A. Karipides, C. Forman, R. H. P. Thomas and A. T. Reed, *Inorg. Chem.*, 1974, 13, 811–815.
- 26 It is not known whether the hydrolysis responsible for the generation of compound 5 occurred before or after dissolution in benzene- d_6 and therefore no supporting spectroscopic data are provided.
- 27 K. Ishihara and H. Yamamoto, Eur. J. Org. Chem., 1999, 527-538.
- 28 (a) T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, Organometallics, 2003, 22, 1588–1590; (b) T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, Organometallics, 2004, 23, 5493–5502; (c) T. Beringhelli, G. D'Alfonso, D. Donghi, D. Maggioni, P. Mercandelli and A. Sironi, Organometallics, 2007, 25, 2088–2095; (d) D. Donghi, D. Maggioni, T. Beringhelli, G. D'Alfonso, P. Mercandelli and A. Sironi, *Eur. J. Inorg.* Chem., 2008, 1645–1653.
- 29 Targor GMBH, J. Schottek and C. Fritze, *German Pat.* Appl., DE10009714, 2001; Basell Polyolefine GMBH, R. Kratzer, *German Pat.* Appl., DE10059717, 2001.
- 30 R. Duchateau, S. J. Lancaster, M. Thornton-Pett and M. Bochmann, Organometallics, 1997, 16, 4995–5005.
- 31 A. N. Chernega, A. J. Graham, M. L. H. Green, J. Haggitt, J. Lloyd, C. P. Mehnert, N. Metzler and J. Souter, J. Chem. Soc., Dalton Trans., 1997, 2293–2303.
- 32 C. Bergquist, B. M. Bridgewater, C. J. Harlan, J. R. Norton, R. A. Friesner and G. Parkin, *J. Am. Chem. Soc.*, 2000, **122**, 10581–10590.
- 33 Y. Sarazin, J. A. Wright, D. A. J. Harding, E. Martin, T. J. Woodman, D. L. Hughes and M. Bochmann, *J. Organomet. Chem.*, 2008, 693, 1494–1501.
- 34 M. Weidenbruch, M. Herrndorf, A. Schäfer, S. Pohl and W. Saak, J. Organomet. Chem., 1989, 361, 139–145.
- 35 The torsion angles describing the extent of the twist vary between 109.4 and 126.3° and are included as supplementary information[†].
- 36 Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, S. Tokito and Y. Taga, J. Am. Chem. Soc., 2000, 122, 1832–1833.
- 37 R. Hooft, COLLECT: Data collection software, Nonius, B.V., 1998.
- Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307–326.
 Programs CrysAlis-CCD and -RED, Oxford Diffraction Ltd., Abingdon, UK, 2005.
- 40 G. M. Sheldrick, Acta Crystallogr., Sect. A, 2008, A64, 112-122.