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Citation for published version:

Digital Object Identifier (DOI):
10.1002/ejic.201700600

Link:
Link to publication record in Heriot-Watt Research Portal

Document Version:
Publisher's PDF, also known as Version of record

Published In:
European Journal of Inorganic Chemistry

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Aminoborylene Complexes

Fluoroarene Complexes with Small Bite Angle Bisphosphines: Routes to Amine–Borane and Aminoborylene Complexes


Abstract: Fluoroarene complexes of the small bite angle bisphosphine Cy2PCh2PCy2 (dcpm) have been prepared: [Rh(dcpm)(η6-1,2-F2C6H4)][Al{OC(CF3)3}4] and [Rh(dcpm)(η6-1,2,3-F3C6H3)][Al{OC(CF3)3}4]. These complexes act as precursors to a previously inaccessible σ-amine–borane complex [Rh(dcpm)(η2-H3B·NMe3)][Al{OC(CF3)3}4] of a small bite-angle phosphine. This complex is a poor catalyst for the dehydrocoupling of H3B·NMe3·H. Instead, formation of the bridging borylene complex [[RhH(μ-dcpm)]2(μ-H)(μ-BNMe2)][Al{OC(CF3)3}4] occurs, which has been studied by NMR, mass spectrometry, crystallographic and DFT techniques. This represents a new route to bridging borylene complexes.

Introduction

The transition metal catalysed dehydrocoupling and dehydro-polymerisation of amine–boranes has been the subject of considerable recent attention due to both fundamental interest in BH/NH activation processes and as routes to new BN-based materials.[1–3] Amine–borane σ-complexes[4] are often implicated as intermediates in such processes. Although a wide variety of amine–borane σ-complexes are now known,[4–6] previous attempts to prepare such species with small bite angle bisphosphine coligands have been unsuccessful.[7] Studying the reactivity of [Rh{Ph2P(CH2)xPPh2}](η6-FC6H5)][BArF4] with H3B·NMe3 to form [Rh{Ph2P(CH2)xPPh2}](η2-H3B·NMe3)][BArF4] [x = 2–5, Ar = 3,5-(CF3)2C6H3] revealed a dependence of the relative strengths of the metal-borane/metal–arene interactions on the P–Rh–P bite angle (Scheme 1a).[8,9] Larger bite angles were noted to give rise to stronger Rh–B and Rh–H interactions, as evidenced by downfield 11B NMR chemical shifts and upfield 1H NMR chemical shifts. Notably, a σ-borane complex did not form for x = 2 (i.e. Ph2PCH2CH2PPh2), which demonstrates the tipping point where η6-binding of the FC6H5 solvent outcompetes η2-H3B·NMe3 coordination. These weak rhodium-borane interactions were found to be advantageous in catalysis, with small bite angles promoting faster dehydrocoupling of H3B·NMe3·H to form [H2BNMe2]2, e.g. TOFs from 180 h–1 (x = 5) to 1250 h–1 (x = 3).[7] For x = 2 no dehydrocoupling was observed, likely due to preferential binding of FC6H5 over η2-complexation of the amine–borane. Demonstration of this comes from comparison of the binding mode of the B-phenyl-substituted amine–borane H2PhB·NMe3 with {Rh(PR3)2}+ fragments: wide bite angles favour amine–borane σ-coordination, tighter ones arene coordination, e.g. [Rh(PiPr3)2(η2-(BH)-H2PhB-NMe3)][BArF4], [P–Rh–P = (a) P–Rh–P bite angle affects amine–borane coordination

(b) Increasing fluorination favours [BArF4]- zwitterion

(c) This work (weakly bound fluoroarenes)

Scheme 1. (a) Displacement of FC6H5 by H3B·NMe3 (x = 3–5). [BArF4]- anion not shown.[7] (b) Zwitterion formation from fluoroarene complexes.[11] (c) Preparation of fluoroarene complexes in this work. [Al{OC(CF3)3}4]+ anion not shown.

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DOI: 10.1002/ejic.201700600
Empirically the P–Rh–P bite angle has an inverse effect on arene binding in [Rh(bisphosphine)(arene)]+ cations, with η1-arene binding more favourable for smaller bite angle ligands,[2,12,13] for which we also suggest amine–borane α-complexation is weaker. One way to mitigate these competing effects is to use more weakly binding arene ligands, η6-Fluoroarenes are increasingly popular as weakly binding ligands that offer an operationally unsaturated metal centre.[14] However, the vast majority of cases are limited to FC6H5 examples, with [Al{OC(CF3)3}4]– was employed, the use of which has been pioneered[7,12,13] for which we also suggest amine–borane complexes.

Results and Discussion

To avoid competition from zwitterion formation through coordination of [BARh]4–, the very weakly coordinating anion [Al(O)CF3]3Al– was employed, the use of which has been pioneered[2,26] and widely applied by Krossing.[25,26] Hydrogenation of [Rh(dcpm)(COD)][Al(O)CF3]3Al (COD = cyclooctadiene) in 1,2-F2C6H4 or 1,2,3-F3C6H3 solution gave the corresponding fluoroarene complexes [Rh(dcpm)(F2C6H4–)](Al(O)CF3)3Al [n = 2 (1), 3 (2)], Scheme 2. Scheme 2: Trace quantities of other, more strongly coordinating, arenes in the commercially available solvents lead to impurities of the form [Rh(dcpm)(arene)](Al(O)CF3)3Al.[27] In the case of 1 these are minimal (<10 %), but for 2 considerable quantities are observed. This can be simply overcome by performing the synthesis of 2 in concentrated solution (0.1 M, 100 mg in 0.4 cm3), thereby decreasing the ratio of [impurities]:[Rh] such that 2 is formed in >95 % spectroscopic yield. Both complexes 1 and 2 can be isolated as synthetically pure yellow crystals in 78 % and 82 % yields respectively after crystallisation by addition of pentane. For comparison, the analogous [BARh]4– complexes [Rh(dcpm)(F2C6H4–)](BARh)4 (n = 2, 3) were similarly prepared. Both species were observed in situ, and [Rh(dcmp)(1,2,3-F3C6H3)][BARh]4 (3) could be isolated in 82 % yield as the only product. However, [Rh(dcmp)(1,2,3-F3C6H3)][BARh]4 (4) forms the zwitterion complex [Rh(dcmp)(η6-(3,5-(CF3)2C6H3)–BARh)4] (5), upon standing (Scheme 2). For [Rh(dcmp)(1,2,3-F3C6H3)][BARh]4 slower partial conversion to 5 occurs over days,[28] and a single crystal X-ray structural determination confirmed its formulation (Scheme 2). To avoid such complications all future work was conducted exclusively with the [Al(O)CF3]3Al– anion.

In the 31P{1H} NMR spectra of 1 and 2 downfield shifts and increased Rh–P couplings relative to the precursor complexes are observed (1: Δ = −10.4, J(RhP) 168 Hz; 2: Δ = −10.9, J(RhP) 167 Hz; cf. [Rh(dcmp)(COD)][Al(O)CF3]3Al: Δ = −27.4, J(RhP) 126 Hz). In the 19F{1H} NMR spectrum the fluoroarene resonances shift downfield upon complexation, with those of 2 observed at Δ = −146.7 (2 F) and −167.1 (1 F), relative to free 1,2,3-F3C6H3 (Δ = −136.8, −163.5), as described previously for related systems.[29–31]

Characterisation of 1 and 2 included a single-crystal X-ray crystallographic study (Scheme 2b for 2, supporting materials for 1), and complex 2 is the first structurally characterised example of an FC6H4-transition metal complex. Significant disorder of the fluoroarene ring between different rotomers means that discussion of the geometric parameters is not appropriate, but the structure does demonstrate arene binding and the...
acute nature of the P–Rh–P angle [73.06(4)°]. The only previously reported example of 1,2,3-F₂C₆H₅ binding to a transition metal is [Rh(P₂Ph₃)₂CH₂CH₂P₂Ph₃]+[η²-H₃B-NMe₂][BF₄]₂ in a ratio of 9:1 (as measured by ²¹⁷P{¹H} NMR spectroscopy). Addition of a second equivalent of H₃B-NMe₂ decreased this ratio to 4:1, demonstrating that 1,2,3-F₂C₆H₅ binding is competitive with that of H₃B-NMe₂. In contrast, for the more weakly bound 1,2,3-F₂C₆H₅ complex (2) reaction with H₃B-NMe₂ in 1,2,3-F₂C₆H₅ solvent afforded 6 as the major product (81 % by ²¹⁷P{¹H} NMR spectroscopy), Scheme 3, alongside a collection of uncharacterised [Rh{η²-P₂Ph₃}₃±]⁻ species (13 %) and other minor impurities. Moving to more concentrated solutions (0.17 M) did not significantly increase the yield of 6, and clearly these minor impurities bind slightly more strongly than the amine–borane.

The NMR spectra of 6 resemble those of the analogous [Rh{P₂Ph₃(CH₂)₃P₂Ph₃}]+[BF₄]₂ complexes (n = 3–5).[¹⁷] In the ²¹⁷P{¹H} NMR spectrum of 6 a doublet is observed at δ = −3.7 [J(RhP) 145 Hz]. The ¹¹B NMR spectrum contains a broad resonance at δ = 16.3; and the corresponding o-bound Rh–H–B resonances appear at δ = −1.75 as a very broad singlet (integral 3 H) in the ¹H NMR spectrum indicating rapid exchange between bridging and terminal B–H. Unfortunately, 6 did not survive ESI–MS conditions, and attempts to crystallise 6 resulted in decomposition, an indication of its relative instability.

Having access to small bite angle bispaphosphine complexes that were capable of binding amine–boranes, albeit made in situ, their ability to dehydrocouple H₃B-NMe₂ was evaluated, as we have previously shown that the P–Rh–P bite angle has an influence on the rate of this process.[¹⁷] The dehydrocoupling of H₃B-NMe₂ in 1,2,3-F₂C₆H₅ solvent was investigated using 5 mol-% 2 (Scheme 4). The dehydrocoupling proved to be slow with only 14 % H₂B-NMe₂ consumption over 21 h to provide the dimericaminoborane [H₂B(NMe₂)₂]₂ (8 %), alongside small quantities of other common dehydrocoupling products including transient H₂B=NMe₂, H₂B(NMe₂)₂BH₂, H₂B[NMe₂]₂ and H₂B[(μ-H)NMe₂]BH₂ as measured by ¹¹B NMR spectroscopy.[¹⁵,32–34] In the ²¹¹P{¹H} NMR spectrum only one major phosphorus-containing species was observed (7), as a complex second-order multiplet at δ = 55.9, hinting at the formation of a dimeric species.[¹³] A very broad resonance is observed in the ¹¹B NMR spectrum at δ = 59.0, with nothing observed to lower field. In the ¹H NMR spectrum two very well resolved multiplets were observed in the high field region at δ = −4.87 and −7.91, with relative integrals of 2:1 respectively, which do not sharpen upon ¹¹B decoupling, but do simplify on decoupling ³¹P. This suggests there are no significant ¹¹B–¹H interactions. In the ESI–MS spectrum, a peak at m/z = 1080.51 is observed, with an isotope pattern consistent with the gross formulation of a bimetallic monocation ([Rh(dcpm)]₂H₂BNMe₂)⁺. A similar dimerisation has been seen upon reaction of [Rh{R₂P(CH₂)₃PR₂}²-H₃B-NMe₂]⁺, where the bridgingaminoborane [Rh{(η²-P₂Ph₃)₂PR₂}⁺(μ-H)⁺(μ-H₂BNMe₂)][BF₄]₂ [R = (η²-P₂Ph₃)₂] is formed, and the data for 7 are similar.[³⁶]

Scheme 4. Attempted dehydrocoupling of H₃B-NMe₂ and formation of [Rh{(η²-P₂Ph₃)₂PR₂}⁺(μ-H)⁺(μ-BNMe₂)][BF₄]₂ anion not shown.

Crystalline material of complex 7 was obtained by recrystallisation from 1,2,3-F₂C₆H₅/pentane. In the bulk this was always contaminated with a boron-containing species identified as the boronium salt [H₂B(NMe₂)₂][BF₄]⁺ ([δ(¹¹B) = −2.0 ppm, J(BH) = 115 Hz; lit. δ(¹¹B) = −2.8 ppm, J(BH) = 113 Hz).[³³] This did allow a single-crystal X-ray diffraction study to be performed, the results of which are shown in Figure 1. The solid-state structure shows a rearrangement of the bispaphosphine ligands upon dimerisation, and complex 7 contains bridging dcpm ligand in an A-frame motif and an aminoborylene BΝMe₂ group. The (R₂{(η²-P₂Ph₃)₂})₂ construct resembles that of other bincicular rhodium systems with similar ligands.[³⁸,3₉] Although the hydride ligands were not located in the final Fourier difference map, the combination of NMR spectroscopic evidence and DFT studies (vide infra) confirm the presence of one bridging hydride trans-disposed to one terminal Rh–H at each Rh centre, with the overall formulation [Rh{(η²-P₂Ph₃)₂}(μ-H)(μ-BNMe₂)]⁻[Al{OC(CF₃)₃}₄]⁺ (7). The geometry about each Rh is pseudo-square pyramidal, interestingly with a vacant coordination site trans to the borylene ligand. The cation has overall non-crystallographic C₂ᵥ symmetry. The Rh–B distances [2.015(6) and 1.983(7) Å] are shorter than those in the related bridging aminoborylene complex [Rh{(η²-C₂H₅)CO}_{₂}(μ-BN(SiMe₃)₂)]⁻[Al{OC(CF₃)₃}₄]⁻[Al{OC(CF₃)₃}₄]⁺ [2.054(2) Å][⁴⁰] and aminoborane complex [Rh{P₂Ph₃(CH₂)₃}⁺]⁻ with only 14 % H₃B-NMe₂ consumption over 21 h to provide the dimericaminoborane [H₂B(NMe₂)₂]₂ (8 %), alongside small quantities of other common dehydrocoupling products including transient H₂B=NMe₂, H₂B(NMe₂)₂BH₂, H₂B[NMe₂]₂ and H₂B[(μ-H)NMe₂]BH₂ as measured by ¹¹B NMR spectroscopy.[¹⁵,32–34] In the ²¹¹P{¹H} NMR spectrum only one major phosphorus-containing species was observed (7), as a complex second-order multiplet at δ = 55.9, hinting at the formation of a dimeric species.[¹³] A very broad resonance is observed in the ¹¹B NMR spectrum at δ = 59.0, with nothing observed to lower field. In the ¹H NMR spectrum two very well resolved multiplets were observed in the high field region at δ = −4.87 and −7.91, with relative integrals of 2:1 respectively, which do not sharpen upon ¹¹B decoupling, but do simplify on decoupling ³¹P. This suggests there are no significant ¹¹B–¹H interactions. In the ESI–MS spectrum, a peak at m/z = 1080.51 is observed, with an isotope pattern consistent with the gross formulation of a bimetallic monocation ([Rh(dcpm)]₂H₂BNMe₂)⁺. A similar dimerisation has been seen upon reaction of [Rh{R₂P(CH₂)₃PR₂}²-H₃B-NMe₂]⁺, where the bridgingaminoborane [Rh{(η²-P₂Ph₃)₂PR₂}⁺(μ-H)⁺(μ-H₂BNMe₂)][BF₄]₂ [R = (η²-P₂Ph₃)₂] is formed, and the data for 7 are similar.[³⁶]
The $^{11}$B NMR chemical shift observed for $^7$ ($\delta = 59.0$) suggests a bridging aminoborane motif [cf. $^1$, $\delta(^{11}$B) 51.1] [36]. However, the sharp signals observed for the hydrides in the $^1$H NMR spectrum, that are unaffected by $^{11}$B coupling, point to a bridging dihydrido aminoborylene motif, which would be expected to show lower field chemical shifts in the $^{11}$B NMR spectra (>90 ppm) [40,44], although examples have been observed as far upfield as 74 ppm [45]. An obvious geometric distinction between a bridging aminoborane ($\mu$-H$_2$BNR$_2$) and a bridging aminoborylene dihydride ($\mu$-BNR$_2$) structure is the orientation of the NR$_2$ moiety with respect to the RhBRh plane, as depicted in Figure 2. In the former case, e.g. $^1$, a significant twist angle of 30.92° is observed between the RhBRh and CNC planes of $^1$ so as to maximise the orbital overlap between the B–H bonds.
and Rh2/H2. The associated bond critical points (BCPs) exhibit negative values of the total energy density $\nabla^2 \rho$ and low ellipticities, $\epsilon$, characteristics of $\sigma$-bonding that is predominantly covalent in nature. This contrasts with the $\mu$-H$_2$BNMe$_2$ motif in I where the BCPs associated with the Rh–H and Rh–B bond paths have large ellipticities of about 0.5 au reflecting the anisotropic $\pi$-agostic Rh←H–B interaction. The presence of the bridging hydride in 7 means that a ring critical point is seen between the Rh centres. The computed Rh1←Rh2 distance of 2.85 Å is in good agreement with the experimental value of 2.8266(5) Å. The lack of any Rh1←Rh2 interaction is confirmed in the NBO analysis which highlights three Rh-based (d-orbital) lone pairs, as well as Rh1←H/Rh2←H and Rh1←B/Rh2←B bonding orbitals. In contrast NBO calculations on [{Rh(η$^5$-C$_5$H$_5$)(CO)}$_2$]$\mu$-BN(SiMe$_3$)$_2$] clearly locate a Rh–Rh bonding orbital consistent with the presence of a metal–metal bond (see Supporting Information).

The formation of 7 is postulated to proceed in a similar manner to I and II (Scheme 5). Displacement of the fluoroarene ligand enables initial formation of a $\sigma$-H$_2$BNMe$_2$H complex (A), analogous to complex 6. Subsequent B–H oxidative cleavage yields the intermediate aminoborylene B, from which elimination of the boronium salt H$_2$B(NMe$_2$H)$_2$+$\nu$ (observed at the end of the reaction) generates a neutral "[Rh(dcpm)H]" fragment C. NMe$_2$H arises from H$_2$B-NMe$_2$H dissociation, consistent with the observation of H$_2$B($\mu$-HNMe$_2$B)$_2$ in the reaction. It has previously been shown that hydrogenation of [Rh($\mu$-Pr$_2$PCH$_2$PPr$_2$)-($\eta^1$-C$_3$H$_5$Ph)] ($R = Cy, iPr)$ affords the A-frame bridging bisphosphine complex [RhH($\mu$-Pr$_2$PCH$_2$PPr$_2$)]($\mu$-H)$_2$ and an equivalent rearrangement has been noted in the reaction of [Rh($\mu$-Pr$_2$PCH$_2$PPr$_2$)Cl$_2$](CO)($\eta^1$-C$_3$H$_5$)] with H$_2$ to form [Rh($\mu$-IP$_2$PCH$_2$PPr$_2$)(CO)($\mu$-H)]$_2$. Presumably these dimerisations are driven by ring strain. We thus propose that dimerisation of C first forms a neutral bridging A-frame complex, [RhH(dcpm)$_2$]$_2$ which then undergoes protonation by a half equivalent of H$_2$B(NMe$_2$H)$_2$ to form a bridging aminoborane D. Complex 7 then results from a double B–H activation of D to form a bridging aminoborylene dihydride. Interestingly this does not occur with the R$_2$P(CH$_2$)$_3$PPr$_2$ ligands in I and II in which there is not an A-frame motif. Similar geminal C–H activations of alkenes are effected by [{Ir(μ-Et$_2$PCH$_2$PPh$_2$)(CO)}$_2$]$\mu$-H($\mu$-CO)]$_2$ and [{Ir(μ-P$_2$Ph$_2$PCH$_2$PPh$_2$)$_2$}(μ-CO)](CH$_3$)(CO)]$_2$.[48,49] Such C–H activations are proposed to proceed via a cooperative mechanism wherein $\pi$-complexation of H$_2$C=CHR to one metal enables $\sigma$-CH complexation at the other metal and consequently C–H cleavage. This bears parallels with the double B–H activation of transient H$_2$B=NM$_2$ observed here, although aminoboranes bind end-on rather than the side-on mode adopted by alkynes.[50,51] Aminoborane to aminoborylene transformations by double B–H activation of H$_2$B=NR$_2$ ($R = Cy, iPr$) have been observed with mononuclear iridium and ruthenium complexes,[52,53] and related transformations on boranes are also known.[54,55] However, to the best of our knowledge the complete amine–borane to aminoborylene transformation is unprecedented, and represents a new method for the preparation of bridging borylenes.

### Conclusions

The marriage of the very weakly coordinating anion [Al(OCCF$_3$)$_3$]$^-$ and fluoroarenes 1,2-F$_2$C$_6$H$_4$ and 1,2,3-F$_3$C$_6$H$_3$ enables the synthesis and isolation of a previously inaccessible $\sigma$-amine–borane complex of a small bite angle phosphine. The ring strain imposed by the dcpm ligand leads to unprecedented chemistry with amine–boranes, culminating in formation of a bimetallic aminoborylene [{RhH($\mu$-dcpm)]$_2$($\mu$-H)]($\mu$-BNMe$_2$) and [Al(OCCF$_3$)$_3$]$^-$, the nature of which is confirmed by DFT calculations and QTAIM and NBO analyses.

### Experimental Section

All manipulations, unless otherwise stated, were performed under an argon atmosphere using standard Schlenk line and glovebox techniques. Glassware was oven dried at 130 °C overnight and flame dried under vacuum prior to use. Pentane and CH$_2$Cl$_2$ were dried using a Grubbs type solvent purification system (MBrann SPS-800) and degassed by three successive freeze-pump-thaw cycles. 1,2-F$_2$C$_6$H$_4$ (purchased from Fluorochem, pretreated with alumina), 1,2,3-F$_3$C$_6$H$_3$ and CD$_2$Cl$_2$ were dried with CaH$_2$, vacuum distilled and stored over 3 Å molecular sieves. H$_2$B(NMe$_2$) and H$_2$B-NMe$_2$H were purchased from Sigma–Aldrich and sublimed prior to use. Li[Al(OCCF$_3$)$_3$]$^-$[52] and [Rh(COD)[Cl]]$_2$[56] were prepared by literature methods. All other chemicals were obtained from commercial sources and used as received.

NMR spectra were recorded with a Bruker AVIIHD 500 or Bruker AVIIHD 400 nanobay spectrometer at room temperature, unless otherwise stated. In 1,2-F$_2$C$_6$H$_4$ and 1,2,3-F$_3$C$_6$H$_3$. $^1$H NMR spectra were prelocked to a sample of CD$_2$Cl$_2$ (25 %) and 1,2-F$_2$C$_6$H$_4$ (75 %).
analyses were performed by Stephen Boyer at London Metropolitan Bruker MicrOTOF instrument interfaced with a glove-box. Micro-
and coupling constants (J) in Hz. ESI-MS data were recorded with a 7.07 and 6.96 ppm, respectively. 31P, 11Ba and 19F NMR spectra were
4 H, COD-CH), 3.00 (td, 2 H, PCH3P), 2.33 (s, 8 H, COD-CH2) ppm. 31P{1H} NMR (202 MHz, CD2Cl2, 298 K): δ = –75.8 (d, JRhP = 168 Hz) ppm. 19F{1H} NMR (376 MHz, CD2Cl2, 298 K): δ = –75.8 (s, 36 F, CF3), –146.3 (d, JFF = 3 Hz, 2 F, F2C6H4) ppm. ESI-MS (1,2-F2C6H4, 60 °C, 4.5 kV): m/z 619.32 (calculated 619.31 for [Rh(dcpm)(COD)]+ fragment). C47H50AlF38O4P2Rh (1592.67): calcd 625.24 for [Rh(dcpm)(1,2-F2C6H4)]+ fragment. C47H50AlF39O4P2Rh (1610.66): calcd. C 35.44, H 3.16; found C 35.51, H 3.19.

[Rh(dcpm)(1,2,3-F3C6H3)][Al{OC(CF3)3}4](1): Prepared according to the literature procedure for [Rh(dcpm)(COD)][BARF]4.[58] A solution of [Rh(COD)Cl]2 (0.585 g, 1.19 mmol) and 1,5-cyclooctadiene (0.2 mL) in CH2Cl2 (20 mL) was degassed by bubbling argon through the solution for 15 min. The solution was then added dropwise to a colourless slurry of Li[Al(OCCF3)4] (2.31 g, 2.37 mmol) in CH2Cl2 (60 mL) with vigorous stirring at ambient temperature. The colour of the slurry immediately changed to dark red. The reaction mixture was stirred at ambient temperature for a further 16 h and then filtered. The supernatant was then concentrated under vacuum (ca. 50 mL). Cooling to –20 °C overnight afforded a red crystalline solid which was isolated by decanting, washed with pentane (2 × 2 mL) and dried under vacuum. Further concentration followed by cooling afforded a second crop. Yield 436.9 mg (0.2753 mmol, 89 %). The powder was then extracted into the minimum amount of pentane and dried under vacuum. Crystals of [Rh(dcpm)(1,2,3-F3C6H3)][Al{OC(CF3)3}4] did not persist under ESI-MS conditions. C47H49AlF39O4P2Rh (1610.66): calcd. C 35.05, H 3.07; found C 35.19, H 3.01.

[Rh(dcpm)(COD)][Al(OCCF3)4]2(2): Prepared according to the literature procedure for [Rh(dcpe)(COD)][BARF]4.[58] A solution of 1,5-cyclooctadiene (0.2 mL) was treated dropwise with a solution of dcpm (127.1 mg, 0.3111 mmol) in CH2Cl2 (10 mL) at –78 °C with vigorous stirring. Upon complete addition the colour of the reaction mixture changed from burgundy to orange. The reaction mixture was warmed to ambient temperature and stirred for 16 h. The solution was concentrated to 10 mL under vacuum and pentane (50 mL) was added to precipitate an orange solid which was isolated by filtration, washed with pentane (3 × 10 mL) and dried under vacuum. Yield 88 mg (55 μmol, 82 %). ESI-MS (1,2-F2C6H4, 60 °C, 4.5 kV): m/z 619.32 (calculated 619.31 for [Rh(dcpm)(COD)]+ fragment). C47H50AlF38O4P2Rh (1592.67): calcd. C 35.44, H 3.16; found C 35.51, H 3.19.

[Rh(dcpe)(COD)][BARF]4(3): Prepared according to the literature procedure for [Rh(dcpe)(COD)][BARF]4.[58] A solution of [Rh(COD)Cl]2 (0.585 g, 1.19 mmol) and 1,5-cyclooctadiene (0.2 mL) in CH2Cl2 (20 mL) at –78 °C with vigorous stirring. Upon complete addition the colour of the reaction mixture changed from burgundy to orange. The reaction mixture was warmed to ambient temperature and stirred for 16 h. The solution was concentrated to 5 mL under vacuum and pentane (50 mL) was added to precipitate an orange solid which was isolated by filtration, washed with pentane (3 × 10 mL) and dried under vacuum. Yield 406 mg (0.275 mmol, 93 %). The powder was then extracted into the minimum amount of CH2Cl2 and layered with pentane, which afforded large orange crys-
tals suitable for an X-ray diffraction study. 1H NMR (500 MHz, CD2Cl2, 298 K): δ = 7.72 (s, 8 H, ortho-BARF), 7.56 (s, 4 H, para-BARF), 5.37 (br, s, 4 H, COD-CH2), 2.99 (t, JPH = 10 Hz, 2 H, PCH3P), 2.31 (s, 8 H, COD-CH2), 2.08–1.76 (br. m, 24 H, Cy), 1.43–1.20 (br. m, 20 H, Cy, Cy) ppm. 31P{1H} NMR (202 MHz, CD2Cl2, 298 K): δ = –27.5 (d, JRhP = 126 Hz) ppm. 19F{1H} NMR (470 MHz, CD2Cl2, 298 K): δ = –62.9 (s) ppm. ESI-MS (1,2-F2C6H4, 60 °C, 4.5 kV): m/z 619.32 (calculated

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H, Cy), 1.39−1.03 (br. m, 20 H, Cy) ppm.31P{1H} NMR (162 MHz, CD2Cl2, 298 K): δ = −10.3 (d, Jphosph = 169 Hz) ppm.19F{1H} NMR (376 MHz, CD2Cl2, 298 K): δ = −62.9 (s, 36 F, BArF4), −146.2 (br. s, 2 F, F3C6H3) ppm. ESI-MS (1,2-F3C6H3, 60 °C, 4.5 kV): m/z 625.24 (calculated 625.24 for [Rh(dcpm)·(1,2-F3C6H3)]+ fragment). C32H24BF26P2Rh (1488.79): calc. C 50.82, H 4.20; found C 50.93, H 4.26.

In-situ Preparation of [Rh(dcpm)(1,2,3-F3C6H3)][BArF4] (4) and Isolation of [Rh(dcpm)(μ-3-(CF3)2C6H3)BArF4]3+ (5): [Rh(dcpm)·(COD)BArF4] (54 mg, 36.4 μmol) was dissolved in 1,2,3-F3C6H3 (0.4 mL) in a high pressure J. Young NMR tube. The solution was stirred for 4 h, over which time the solution changed from orange to yellow. Excess H2 was removed by three freeze-pump-thaw degassed and stirred solutions for 1 min. The solution turned red, and pentane (ca 3 mL) was added to give a red oil, which, upon sonicating, afforded a red oily solid. In-situ Preparation of [Rh(dcpm)(1,2,3-F3C6H3)][BArF4] (4) and Isolation of [Rh(dcpm)(μ-3-(CF3)2C6H3)BArF4]3+ (5): [Rh(dcpm)·(COD)BArF4] (54 mg, 36.4 μmol) was dissolved in 1,2,3-F3C6H3 (0.4 mL) in a high pressure J. Young NMR tube. The solution was stirred for 4 h, over which time the solution changed from orange to yellow. Excess H2 was removed by three freeze-pump-thaw degassed and stirred solutions for 1 min. The solution turned red, and pentane (ca 3 mL) was added to give a red oil, which, upon sonicating, afforded a red oily solid.

Acknowledgments

The Engineering and Physical Sciences Research Council (EPSRC) (A. S. W. and S. A. M., EP/M024210/1; N. A. B., DTP Studentship).

Keywords: Amines · Rhodium · Boranes · Fluoroarenes · Phosphines

1,2,3-F$_3$C$_6$H$_3$ was purchased from Fluorochem, treated with alumina, dried with CaH$_2$ and vacuum distilled before use. GC–MS analysis of the purified solvent identified the arenes FC$_6$H$_5$, F$_2$C$_6$H$_4$, FCl$_2$C$_6$H$_3$, F$_2$Cl$_2$C$_6$H$_2$, F$_3$ClC$_6$H$_2$, and F$_3$BrC$_6$H$_2$ as trace impurities. This reactivity profile suggests a dissociative process for substitution.

See Supporting Information for full details and references.

Received: May 21, 2017