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A study of representative alcohol, alkoxide, thiol and thiolate complexes of $B(C_6F_5)_3$; their roles as activators of zirconocene olefin polymerization initiators

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Abstract

The highly electrophilic borane $B(C_6F_5)_3$ reacts with *n*-octadecanol ($n\text{-}C_{18}H_{37}OH$) and *n*-octadecanethiol ($n\text{-}C_{18}H_{37}SH$) to form equilibrium mixtures of reactants and the 1:1 adducts $(n\text{-}C_{18}H_{37}EH)B(C_6F_5)_3$ (E = O, S); equilibrium constants for adduct formation are determined. The adducts are deprotonated by 1,8-bis(dimethylamino)naphthalene (proton sponge) to form the salts $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}O)B(C_6F_5)_3]$ and $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]$, respectively, and by Cp_2ZrMe_2 to give methane and, apparently, the unstable zirconium complexes $[Cp_2ZrMe][(n\text{-}C_{18}H_{37}E)B(C_6F_5)_3]$. The alcohol, alkoxide, thiol and thiolate systems are characterized in solution by ^1H, ^{19}F, $^{13}C\{^1H\}$ and ^{11}B NMR spectroscopy and in the solid state by FAB mass spectrometry, and it is also shown that proton sponge can coordinate in monodentate fashion to $B(C_6F_5)_3$. © 2002 Published by Elsevier Science B.V.

Keywords: Borate complexes; Alkoxide complexes; Thiolate complexes; Olefin polymerization

1. Introduction

Recent years have seen huge advances in the development of well–defined, cationic substituted cyclopentadienyl (Cp′) complexes of the Group 4 metals as alkene polymerization catalysts [1]. In the most studied catalyst systems, the active species are generated from neutral metallocene precursors as in Eqs. (1) and (2), reactions which involve the abstraction of methyl carbanions from the metals by $B(C_6F_5)_3$ and trityl ion, respectively.

$$\begin{tikzcd} \mathrm{Cp'_2ZrMe_2 + B(C_6F_5)_3} \arrow[r] & \mathrm{Cp'_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3} \arrow[d, shift left] \\ & \text{"}\mathrm{[Cp'_2ZrMe]}\text{"}^{+} + \mathrm{[MeB(C_6F_5)_3]^-} \arrow[u, shift left] \end{tikzcd} \qquad (1)$$

$$\begin{tikzcd} \mathrm{2Cp'_2ZrMe_2 + [Ph_3C][B(C_6F_5)_4]} \arrow[r] & \mathrm{[Cp'_2ZrMe(\mu\text{-}Me)ZrMeCp'_2][B(C_6F_5)_4] + Ph_3CMe} \arrow[d, shift left, "\mathrm{[Ph_3C][B(C_6F_5)_4]}"'] \\ & 2\text{"}\mathrm{[Cp'_2ZrMe]}\text{"}^{+} + \mathrm{2[B(C_6F_5)_4]^- + Ph_3CMe} \arrow[u, shift left] \end{tikzcd} \qquad (2)$$

The methylborate anion of Eq. (1) coordinates relatively strongly to the electron deficient cations, and the dissociation postulated is evidenced only from the chemistry of the complexes formed. In contrast, the tetrakis(pentafluorophenyl)borate anion of Eq. (2) forms such weakly associated ion pairs that the equilibrium shown lies well toward the dizirconium species. Again, however, the chemistry of the complexes formed implies the ready availability of $[Cp_2'ZrMe]^+$ [1]. Of course, in order for an initiator system to exhibit high activity, the monomer must be able to coordinate readily. Since this generally involves accessing the putative 14-electron intermediate $[Cp_2'ZrMe]^+$ by displacement of the counteranions, considerable attention has been paid to determining the coordinating abilities of anionic species such as $[MeB(C_6F_5)_3]^-$ and $[B(C_6F_5)_4]^-$, and correlating their ease of dissociation with catalyst activities [2].

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Considerable research has also been carried out in efforts to design new anions which are even more weakly coordinating than those mentioned above [3]. The approaches are generally based on the premise that delocalization of negative charge over as many atoms as possible in a large anion will be of advantage, and a wide variety of anionic species has been reported [3]. In metallocene catalyst chemistry, the synthetic methodologies have often involved modification of the borate anion of Eq. (1), for instance, by substitution of the groups on boron by more complex fluoroaryl groups [2d,2e,4]. The bulkier anions do indeed coordinate less well than does $[MeB(C_6F_5)_3]^-$, and form more active catalysts.

An alternative and rather simpler procedure synthetically involves the interaction of $B(C_6F_5)_3$ with various anions X^- (X^- = e.g. OH^- [5], CN^- [2f,6], N_3^- [6b], OR^- [5b,5c,5d,5k], SR^- [5b,5c,5d]-imidazolate [7]) to form complex anions of the types $[XB(C_6F_5)_3]^-$ and $[(\mu\text{-}X)\{B(C_6F_5)_3\}_2]^-$. Research on the hydroxyl system has a long history, and it has been well established that, because of the strongly electron withdrawing character of $B(C_6F_5)_3$, the aqua complex $H_2OB(C_6F_5)_3$ is a strong Brønsted acid capable of acid cleavage of metal-carbon bonds as in Eq. (3) [5a,5c,5d,5e].

$$Cp'_2ZrMe_2 + H_2OB(C_6F_5)_3 \rightarrow [Cp'_2ZrMe][(HO)B(C_6F_5)_3] + CH_4 \quad (3)$$

There result organometallic complexes, similar to those shown in Eqs. (1) and (2), which have been shown to catalyze alkene polymerization [5b,5c,5d,5e]. Coordination of alcohols ROH (R = alkyl) to $B(C_6F_5)_3$ similarly gives the 1:1 adducts $(ROH)B(C_6F_5)_3$ [5b,5c,5d,5k], and these appear to exhibit sufficiently enhanced acidity that they also cleave metal-carbon bonds (Eq. (4)) to give the cationic products which behave as alkene polymerization catalysts [5b,5c,5d].

$$Cp'_2ZrMe_2 + (ROH)B(C_6F_5)_3 \rightarrow [Cp'_2ZrMe][(RO)B(C_6F_5)_3] + CH_4 \quad (4)$$

Thus a wide variety of new, readily synthesized activators containing bulky counteranions is now apparently available. However, few such systems have as yet been studied in detail, and while crystalline alcohol adducts of $B(C_6F_5)_3$ can be isolated from non-polar solvents such as pentane [5c,5k], in fact little is known of their solution chemistry. Indeed, 1:1 adducts with a variety of N- [5k,8a] O- [5k,8b] and P-donors [8c] exhibit relatively small association constants and high labilities, while $B(C_6F_5)_3$ itself undergoes B–C cleavage in the presence of proton sources [8c]. In addition, Zr–O bonds are generally stronger than B–O bonds [9], leading to the possibility of ligand exchange and the formation of alkoxy-zirconium compounds, while simple alcohols can induce the same methyl protonation shown in Eq. (4) even in the absence of $B(C_6F_5)_3$ [10]. Thus, in a solution containing *e.g.* Cp'_2ZrMe_2, an alcohol and $B(C_6F_5)_3$, one wonders what species might actually be present.

We describe here the results of an investigation of the *solution* chemistry, in the presence and absence of base, of Brønsted acidic alcohol (*n*-octadecanol, *n*-$C_{18}H_{37}OH$) and thiol (*n*-octadecanethiol, *n*-$C_{18}H_{37}SH$) adducts of $B(C_6F_5)_3$. Anticipating further investigations of the adducts as co-initiators, with Cp'_2ZrMe_2, for alkene polymerization, we have also studied reactions of the alcohol and alcohol adducts in solution with Cp_2ZrMe_2. The high molecular weight, long chain *n*-octadecanol and *n*-octadecanethiol were chosen in part because measuring of millimole quantities would be more accurate than with low molecular weight analogues, in part with the expectation that ionic species of the type formed in Eq. (4) might exhibit better solubilities and hence more useful catalytic properties in non-polar solvents.

2. Results and discussion

2.1. Adduct formation with primary alcohol and thiol

The adducts of $B(C_6F_5)_3$ with *n*-octadecanol (*n*-$C_{18}H_{37}OH$, **1**) and *n*-octadecanethiol (*n*-$C_{18}H_{37}SH$, **4**) form rapidly on mixing $B(C_6F_5)_3$ and *n*-octadecanol or *n*-octadecanethiol in CD_2Cl_2 or toluene-d_8.

$$B(C_6F_5)_3 + nC_{18}H_{37}EH \rightleftharpoons (nC_{18}H_{37}EH)B(C_6F_5)_3 \quad E = O(\mathbf{2}),\ S(\mathbf{5}) \quad (5)$$

The adducts have previously been reported by Siedle et al. [5c,5d], but no characterizing data were presented. The reactions can, however, be conveniently studied by NMR spectroscopy using a range of nuclei, ^1H, ^{13}C, ^{11}B and ^{19}F, which are highly sensitive to the coordination and electronic environment. Thus, on adding one molar equivalent of $B(C_6F_5)_3$ to a solution of *n*-octadecanol (~1 mM) in CD_2Cl_2, the O*H* resonance shifted from δ 1.38 (m) to δ 6.19 (broad singlet), indicating significant exchange of coordinated alcohol with, presumably, a small amount of free *n*-octadecanol remaining in solution under these circumstances (see below). Similarly the OC*H₂* ^1H and O*C*H₂ $^{13}C\{^1H\}$ resonances shifted from δ 3.58 (triplet, $^3J_{HH}$ 6.5 Hz) and 63.3 to δ 4.02 (triplet, $^3J_{HH}$ 6.9 Hz) and 70.5, respectively. On the addition of 0.1 or greater molar equivalents of $B(C_6F_5)_3$, however, the O*H* resonance changed to a well-resolved triplet and the OC*H₂* resonance to a double triplet, suggesting that the concentration of the free alcohol had been effectively reduced to the point that exchange was now no longer observable.

The other ^{1}H and ^{13}C resonances shift relatively little, but the ^{11}B resonance of $B(C_6F_5)_3$ shifts from δ 63.3 to 3.8 and the *o*-F, *m*-F and *p*-F ^{19}F resonances shift from δ −129.1, −162.0 and −144.7 to δ −134.9, −168.3 and −164.9, respectively. The changes in the ^{11}B and the ^{19}F NMR spectra are all consistent with change in the coordination number of the boron from three to four [5i,8a,11]. Similar changes were observed on the addition of one molar equivalent of $B(C_6F_5)_3$ to a solution of *n*-octadecanethiol in CD_2Cl_2, the S*H* resonance shifting from δ 1.35 (triplet, $^{3}J_{HH}$ 7.9 Hz) to δ 3.35 (triplet, $^{3}J_{HH}$ 8.0 Hz), the SC*H₂* ^{1}H and S*C*H₂ $^{13}C\{^{1}H\}$ resonances shifting from δ 2.51 and 65.1 to δ 2.54 and 24.9, respectively. Important NMR data for these systems are listed in Table 1.

Since alcohols contain two lone pairs, the 2:1 adduct $\{(n\text{-}C_{18}H_{37}OH)\{B(C_6F_5)_3\}_2$ could in principle also form and play a role in dimethyl zirconocene activation analogous to the chemistry depicted in Eq. (4). The stoichiometry of the *n*-octadecanol reaction was therefore determined using the mole ratio method [12]. The concentration of the *n*-octadecanol was kept constant and the ratio with respect to the borane was varied from 0.6:1 to 5:1. The chemical shift of the OC*H₂* protons of *n*-octadecanol was observed using ^{1}H NMR spectroscopy, as this is highly sensitive to coordination. The experimental data are presented as supplementary information (Table S1) and, as shown in Fig. 1, a plot of the change in chemical shift, $\Delta\delta$, as a function of borane concentration resulted in two lines intersecting at an approximate ratio of 1:1 and well away from the intersection point for a 2:1 reaction, confirming the anticipated 1:1 stoichiometry.

During this study, some decomposition of the product was noted at higher $B(C_6F_5)_3$ to *n*-octadecanol ratios, a weak ^{1}H resonance of C_6F_5H being observed at δ 6.96 (m). This observation suggests the partial metathesis of the adduct to C_6F_5H and $B(OC_{18}H_{37})(C_6F_5)_2$, but the decomposition was only on the order of 1–3% and did not seriously affect the determination of stoichiometry. Equilibrium constant measurements for the 1:1 complex were carried out, using the dilution procedure [13], with solutions sufficiently dilute (7×10^{-4}–2×10^{-2} mol l^{-1}) that C_6F_5H did not form. The procedure involved diluting portions of a standard solution to known concentrations, *x*, while monitoring the ^{1}H chemical shifts of the OC*H₂* protons of the *n*-octadecanol. The data, which are presented as supplementary information (Table S2), were fitted to Eq. (6) [13]. In Eq. (6), Δ is the difference between the observed chemical shift of the probe protons in the solutions of the 1:1 adduct at equilibrium and that of the same proton in the free component, Δ_0 ($\delta_{comp} - \delta_{free}$) is the difference between the limiting chemical shift of the probe protons in the 1:1 adduct and that of the protons in the free component ($\delta_{100\%\ comp} - \delta_{free}$) and *x* is the concentration (in mol l^{-1}) of the 1:1 adduct.

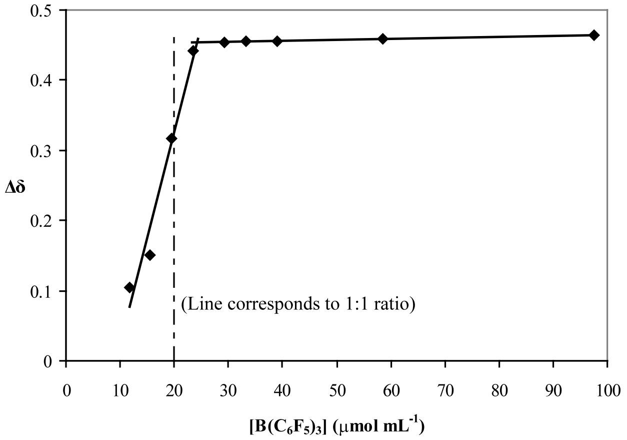


Fig. 1. Plot of the change in chemical shift, $\Delta\delta$, of the OC*H₂* protons of *n*-octadecanol vs. borane concentration.

Table 1
Selected NMR spectroscopy data (δ) for **1**–**6** in CD_2Cl_2 and toluene-d$_8$ (E = O, S)

Data	CD_2Cl_2			Toluene-d$_8$				
	^{1}H, E*H*	^{1}H, EC*H₂*	^{13}C, E*C*H₂	^{1}H, E*H*	^{1}H, EC*H₂*	^{13}C, E*C*H₂		
1	1.38	3.58	63.3	0.43	3.33	62.7		
2 [a]	6.19	4.02	70.5	5.93	3.35	67.9		
3	–	3.62	65.1	–	3.07	65.3		
4	1.35	2.51	24.9	1.06	2.18	24.6		
5 [a]	3.35	2.54	29.4	2.57	2.00	29.0		
6	–	1.93	29.7	–	2.41	30.3		
	B(C₆F₅)₃	*o*-F	*m*-F	*p*-F	*B*(C₆F₅)₃	*o*-F	*m*-F	*p*-F
B(C₆F₅)₃	57.9	−129.1	−162.0	−144.7	60.0	−129.7	−161.1	−142.8
2 [a]	3.8	−134.9	−168.3	−164.9	3.2	−135.5	−163.0	−155.1
3	−2.4	−133.9	−168.4	−165.0	−3.1	−135.6	−167.4	−164.0
5 [a]	12.9	−131.9	−163.6	−153.1	9.6	−131.9	−162.7	−152.1
6	−11.2	−132.9	−168.4	−164.6	−10.4	−131.8	−167.4	−163.3

[a] The chemical shifts noted for **2** and **5** are averages of the chemical shifts of the free and coordinated species. The concentrations used to acquire these data may be found in Section 3.

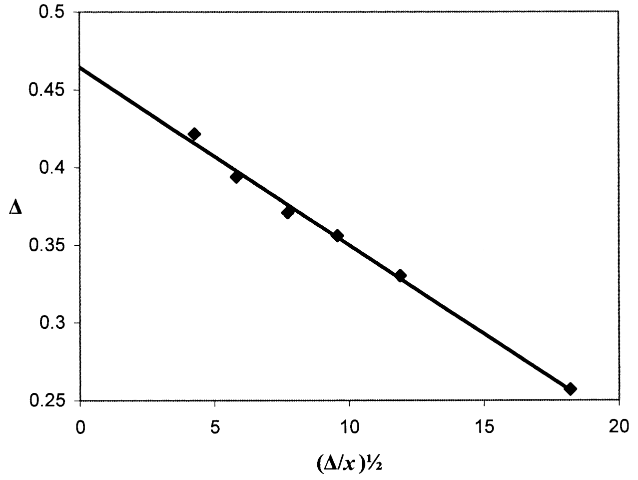


Fig. 2. Plot of Δ vs. $(\Delta/x)^{1/2}$.

$$\Delta = \Delta_0\text{-}(\Delta/x)^{1/2}(\Delta_0/K_{eq})^{1/2} \quad (6)$$

The results are shown in Fig. 2, where the slope $(-(\Delta_0/K_{eq})^{\frac{1}{2}})$ yields an equilibrium constant K_{eq} of 3600 ± 180 mol^{-1} l^{-1} at 298 K.

The above method for the derivation of K_{eq} relies on the reliable determination of the chemical shifts of free, unassociated n-octadecanol. In CD_2Cl_2, the chemical shifts of the OH and OCH_2 resonances were found to be concentration dependent above 0.1 mol l^{-1}, indicating varying amounts of hydrogen-bonding, but not in the range $0.1-3 \times 10^{-3}$ mol l^{-1}, where presumably essentially unassociated, monomeric n-octadecanol molecules pertained. When the same system was examined in toluene-d_8, however, the chemical shifts of the OH and OCH_2 resonances varied over the entire useful concentration range ($0.1-3 \times 10^{-3}$ mol l^{-1}), and thus some degree of molecular association in the form of hydrogen bonding was apparently present at all concentrations. For this reason, neither the stoichiometry nor the equilibrium constant for the reaction of n-octadecanol and $B(C_6F_5)_3$ could be determined in this solvent.

The mole ratio analysis was also applied to the n-octadecanethiol system in CD_2Cl_2 and toluene-d_8 to ascertain the stoichiometry; in contrast to the n-octadecanol-borane system, decomposition of the adduct to C_6F_5H was not observed at high borane to n-octadecanethiol ratios (5–20:1). The data again indicated a 1:1 stoichiometry, and this was confirmed using the program EQNMR by modeling the 2:1 and 1:1 cases [14]. The thiol proton was observed throughout the whole range of $B(C_6F_5)_3$:n-octadecanethiol ratios, 20:1–1:5. No exchange of this proton was observed, as in the case of n-octadecanol, allowing us to use this as a probe to measure K_{eq} in CD_2Cl_2 and toluene-d_8. The program EQNMR was used in this case to extract K_{eq} giving values of 462 ± 30 and 370 ± 30 mol^{-1} l^{-1} at 298 K in CD_2Cl_2 and toluene-d_8, respectively.

All attempts to isolate the pure 1:1 adducts, $(n\text{-}C_{18}H_{37}EH)B(C_6F_5)_3$ (E = O, S) failed, presumably in part because the n-$C_{18}H_{37}$ chains ensured that oils were inevitably obtained, in part because of facile dissociation. Indeed, plots showing the extent of coordination of both ligands as a function of borane concentration (Fig. 3) indicate that, at 1:1 ratios, there are appreciable fractions, 0.12 and 0.30, of free n-octadecanol and n-octadecanethiol, respectively. Thus, as expected, the presumably hard Lewis acidic borane exhibits a distinct preference for the relatively hard alcohol.

The equilibrium constants obtained for n-octadecanol and n-octadecanethiol are similar to those reported by Piers et al. [8b] for reactions of $B(C_6F_5)_3$ with a series of carbonyl compounds in benzene-d_6. From the value for K_{eq}, we can derive a value of ΔG^0 of -20.3 kJ mol^{-1} for n-octadecanol in CD_2Cl_2, and -15.2 and -14.7 kJ mol^{-1} for n-octadecanethiol in CD_2Cl_2 and toluene-d_8, respectively.

2.2. Deprotonation of $(n\text{-}C_{18}H_{37}EH)B(C_6F_5)_3$ (E = O, S)

We can infer from the downfield shifts of the alcohol OH and thiol SH protons on coordination that the electron withdrawing power of the $B(C_6F_5)_3$ induces significant increases in the alcohol and thiol acid strengths. In agreement with this deduction, ^1H NMR spectroscopy showed that while neither n-octadecanol nor n-octadecanethiol react in CD_2Cl_2 with the strong, non-nucleophilic base 1,8-bis (dimethylamino) naphthalene [15] (proton sponge, $C_{10}H_6(NMe_2)_2$), addition of one molar equivalent of proton sponge to a 1:1 mixture of n-octadecanol or n-octadecanethiol and $B(C_6F_5)_3$ resulted in the rapid formation of the protonated amine (δ 19.34) and the anion, (Eq. (7), E = O, S).

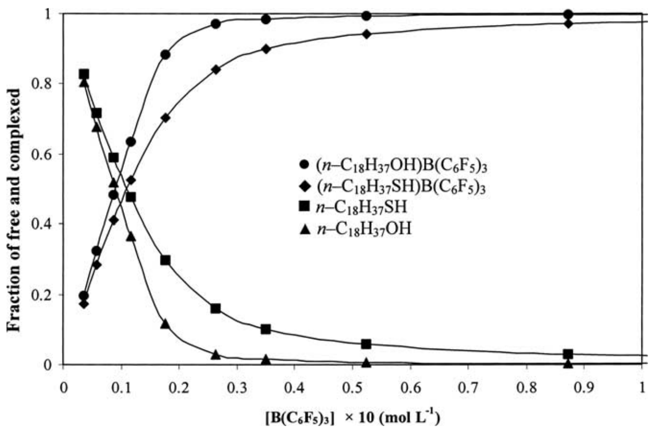
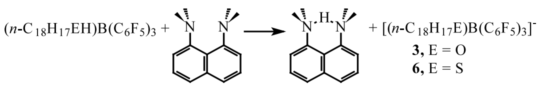


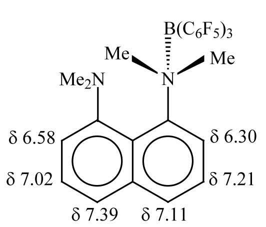
Fig. 3. Plots showing fraction of free and complexed n-octadecanol and n-octadecanethiol, (both 1.75×10^{-2} mol l^{-1} initial concentration), as a function of increasing borane concentration in CD_2Cl_2.



(7)

In the case of n-octadecanol, ^1H and ^{19}F NMR spectroscopy indicated that conversion to the cation and anion was rapid and quantitative, and the product was obtained in 84% isolated yield (see Section 3). As anticipated, deprotonation of the 1:1 adduct results in upfield shifts of the OCH_2 ^1H and OCH_2 ^{13}C resonances, by 0.40 and 5.4 ppm, respectively. The ^{11}B and ^{19}F chemical shifts also change, as indicated in Table 1. Similar results were obtained in CD_2Cl_2 with the thiol, the SH resonance disappearing and being replaced by the NH resonance at δ 19.34. There were complementary shifts of the SCH_2 ^1H and SCH_2 ^{13}C resonances, as well as of the ^{11}B and ^{19}F resonances (Table 1), and the product was obtained in 48% isolated yield (see Section 3).

The lowered isolated yield may come about in part because a small portion of the proton sponge coordinates in an unusual *monodentate* fashion to the borane. A ^1H NMR spectrum of a 1:1:1 ratio of thiol, proton sponge and $B(C_6F_5)_3$ in CD_2Cl_2 at 298 K revealed, in addition to the expected resonances of $[C_{10}H_7(NMe_2)_2][(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]$, a set of weak resonances tentatively attributable to the 1:1 adduct $[(C_{10}H_6(NMe_2)_2)B(C_6F_5)_3]$. While the latter has not been isolated, the ^1H NMR spectrum clearly shows that *both* planes of symmetry of the proton sponge framework have been lost. Thus there are six single-hydrogen aromatic resonances at δ 7.39 (d, $J = 7.2$ Hz), 7.21 ('t', $J = 8.0$ Hz), 7.11 (d, $J = 7.8$ Hz), 7.02 ('t', $J = 8.1$ Hz), 6.58 (d, $J = 7.5$ Hz) and 6.30 (d, $J = 7.5$ Hz), in addition to a broad, six-hydrogen methyl resonance at δ 2.33 and two three-hydrogen methyl resonances at δ 2.54 and 2.61. Thus the structure would appear to be as in **A**, with the N–B bond more or less perpendicular to the $C_{10}H_6$ plane.



A

The three-hydrogen methyl resonances are reasonably attributed to the NMe_2 group coordinated to the borane, and are presumably rendered non-equivalent because of restricted rotation about the N–aryl bond. The resulting asymmetry results in non-equivalence of the free NMe_2 methyl groups, resulting in their six-hydrogen resonance being broad. The ring hydrogen resonances have been assigned using a COSY experiment, and the resulting assignments are also shown.

The compounds $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}EH)B(C_6F_5)_3]$ (E = O, S) could not be characterized satisfactorily by elemental analyses as apparent inclusion of free alcohol or thiol could seemingly not be avoided. However, they were readily characterized by fast atom bombardment (FAB) mass spectrometry, the positive ion of both being confirmed as the protonated proton sponge ion, $[C_{10}H_6(NMe_2)_2H]^+$ (FAB+ m/e 215.3), the molecular ions of $[(n\text{-}C_{18}H_{37}O)B(C_6F_5)_3]^-$ and $[(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]^-$ also being observed at m/e values of 781.1 and 797.2, respectively.

Interestingly, addition of excess borane to a solution of $[C_{10}H_6(NMe_2)_2][(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]$ in CD_2Cl_2 resulted in changes of the chemical shifts of the ^1H NMR and ^{19}F resonances. The changes were small, generally < 1 ppm in the ^1H NMR spectra, but the ^{19}F resonances of the anion and the free borane were averaged, suggesting a facile equilibrium between $[(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]^-$ and the 2:1 species $[(n\text{-}C_{18}H_{37}S)\{B(C_6F_5)_3\}_2]^-$. Similar observations were not made with the n-octadecanol system, possibly because the smaller oxygen cannot accommodate two borane molecules.

2.3. Reactions between Cp_2ZrMe_2 and *n*-octadecanol

The reaction of Cp_2ZrMe_2 with an equivalent of n-octadecanol in CD_2Cl_2 at −50 °C resulted in the formation of methane (δ 0.18) and, apparently, two new Cp-zirconium compounds. A ^1H NMR spectrum run immediately showed, in addition to the resonances of unreacted n-octadecanol and Cp_2ZrMe_2, two new Cp resonances at δ 5.92 and 5.98, two apparent Zr–Me resonances at δ −0.094 and −0.17 and a triplet OCH_2 resonance at δ 3.76. On warming to 20 °C, the NMR spectrum indicated that the reaction had proceeded further, but the resonances of Cp_2ZrMe_2 and n-octadecanol were still present. On prolonged standing at 20 °C, the spectrum became very complicated. Reaction of Cp_2ZrMe_2 with 0.5 equiv. of n-octadecanol at −50 °C resulted in little reaction after 10 min, but reaction of Cp_2ZrMe_2 with 2 equiv. of n-octadecanol at 20 °C resulted in immediate disappearance of the resonances of the Cp_2ZrMe_2 and the appearance of the resonance of methane, of the Cp and Zr–Me resonances mentioned above and of the OCH_2 resonance mentioned above. We suspect the formation of the alkoxy species $Cp_2Zr(Me)(OC_{18}H_{37})$, but all attempts to synthesize this resulted in the formation of a waxy mixture with a complicated NMR spectrum.

2.4. Reactions of Cp_2ZrMe_2 with 1:1:1 *n*-octadecanol, $B(C_6F_5)_3$ and proton sponge

A reaction of Cp_2ZrMe_2 with an equimolar amount of $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}O)B(C_6F_5)_3]$ in CD_2Cl_2

at −20 °C was monitored by ^1H NMR spectroscopy. After 10 min, in addition to resonances of the starting materials (~ 70% of the original intensities), the spectrum exhibited a methane resonance at δ 0.186, two new Cp resonances at δ 5.94 and 5.99, two new Zr–Me resonances at δ −0.07 and −0.11 and an OCH_2 resonance at δ 3.82. Some of these are probably to be attributed to the above mentioned $Cp_2Zr(Me)(OC_{18}H_{37})$, but again warming the reaction mixture resulted in considerable decomposition. A similar reaction but in the presence of a second equivalent of $B(C_6F_5)_3$ resulted in a complex ^1H NMR spectrum which exhibited the resonances of protonated proton sponge and of the borate anion $[MeB(C_6F_5)_3]^-$ (δ 0.42), but no methane resonance. Interestingly, only a single set of ^{19}F resonances were observed, attributable to $[MeB(C_6F_5)_3]^-$, and it appears that in this case the major species formed are alkoxy zirconium compounds and $[C_{10}H_6(NMe_2)_2H]$-$[MeB(C_6F_5)_3]$. Certainly the anticipated catalytic cation $[Cp_2ZrMe]^+$ is not a major species in solution [5b,5c,5d,5e].

3. Experimental

All operations were performed under purified argon using normal Schlenk techniques or an MBraun Labmaster glove box. Solvents were purified by standard methods, and distilled and degassed before use. All 1D ^1H, ^{11}B, $^{13}C\{^1H\}$ and ^{19}F NMR spectra and 2D COSY, HMQC and HSQC spectra, (used for assignment), were recorded using Bruker AC-200 or Avance 300, 400 or 500 spectrometers, chemical shifts being determined by reference to residual ^1H and ^{13}C solvent peaks for ^1H and $^{13}C\{^1H\}$ studies, external $CFCl_3$ for ^{19}F studies and $BF_3 \cdot Et_2O$ for ^{11}B. The compounds Cp_2ZrMe_2 [9] and $B(C_6F_5)_3$ [8d] were prepared according to published procedures. 1,8-(Dimethylamino) naphthalene was purchased from Aldrich and sublimed before use. Toluene-d_8 and CD_2Cl_2 were dried over sodium–benzophenone and CaH_2, respectively, and vacuum transferred prior to use. The ‘’ in the text indicates a resonance of a deceptively simple nature.

n-Octadecanol (**1**) and *n*-octadecanethiol (**4**) were purchased from Aldrich and recrystallized before use. Full NMR data are given in the supplementary material.

3.1. Formation of $(n\text{-}C_{18}H_{37}OH)B(C_6F_5)_3$ (**2**)

To $B(C_6F_5)_3$ (10 mg, 18.5 μmol) and **1** (5 mg, 18.5 μmol) in a 5 mm NMR tube was added 1 ml of deuterated solvent at room temperature (r.t.). ^1H NMR (298 K, CD_2Cl_2) 6.19 (br s, 1H, O*H*) 4.02 (t, *J* = 6.9 Hz, 2H, OC*H*$_2$); 1.79 (m, 2H, -C*H*$_2$); 1.26 (m, 30H, C*H*$_2$); 0.86 (t, *J* = 6.7 Hz, 3H, C*H*$_3$). (298 K, toluene-d_8) 5.93 (br s, 1H, O*H*) 3.35 (t, *J* = 6.2 Hz, 2H, OC*H*$_2$); 1.39–0.78 (m, 35H, C*H*$_2$). $^{13}C\{^1H\}$ (298 K, CD_2Cl_2): 148.2 (dm, J_{FC} = 239.4 Hz, *ortho* *C*F); 140.9 (dm, J_{FC} = 253.4 Hz, *para* *C*F); 137.6 (dm, J_{FC} = 249.0 Hz, *meta* *C*F) 116.2 (*ipso C*); 70.5 (O*C*H$_2$); 32.3, 30.7, 30.1, 30.0, 29.9, 29.8, 29.4, 25.4, 23.1 (*C*H$_2$); 14.3 (*C*H$_3$). (298 K, toluene-d_8) 147.8 (dm, J_{FC} = 244.6 Hz, *ortho* *C*F); 140.4 (dm, J_{FC} = 256.5 Hz, *para* *C*F); 137.2 (dm, J_{FC} = 252.8 Hz, *meta* *C*F) 115.2 (*ipso C*); 67.9 (O*C*H$_2$); 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 24.7, 22.7 (*C*H$_2$); 13.8 (*C*H$_3$). ^{19}F NMR: (298 K, CD_2Cl_2) −134.9 (d, *J* = 21.7 Hz, 2F, *ortho*); −164.9 (t, *J* = 20.9 Hz, 1F, *para*); −168.3 (m, 2F, *meta*). (298 K, toluene-d_8) −135.5 (d, *J* = 21.5 Hz, 2F, *ortho*); −155.1 (t, *J* = 20.3 Hz, 1F, *para*); −163.0 (m, 2F, *meta*). ^{11}B NMR: (298 K, CD_2Cl_2) 3.8. (298 K, toluene-d_8) 3.2.

3.2. Formation of $(n\text{-}C_{18}H_{37}SH)B(C_6F_5)_3$ (**5**)

To $B(C_6F_5)_3$ (8.9 mg, 15.5 μmol) and **4** (5.0 mg, 15.5 μmol) in a 5 mm NMR tube was added 1 ml of deuterated solvent at r.t. ^1H NMR (298 K, CD_2Cl_2) 3.35 (t, *J* = 8.0 Hz, 1H, S*H*); 2.54 (‘q’, *J* = 7.6 Hz, 2H, SC*H*$_2$); 1.67 (‘q’, *J* = 7.04 Hz, 2H, C*H*$_2$); 1.35 (m, 2H, C*H*$_2$); 1.26 (m, 28H, C*H*$_2$); 0.88 (t, *J* = 7.0 Hz, 3H, C*H*$_3$). (298 K, toluene-d_8) 2.57 (t, *J* = 7.8 Hz, 1H, S*H*); 2.00 (‘q’, *J* = 7.4 Hz, 2H, SC*H*$_2$); 1.34 (m, 24H, C*H*$_2$); 1.16 (m, 2H, C*H*$_2$); 1.12 (m, 2H, C*H*$_2$); 1.04 (m, 2H, C*H*$_2$); 0.96 (m, 2H, C*H*$_2$); 0.92 (t, *J* = 7.1 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ (298 K, CD_2Cl_2): 148.5 (dm, J_{FC} = 243.9 Hz, *ortho* *C*F); 142.1 (dm, J_{FC} = 243.5 Hz, *para* *C*F); 137.7 (dm, J_{FC} = 261.5 Hz, *meta* *C*F) 114.3 (*ipso C*); 32.3 (ρ-*C*H$_2$); 31.6 (β-*C*H$_2$); 30.1, 30.0, 29.9, 29.8, 29.7 (*C*H$_2$); 29.4 (α-*C*H$_2$); 29.2 (*C*H$_2$); 28.7 (γ-*C*H$_2$); 23.1 (θ-*C*H$_2$); 14.3 (*C*H$_3$). (298 K, toluene-d_8) 148.5 (dm, J_{FC} = 261.0 Hz, *ortho* *C*F); 142.2 (dm, J_{FC} = 257.1 Hz, *para* *C*F); 137.8 (dm, J_{FC} = 257.3 Hz, *meta* *C*F) 114.4 (*ipso C*); 32.4, 31.1, 30.3, 30.2, 30.1, 29.9, 29.8, 29.3 (*C*H$_2$); 29.0 (S*C*H$_2$); 28.4, 23.2 (*C*H$_2$); 14.4 (*C*H$_3$). ^{19}F NMR: (298 K, CD_2Cl_2) −131.9 (d, *J* = 16.6 Hz, 2F, *ortho*); −153.1 (s, 1F, *para*); −163.6 (m, 2F, *meta*). (298 K, toluene-d_8) −131.9 (s, 2F, *ortho*); −152.1 (s, Hz, 1F, *para*); −162.7 (m, 2F, *meta*). ^{11}B NMR: (298 K, CD_2Cl_2) 12.9. (298 K, toluene-d_8) 9.6.

3.3. Determination of the stoichiometry of the reaction of *n*-octadecanol and $B(C_6F_5)_3$

A series of solutions was prepared by dissolving *n*-octadecanol (5 mg, 20 μmol) and varying amounts of $B(C_6F_5)_3$ (0.6:1–5:1) in 1 ml CD_2Cl_2 in several 5 mm NMR tubes. The solutions were allowed to react for 1 h before measurement of the ^1H NMR spectra; see Table S1, supplementary material, for data.

3.4. Measurement of equilibrium constant of the reaction of *n*-octadecanol and $B(C_6F_5)_3$

The equilibrium constant for the adduct formation was measured using ^{1}H NMR methods. Samples for observing the complexed proton shift were prepared from a stock solution of $B(C_6F_5)_3$ (40 mg, 8×10^{-5} mol) and *n*-octadecanol (21 mg, 8×10^{-5} mol), dissolved in CD_2Cl_2 (1 ml, 1.362 g). The vessel was sealed and left to react for 1 h. Portions of this solution were then placed in 5 mm NMR tubes and the volumes were adjusted to 1000 μl with the appropriate amount of CD_2Cl_2 (see Table S2, supplementary material, for data).

3.5. Reaction with 2:1 stoichiometry

To $B(C_6F_5)_3$ (20 mg, 39 μmol) and *n*-$C_{18}H_{37}OH$ (5 mg, 18.5 μmol) in a 5 mm NMR tube was added 1 ml of deuterated solvent at r.t. ^{1}H NMR (298 K, CD_2Cl_2) 6.24 (t, $J = 4.4$ Hz, 1H, O*H*); 4.03 (dt, $J = 4.4$, 6.9 Hz, 2H, OC*H*$_2$); 1.80 (m, 2H, -C*H*$_2$); 1.26 (m, 30H, C*H*$_2$); 0.87 (t, $J = 6.8$ Hz, 3H, C*H*$_3$). (298 K, toluene-d$_8$) 5.94 (t, $J =$ 4.4 Hz, 1H, O*H*); 3.37 (dt, $J = 4.4$, 6.6 Hz, 2H, α-C*H*$_2$); 1.39–0.78 (m, 35H, C*H*$_2$).

3.6. Determination of the stoichiometry and equilibrium constant of the reaction of *n*-octadecanethiol and $B(C_6F_5)_3$

A series of solution was prepared by dissolving *n*-octadecanethiol (5.0 mg, 17.5 μmol) and varying amounts of $B(C_6F_5)_3$ (1:5–5:1) in 1 ml of deuterated solvent in several 5 mm NMR tubes. The solutions were allowed to react for 1 h before measurement of the ^{1}H NMR spectra; see Table S3 and S4, supplementary material, for data in CD_2Cl_2 and toluene-d$_8$.

3.7. Synthesis of $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}O)B(C_6F_5)_3]$ (**3**)

$B(C_6F_5)_3$ (175 mg, 340 μmol) and **1** (92 mg, 340 μmol) were dissolved in dichloromethane (30 ml) at −78 °C. They were allowed to slowly warm to r.t., where they were allowed to stir for a further 1 h. To this solution, cooled to −78 °C, was added proton sponge (74 mg, 340 μmol) drop-wise in dichloromethane (15 ml). The solution was allowed to warm slowly to r.t. and was stirred for a further 3 h. The solvent was removed in vacuo to leave a colorless, viscous oil. Hexanes (10 ml) were added to the flask, and the mixture was sonicated for 1 h, during which time the oil turned into a white precipitate. The supernatant was decanted and the solid was washed with hexanes (2 × 10 ml). The solvent was removed in vacuo, and the white solid was isolated 284 mg (285 μmol, 84%). *Anal.* Calc. for $C_{50}H_{56}B_1F_{15}N_2O_1$: C, 60.3; H, 5.7; N, 2.8. Found: C, 57.7; H, 5.2; N, 2.9%. ^{1}H NMR (298 K, CD_2Cl_2): 19.39 (m, 1H, N*H*); 8.04 (d, $J = 8.3$ Hz 2H, C*H*); 7.76 (d, $J = 7.8$ Hz, 2H, C*H*); 7.71 (‘t’, $J = 7.9$, 2H, C*H*); 3.14 (d, $J = 2.6$ Hz, 12H, NC*H*$_3$); 3.07 (t, $J = 6.6$ Hz, 2H, OC*H*$_2$); 1.41 (m, 2H, β-C*H*$_2$); 1.26 (m, 30H, C*H*$_2$); 0.88 (t, $J = 6.5$ Hz, 3H, C*H*$_3$). (298 K, toluene-d$_8$): 18.32 (br s, 1H, N*H*); 7.44 (d, $J = 8.0$ Hz 2H, C*H*); 7.17 (‘t’, $J = 7.6$ Hz, 2H, C*H*); 6.88 (d, $J = 6.9$, 2H, C*H*); 3.62 (t, $J = 7.1$ Hz, 2H, OC*H*$_2$); 2.23 (d, $J =$ 1.8 Hz, 12H, NC*H*$_3$); 1.76 (m, 2H, -C*H*$_2$); 1.44 (m, 2H, ?-C*H*$_2$); 1.31 (m, 28H, C*H*$_2$); 0.92 (t, $J = 6.7$ Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR(298 K, CD_2Cl_2): 148.3 (dm, $J_{FC} = 242.7$ Hz, *ortho* CF); 143.3 (*ipso C*); 138.4 (dm, $J_{FC} = 241.1$ Hz, *para* CF); 136.7 (dm, $J_{FC} = 254.1$ Hz, *meta* CF); 135.7 (*ipso C*); 130.5 (CH); 127.7 (CH); 121.5 (CH); 118.8 (*ipso C*); 109.8 (*ipso C*); 65.1 (OCH$_2$); 46.8 (NCH$_3$); 33.2, 32.3, 30.1, 26.7, 23.1 (CH$_2$); 14.2 (CH$_3$). (298 K, toluene-d$_8$): 148.9 (dm, $J_{FC} = 245.6$ Hz, *ortho* CF); 143.1 (*ipso C*); 139.7 (low field part of doublet, *para* CF); 137.1 (dm, $J_{FC} = 248.8$ Hz, *meta* CF); 135.6 (*ipso C*); 129.9 (CH); 127.1 (CH); 120.8 (CH); 118.4 (*ipso C*); 65.3 (OCH$_2$); 45.2 (NCH$_3$); 33.8, 32.4, 30.6, 30.5, 30.3, 30.2, 29.9, 27.0, 23.2 (CH$_2$); 14.4 (CH$_3$). ^{19}F NMR (298 K, CD_2Cl_2): −133.9 (d, $J = 23.0$ Hz, 2F, *ortho*); −165.0 (t, $J = 19.9$ Hz, 1F, *para*); −168.4 (m, 2F, *meta*). (298 K, toluene-d$_8$): −135.6 (d, $J = 24.4$ Hz, 2F, *ortho*); −164.0 (m, 1F, *para*); −167.4 (m, 2F, *meta*). ^{11}B NMR: (298 K, CD_2Cl_2) −2.4. (298 K, toluene-d$_8$) −3.1. MS(FAB, nitrobenzyl alcohol): FAB$^+$ *m/e* 215.1 $[C_{10}H_6(NCH_3)_2H]^+$; FAB$^-$ *m/e* 781.1 $[(n\text{-}C_{18}H_{37}O)B(C_6F_5)_3]^-$.

3.8. Synthesis of $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]$ (**6**)

$B(C_6F_5)_3$ (0.5360 g, 1.05 mmol) and **4** (0.3000 g, 1.05 mmol) were dissolved in dichloromethane (30 ml) at −78 °C. They were allowed to slowly warm to r.t., where they were allowed to stir for a further 1 h. To this solution, cooled to −78 °C, was added proton sponge (0.2244 g, 1.05 mmol) drop-wise in dichloromethane (15 ml). The solution was allowed to warm slowly to r.t. and was stirred for a further 3 h. The solution was concentrated, in vacuo to 5 ml, cooled to 0 °C and hexanes, (30 ml), added to give a white precipitate. The supernatant was decanted and the solid was washed with hexanes (2 × 10 ml). The solvent was removed in vacuo, and a waxy pale yellow solid was isolated 0.5062 g (0.50 mmol, 48%). *Anal.* Calc. for $C_{50}H_{56}B_1F_{15}N_2S_1$: C, 59.3; H, 5.6; N, 2.8. Found: C, 57.8; H, 5.1; N, 2.8%. ^{1}H NMR (298 K, CD_2Cl_2): 19.34 (m, 1H, N*H*); 8.04 (d, $J = 8.6$ Hz 2H, C*H*); 7.78 (d, $J = 8.6$ Hz, 2H, C*H*); 7.71 (d, $J = 8.0$, 2H, C*H*); 3.15 (d, $J = 2.8$ Hz, 12H, NC*H*$_3$); 1.93 (t, $J = 7.8$ Hz, 2H, SC*H*$_2$); 1.27 (m, 32H, C*H*$_2$); 0.88 (t, $J = 6.8$ Hz, 3H, C*H*$_3$). (298 K, toluene-d$_8$): 18.36 (m, 1H, N*H*); 7.34 (d, $J = 8.0$ Hz 2H, C*H*); 7.15 (‘t’, $J = 8.3$ Hz, 2H, C*H*); 6.88 (d, $J = 7.6$, 2H, C*H*); 2.41 (t, $J = 7.5$

Hz, 2H, $\mathrm{SC}H_2$); 2.31 (d, $J = 2.5$ Hz, 12H, $\mathrm{NC}H_3$); 1.52 (m, 2H, -$\mathrm{C}H_2$); 1.31 (m, 30H, $\mathrm{C}H_2$); 0.92 (t, $J = 6.8$ Hz, 3H, $\mathrm{C}H_3$). $^{13}C\{^1H\}$ NMR(298 K, CD_2Cl_2): 148.5 (dm, $J_{FC} = 235.2$ Hz, *ortho* CF); 143.5 (*ipso* C); 138.5 (dm, $J_{FC} = 247.0$ Hz, *para* CF); 136.9 (dm, $J_{FC} = 250.7$ Hz, *meta* CF); 136.0 (*ipso* C); 130.4 (CH); 127.7 (CH); 121.5 (CH); 118.8 (*ipso* C); 113.0(*ipso* C); 46.8 ($\mathrm{N}CH_3$); 32.9 (β-CH_2); 32.3, 30.1, 29.9, 29.8 (CH_2); 29.7 ($\mathrm{S}CH_2$); 14.2 (CH_3). (298 K, toluene-d_8): 149.0 (dm, $J_{FC} = 242.5$ Hz, *ortho* CF); 143.3 (*ipso* C); 139.9 (low field part of doublet, *para* CF); 137.2 (dm, $J_{FC} = 246.5$ Hz, *meta* CF); 135.6 (*ipso* C); 129.7 (CH); 127.1 (CH); 120.9 (CH); 118.5 (*ipso* C); 45.2 ($\mathrm{N}CH_3$); 33.5 (β-CH_2); 32.4, (CH_2); 30.3 ($\mathrm{S}CH_2$); 30.3, 30.2, 29.9, 23.2 (CH_2); 14.4 (CH_3). ^{19}F NMR (298 K, CD_2Cl_2): −132.9 (d, $J = 20.4$ Hz, 2F, *ortho*); −164.6 (t, $J = 20.4$ Hz, 1F, *para*); −168.4 (m, 2F, *meta*). (298 K, toluene-d_8): −131.8 (d, $J = 20.5$ Hz, 2F, *ortho*); −163.3 (t, $J = 21.9$ Hz, 1F, *para*); −167.4 (m, 2F, *meta*). ^{11}B NMR: (298 K, CD_2Cl_2) −11.2. (298 K, toluene-d_8) −10.4. MS(FAB, glycerol): FAB^+ *m/e* 215.1 $[C_{10}H_6(NCH_3)_2H]^+$; FAB^- *m/e* 797.2 $[(n\text{-}C_{18}H_{37}S)B(C_6F_5)_3]^-$.

3.9. Reactions between Cp_2ZrMe_2 and *n*-octadecanol

To a solution of 15 mg (0.06 mmol) of Cp_2ZrMe_2 (δ_{Cp} 6.07, δ_{Me} −0.51) in 0.5 ml CD_2Cl_2 at −50 °C was added a solution of 15.8 mg (0.058 mmol) of **1** in a small amount of CD_2Cl_2. A ^1H NMR spectrum run immediately showed, in addition to the resonances of **1** (δ 3.58, 1.53, 1.26, 0.88) and Cp_2ZrMe_2 (δ 6.07, −0.51), at ~70% of the original intensities, the resonance of methane at δ 0.18, two new Cp resonances at δ 5.98 and 5.92 (2:1 ratio) and two new methyl resonances at δ −0.094 and −0.17 (1:2 ratio). There was also an $\mathrm{OC}H_2$ product resonance at δ 3.76 (t, J_{HH} 6.1 Hz). On warming to 20 °C, the NMR spectrum exhibited new resonances (δ_{Cp} 6.009, 5.96; δ_{Me} −0.019, −0.064), indicating that the reaction had proceeded further, but the resonances of Cp_2ZrMe_2 and *n*-octadecanol were still present. On prolonged standing at 20 °C, the spectrum became very complicated.

Reaction of Cp_2ZrMe_2 (19 mg, 0.07 mmol) with 0.5 equiv. of **1** at −50 °C resulted in little reaction after 10 min, but reaction of Cp_2ZrMe_2 (8.83 mg, 0.035 mmol) with 2 equiv. of *n*-octadecanol (19 mg, 0.07 mmol) at 20 °C (mixed at −20 °C) resulted in immediate disappearance of the resonances of the Cp_2ZrMe_2 and the appearance of the resonance of methane at δ 0.21, of new Cp and methyl resonances at δ 6.01 and −0.059, respectively, and of a new $\mathrm{OC}H_2$ resonance at δ 3.816 (t, J_{HH} 6.1 Hz). The product is almost certainly an alkoxy species such as $Cp_2ZrMe\ (OC_{18}H_{37})$, but all attempts to synthesize it on a larger scale resulted in the formation of a waxy mixture with a complicated NMR spectrum.

3.10. Reactions of Cp_2ZrMe_2 with 1:1:1 *n*-octadecanol, $B(C_6F_5)_3$ and proton sponge

Solid Cp_2ZrMe_2 (4.91 mg, 0.02 mmol) was dissolved in a solution of $[C_{10}H_6(NMe_2)_2H][(n\text{-}C_{18}H_{37}O)B(C_6F_5)_3]$ (0.02 mmol) in 0.5 ml CD_2Cl_2 at −20 °C, and the reaction was monitored by ^1H NMR spectroscopy. After 20 min, in addition to resonances of the starting materials (~70% of the original intensities), there were observed a methane resonance at δ 0.186, two new Cp resonances at δ 5.99 and 5.94, two new Zr–Me resonances at δ −0.07 and −0.11 and a $\mathrm{OC}H_2\mathrm{R}$ resonance at δ 3.82 (t, J_{HH} 5.9 Hz). Some of these are probably to be attributed to the above mentioned compound $Cp_2Zr\ (Me)(OCH_2R)$, but again warming the reaction mixture resulted in considerable decomposition.

The same reaction in the presence of a second equivalent of $B(C_6F_5)_3$ resulted in a complex ^1H NMR spectrum which exhibited the resonances of protonated proton sponge and of the borate anion $[MeB(C_6F_5)_3]^-$ (δ 0.42), but only a very weak methane resonance. Since only a single set of ^{19}F resonances were observed, those of $[MeB(C_6F_5)_3]^-$ at δ −134.2 (d, J_{FF} 18.8 Hz), −166.10 (t, J_{FF} 20.69 Hz) and −168.7 (dt, J_{FF} 18.8 Hz), it appears that the major species formed are alkoxy zirconium compounds and $[C_{10}H_6(NMe_2)_2H]$-$[MeB(C_6F_5)_3]$.

3.11. Supporting information available

A listing of all data used in the calculation of the equilibrium constants.

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