Rhodium(III) Complexes Featuring Coordinated CF3 Appendages

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Rhodium(III) Complexes Featuring Coordinated CF₃ Appendages

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Abstract
The synthesis and characterisation of complexes featuring intramolecular CF₃–Rh(III) interactions is described. This bonding is evidenced in the solid state using X-ray diffraction, with Rh–F contacts of 2.36 – 2.45 Å, and in solution using NMR spectroscopy, through detection of time-averaged ¹J_{RhF} and ²J_{PF} coupling.

Introduction
The coordination chemistry of the transition elements is extensive, but notable for the paucity of well-defined complexes featuring explicit C–F→M bonding interactions[1,2]. Indeed, the poor ligating characteristics of organofluorine groups, augmented by the inertness of the associated C–F bonds, lend them to notable application as constituents of weakly coordinating anions, such as [B(C₆F₅)₄]⁻, [B(3,5-(CF₃)₂C₆H₃)₄]⁻ and [Al(OC(CF₃)₃)₄]⁻.[3] Of the limited number of structurally characterised examples, the overwhelming majority are based on the early transition metals; with A – D notable (Chart 1).[4,5] Complexes of the platinum group metals are scarce and only E – G feature M–F contacts < 2.5 Å.[6,7] Building on our recent work, employing the high trans-influence 2,2’-biphenyl (biph) ancillary ligand for the systematic study of agostic interactions,[8] we herein report the synthesis and characterisation of an unprecedented homologous series of late transition metal complexes featuring distinct CF₃→M bonding interactions.

![Chart 1. Selected examples of structurally characterised early and platinum group metal complexes featuring explicit C–F→M bonding interactions.](image-url)
Results and discussion

To temper the extremely low nucleophilicity of the CF₃ group, we focused our efforts on probing the intramolecular coordination chemistry of this commonly used appendage and identified PPh₂ArF as a prospective ditopic ligand (Chart 1).[9] Monomeric Rh(III) complex [Rh(biph)(dtbpm)Cl] (dtbpm = bis(di-tert-butylphosphino)methane) is an established source of the [Rh(biph)Cl] fragment in solution[8,10] and reaction with excess PPh₂ArF in CHCl₃ at RT proceeded as anticipated with substitution of the small bite angle diphosphine alongside precipitation of chloro-bridged dinuclear complex 1 (Figure 1). The structure and purity of this sparingly soluble dimer was corroborated in solution using NMR spectroscopy, in the solid state using single crystal X-ray diffraction, and through microanalysis. Subsequent substitution reactions enabled synthesis of mononuclear derivatives 2 – 5, which were all isolated in high purity and extensively characterised (Figure 1).

The solid-state structures of 1 – 4 are notable for the adoption of distinct CF₃➞Rh bonding interactions, characterised by Rh–F contacts of 2.36 – 2.45 Å that increase in the order 2 < 4 < 1 < 3. There are very few crystallographically characterised transition metal precedents for coordination of the CF₃ appendage and, to the best of our knowledge,[1,2] only first row adduct D, bearing two rigid 2,4,6-tris(trifluoromethyl)phenyl ligands, features a shorter contact (V–F = 2.306(2) Å).[5,11] Coordination of cyclopentadienyl in 5 leads to the nominal monodentate coordination of PPh₂ArF, with the CF₃ group projected away from the metal centre (≤Rh–P–C–CCF₃ = 167.7(1)° and Rh⋯F > 5 Å) demonstrating that this ligand is sufficiently conformationally flexible as to not enforce the chelation observed in 1 – 4.

In CD₂Cl₂ solution at 298 K, coordination of PPh₂ArF in 1 – 5 was confirmed by ³¹P NMR spectroscopy with the associated resonances exhibiting large ¹⁰³Rh coupling (¹JRhP = 124 – 170 Hz). Further coupling to magnetically equivalent ¹⁹F nuclei (²JFP ca. 5 Hz) is evident from the ³¹P{¹H} NMR spectra of 1 – 4, but absent in that of 5, consistent with the presence of weak and time-averaged CF₃➞Rh interactions in solution. At ambient temperature fast rotation of the CF₃ groups on the NMR time scale (400 MHz) and coupling to both ³¹P and ¹⁰³Rh, with ¹JRhF = ²JFP, is also apparent from the ¹⁹F{¹H} NMR spectra of 1 – 4 (δCF₃ = -62.8 – -67.6 ppm). The transient nature of the CF₃➞Rh interaction in solution inferred from this data is fully in line with expectation and further vindicated through pronounced structural dynamics of asymmetric 1 – 3 evident by ¹H NMR spectroscopy at 298 K, that results in higher than expected time-averaged symmetry of the biph ancillary ligand and invokes dissociation of the CF₃ group. Equivalent exchange processes are presumably occurring in 4, although the spectroscopic signatures are asymptomatic due to the inherently higher symmetry of this complex. Further interrogation of 2 – 4 in CD₂Cl₂ was possible by VT NMR spectroscopy (400 MHz; see the Supporting Information), with progressive cooling from 298 to 185 K freezing out the structural dynamics observed for 2 and 3, and inducing the onset of decoalescence for the CF₃ resonances. Moreover, the ¹H ArF signals of 2 – 4 are sharp across the full temperature range, ruling out P–ArF bond rotation on the NMR time scale.
Figure 1. Synthesis and structures of rhodium(III) complexes of PPh₂ArF; [B(3,5-(CF₃)₂C₆H₃)₄]⁻ counter anions omitted for clarity. All reactions were carried out in CH₂Cl₂ at RT; 1 was isolated in 82% yield, and all subsequent substitution reactions proceeded quantitatively by NMR spectroscopy. Solid-state structures drawn with thermal ellipsoids at 50%, and minor disordered components (1×Ph group in 1 and 4) and H atoms are omitted; symmetry equivalent atoms in 1 are generated using the operation (4/3 − x, 5/3 − y, 2/3 − z), only one of the two unique but structurally similar cations shown for 2 and 3 (Z = 2).\textsuperscript{[12]}
Conclusions
Through the isolation and structural characterisation of Rh(III) complexes of PPh₂ArF₁–₄ we have demonstrated the ability of the late transition metal complexes to form well-defined adducts of the widely employed CF₃ functional group. Synthesis of these complexes advances the coordination chemistry of weakly interacting organofluorine compounds, and highlights the use of C–F–M bonding interactions for the stabilisation of transition metal complexes with a low-coordination number; species implicated in many homogenously catalysed reactions.[13] Transient species featuring interactions of this nature could also be invoked in the oxidative addition of C(sp³)–F bonds and our future work will be focused on ascertaining their role in such processes.

Supporting information
- Full experimental details, NMR and ESI-MS spectra of new compounds.
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Acknowledgements
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1. General experimental methods

All manipulations were performed under an atmosphere of argon using Schlenk and glove box techniques. Glassware was oven-dried at 150 °C overnight and flamed under vacuum prior to use. Anhydrous CH₂Cl₂ and hexane (<0.005% H₂O) were purchased from ACROS or Sigma-Aldrich and freeze–pump–thaw degassed three times before being placed under argon over thoroughly vacuum-dried 3 Å molecular sieves. CD₂Cl₂ was freeze–pump–thaw degassed three times before being placed under argon over thoroughly vacuum-dried 3 Å molecular sieves. [Rh(biph)(dtbpm)Cl],¹ PPh₂Ar², Na[acac],³ Na[Cp],⁴ and Na[B(3,5-(CF₃)₂C₆H₃)₄]⁵ were synthesised using literature protocols; 2,2’-bipyridyl was purchased from Sigma-Aldrich and used as supplied. NMR spectra were recorded on either a Bruker Avance III HD 500 MHz or Bruker Avance III 400 MHz spectrometer (all variable temperature measurements). Chemical shifts are quoted in ppm and coupling constants in Hz. High-resolution electrospray ionisation mass spectra (HR ESI-MS) were recorded on a Bruker MaXis II spectrometer. Microanalyses were performed by Stephen Boyer at London Metropolitan University.
2. Preparation of [Rh(biph)(PPh₂Ar²)Cl₂] 1

A solution of [Rh(biph)(dtbpm)Cl] (297.5 mg, 0.500 mmol) and PPh₂Ar² (412.9 mg, 1.250 mmol) in CH₂Cl₂ (3 mL) was stirred at ambient temperature for 18 hours. The resulting yellow microcrystalline precipitate was isolated by filtration, washed with CH₂Cl₂ (3 × 5 mL), and then dried in vacuo to afford the final product. Concentration of the combined filtrate and washings to ca. 5 mL afforded additional product on cooling to 4 °C, which was isolated by filtration, washed with CH₂Cl₂ (3 × 5 mL), and then dried in vacuo. Combined yield: 253.7 mg (82%, yellow solid).

¹H NMR (500 MHz, CD₂Cl₂, 298 K): δ 8.06 (dd, ²J_HH = 8.0, ²J_HP = 3.9, 2H, 6-Ar²), 7.74 (t, ³J_HH = 7.8, 2H, 5-Ar²), 7.50 (t, ³J_HH = 7.7, 2H, 4-Ar²), 7.37 – 7.45 (m, 6H, 3-Ar² + 6-biph), 7.20 (t, ³J_HH = 7.5, 4H, p-Ph), 6.94 – 7.02 (m, 12H, 3-biph + m-Ph), 6.82 (t, ³J_HH = 7.3, 4H, 4-biph), 6.64 (br, 8H, o-Ph), 6.62 (t, ³J_HH = 7.5, 4H, 5-biph).

¹³C(¹H) NMR (126 MHz, CD₂Cl₂, 298 K): δ 158.7 (HMBC, 1-biph), 151.5 (s, 2-biph), 137.3 (s, 3-Ar²), 135.4 (s, 6-biph), 133.8 (d, ²J_PC = 10, o-Ph), 134 (obscured, 2-Ar²), 132.8 (d, ²J_PC = 7, 4-Ar²), 132.0 (s, 5-Ar²), 130.6 (d, ²J_PC = 2, p-Ph), 129.2 (d, ³J_PC = 42, 1-Ar²), 128.6 (br, 6-Ar²), 128 (obscured, i-Ph), 127.8 (d, ³J_PC = 11, m-Ph), 125.2 (s, 5-biph), 124.7 (q, ³J_PC = 277, CF₃), 123.5 (s, 4-biph), 121.3 (s, 3-biph).

³¹P(¹H) NMR (162 MHz, CD₂Cl₂, 298 K): δ 39.1 (dq, ²J_HP = 170, ³J_PP = 4).

¹⁹F(¹H) NMR (376 MHz, CD₂Cl₂, 298 K): δ -62.80 (vbr, fwhm = 15.5 Hz). Processing of this data using sine bell apodization resolved the broad CF₃ signal into an apparent triplet resonance with ²J_HF = ³J_PP = 3 Hz.

HR ESI-MS (positive ion, 4 kV): 626.0718 ([½M–Cl+MeCN]⁺, calcd 626.0726) m/z.

Anal. calcd for C₆₂H₄₃Cl₂F₆P₂Rh₂ (1241.68 g·mol⁻¹): C, 59.97; H, 3.57; N, 0.00. Found: C, 59.90; H, 3.64; N, 0.0.

Figure S1: ¹H NMR spectrum of [Rh(biph)(PPh₂Ar²)Cl₂] 1 (500 MHz, CD₂Cl₂, 298 K).
**Figure S2**: $^{13}$C$^1$H APT NMR spectrum of [Rh(biph)(PPh$_2$Ar$_2$)]Cl$_2$ 1 (126 MHz, CD$_2$Cl$_2$, 298 K).

**Figure S3**: $^{31}$P$^1$H NMR spectrum of [Rh(biph)(PPh$_2$Ar$_2$)]Cl$_2$ 1 (162 MHz, CD$_2$Cl$_2$, 298 K).

**Figure S4**: $^{19}$F$^1$H NMR spectrum of [Rh(biph)(PPh$_2$Ar$_2$)]Cl$_2$ 1 (376 MHz, CD$_2$Cl$_2$, 298 K).
3. Preparation of [Rh(biph)(bipy)(PPh₂Ar⁵)][BAR⁵₄] 2

A suspension of 1 (62.1 mg, 50.0 mmol), Na[B(3,5-(CF₃)₂C₆H₃)₄] (97.5 mg, 110 μmol), and 2,2'-bipyridyl (17.2 mg, 110 μmol) in CH₂Cl₂ (5 mL) was stirred at ambient temperature for 18 h. The resulting yellow solution was filtered, and the product crystallised by the addition of excess hexane (ca. 20 mL). Yield: 137.2 g (85%, yellow solid).
$^1$H NMR (500 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 8.24 (d, $^3$J$_{HH}$ = 8.1, 1H, 3'-bipy), 8.07 – 8.14 (m, 3H, 6-Ar$^f$ + 3-bipy + 4'-bipy), 7.90 (t, $^3$J$_{HH}$ = 7.8, 1H, 4-bipy), 7.87 (t, $^3$J$_{HH}$ = 7.8, 1H, 5-Ar$^f$), 7.75 – 7.78 (m, 1H, 6-bipy), 7.70 – 7.75 (m, 8H, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), 7.63 – 7.69 (m, 2H, 4-Ar$^f$ + 6'-bipy), 7.55 (br, 4H, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), 7.41 (dd, $^3$J$_{HH}$ = 10.9, $^3$J$_{HH}$ = 8.0, 1H, 3-Ar$^f$), 7.27 (t, $^3$J$_{HH}$ = 6.6, 1H, 5'-bipy), 7.20 (t, $^3$J$_{HH}$ = 6.7, 1H, 5-bipy), 5.80 – 8.00 (br m, 18 H, biph + Ph).

$^{13}$C[$^1$H] NMR (126 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 162.3 (q, $^1$J$_{CB}$ = 50, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), 155.94 (d, $^2$J$_{PC}$ = 2, 2/2'-bipy), 155.92 (d, $^2$J$_{PC}$ = 1, 2'/2-bipy), 152.9 (d, $^2$J$_{PC}$ = 2, 6'-bipy), 151.7 (app. t, $^2$J$_{PC}$ = $^3$J$_{PC}$ = 2, 6-bipy), 151.3 (br, tentatively assigned to 1-biph), 140.7 (s, 4'-bipy), 140.5 (s, 4-bipy), 138.5 (d, $^3$J$_{PC}$ = 2, 3-Ar$^f$), 135.4 (s, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), 134.1 (br, tentatively assigned to o-Ph), 133.7 (d, $^4$J$_{PC}$ = 7, 4-Ar$^f$), 133.2 (d, $^4$J$_{PC}$ = 2, 5-Ar$^f$), 132.8 (qd, $^2$J$_{PC}$ = 29, $^2$J$_{PC}$ = 11, 2-Ar$^f$), 129.4 (qq, $^2$J$_{PC}$ = 32, $^3$J$_{CB}$ = 3, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), 128.8 (app p, $^4$J$_{PC}$ = $^4$J$_{PC}$ = 6, 6-Ar$^f$), 127.59 (br, 5-bipy), 127.57 (d, $^4$J$_{PC}$ = 42, 1-Ar$^f$), 127.0 (s, 5'-bipy), 126.9 (s, tentatively assigned to p-Ph), 125.5 (qd, $^4$J$_{PC}$ = 275, $^3$J$_{PC}$ = 2, CF$_3$), 125.3 (br, tentatively assigned to m-Ph), 125.2 (q, $^4$J$_{PC}$ = 272, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), 123.4 – 123.5 (m, 3-bipy + 3'-bipy), 118.0 (sept, $^3$J$_{PC}$ = 4, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$). Due to structural dynamics on the NMR time scale the signals for biph and Ph are either not observed or not unambiguously assigned.

$^{31}$P[$^1$H] NMR (162 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ 32.6 (dq, $^1$J$_{RP}$ = 150, $^2$J$_{PF}$ = 5).

$^{19}$F[$^1$H] NMR (376 MHz, CD$_2$Cl$_2$, 298 K): $\delta$ -62.89 (s, [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$), -67.61 (app t, $^1$J$_{RF}$ ≈ $^2$J$_{RF}$ = 4.0, Ar$^f$).

HR ESI-MS (positive ion, 4 kV): 741.1144 ([M]$^+$, calcld 741.1148) m/z.

Anal. calcld for C$_{73}$H$_{43}$BF$_2$N$_2$PrH (1604.80 g·mol$^{-1}$): C, 54.64; H, 2.64; N, 1.75. Found: C, 54.49; H, 2.80; N, 1.74.

Figure S6: $^1$H NMR spectrum of [Rh(biph)(bipy)(PPh$_3$Ar$^f$)][BAr$^f$$_4$] 2 (500 MHz, CD$_2$Cl$_2$, 298 K).
**Figure S7:** $^{13}$C($^1$H) APT NMR spectrum of [Rh(biph)(bipy)(PPh$_2$Ar$^f$)][BAr$_4$]$^2$ (126 MHz, CD$_2$Cl$_2$, 298 K).

**Figure S8:** $^{31}$P($^1$H) NMR spectrum of [Rh(biph)(bipy)(PPh$_2$Ar$^f$)][BAr$_4$]$^2$ (162 MHz, CD$_2$Cl$_2$, 298 K).

**Figure S9:** $^{19}$F($^1$H) NMR spectra of [Rh(biph)(bipy)(PPh$_2$Ar$^f$)][BAr$_4$]$^2$ (376 MHz, CD$_2$Cl$_2$, 298 K).
Figure S10: VT $^1$H NMR spectra of [Rh(biph)(bipy)(PPh$_2$ArF)][BAr$_4^-$] 2 (400 MHz, CD$_2$Cl$_2$, 298 K).

Figure S11: VT $^{31}$P{$^1$H} NMR spectra of [Rh(biph)(bipy)(PPh$_2$ArF)][BAr$_4^-$] 2 (162 MHz, CD$_2$Cl$_2$, 298 K).

Figure S12: VT $^{19}$F{$^1$H} NMR spectra of [Rh(biph)(bipy)(PPh$_2$ArF)][BAr$_4^-$] 2 (376 MHz, CD$_2$Cl$_2$, 298 K).
**Figure S13:** HR ESI-MS spectrum of [Rh(biph)(bipy)(PPh$_2$Ar)$_3$][BAR$_4$]$_2$.  

| m/z    | Intensity |
|--------|-----------|
| 741.1144 |            |
| 741.4742 |            |
| 742.1176 |            |
| 742.8958 |            |
| 743.1205 |            |
| 743.3845 |            |

The spectrum shows peaks at these m/z values with intensities indicated.
4. Preparation of [Rh(biph)(acac)(PPh₂Ar⁵)] 3

A suspension of 1 (62.1 mg, 50.0 mmol), Na[acac] (13.4 mg, 110 μmol) in CH₂Cl₂ (5 mL) was stirred at ambient temperature for 18 h. The resulting yellow solution was filtered, and the product crystallised by the addition of excess hexane (ca. 20 mL). Yield: 48.4 mg (75%, yellow solid).

**¹H NMR** (500 MHz, CD₂Cl₂, 298 K): δ 8.03 (dd, 3JHH = 8.0, 3JHP = 4.1, 1H, 6-Ar⁵), 7.72 (t, 3JHH = 7.6, 1H, 5-Ar⁵), 7.55 (t, 3JHH = 7.6, 1H, 4-Ar⁵), 7.50 (t, 3JHH = 8.8, 1H, 3-Ar⁵), 7.25 (t, 3JHH = 7.3, 2H, p-Ph), 7.01 – 7.08 (m, 6H, 6-biph + m-Ph), 6.96 (dd, 3JHH = 7.5, 4JHH = 1.6, 2H, 3-biph), 6.88 (app. t, 3JHH ≈ 4JHP = 10, 4H, o-Ph), 6.79 (t, 3JHH = 7.4, 2H, 4-biph), 6.60 (td, 3JHH = 7.5, 4JHH = 1.6, 2H, 5-biph), 5.43 (s, 1H, CH), 1.94 (s, 6H, CH₃).

**¹³C[¹H] NMR** (126 MHz, CD₂Cl₂, 298 K): δ 187.5 (s, CO), 160.8 (br d, ¹JHC = 37, 1-biph), 152.4 (s, 2-biph), 135.8 (s, 3-Ph), 134.5 (d, ²JPC = 10, 1-Ph), 134.2 (s, 6-biph), 132.7 (qd, ²JPC = 30, ³JPC = 11, 2-Ar⁵), 132.3 (d, ³JPC = 6, 4-Ar⁵), 131.5 (d, ³JPC = 2, 5-Ar⁵), 131.1 (d, ⁴JPC = 40, 1-Ar⁵), 130.4 (d, ⁴JPC = 2, p-Ph), 129.0 (d, ¹JPC = 54, i-Ph), 128.5 (app. p, ²JPC ≈ ⁴JPC = 7, 6-Ar⁵), 127.6 (d, ³JPC = 11, m-Ph), 125.2 (qd, ³JPC = 275, ³JPC = 2, CF₃), 124.9 (s, 5-biph), 123.4 (s, 4-biph), 121.2 (s, 3-biph), 99.2 (s, CH), 28.4 (s, CH₃), 28.4 (s, CH₃).

**¹⁹F[¹H] NMR** (376 MHz, CD₂Cl₂, 298 K): δ -64.13 (app. t, ¹JHF = ²JPF = 5).

**HR ESI-MS** (positive ion, 4 kV): 684.0905 ([M]⁺, calcd 684.0907) m/z.

![Figure S14: ¹H NMR spectrum of [Rh(biph)(acac)(PPh₂Ar⁵)] 3 (500 MHz, CD₂Cl₂, 298 K).](image-url)
Figure S15: $^{13}$C{H} APT NMR spectrum of [Rh(biph)(acac)(PPh$_2$Ar$^f$)] $\mathbf{3}$ (126 MHz, CD$_2$Cl$_2$, 298 K).

Figure S16: $^{31}$P{H} NMR spectrum of [Rh(biph)(acac)(PPh$_2$Ar$^f$)] $\mathbf{3}$ (162 MHz, CD$_2$Cl$_2$, 298 K).

Figure S17: $^{19}$F{H} NMR spectrum of [Rh(biph)(acac)(PPh$_2$Ar$^f$)] $\mathbf{3}$ (376 MHz, CD$_2$Cl$_2$, 298 K).
**Figure S18:** VT $^1$H NMR spectra of [Rh(biph)(acac)(PPh$_2$Ar$_F$)$_3$] 3 (400 MHz, CD$_2$Cl$_2$, 298 K).

**Figure S19:** VT $^{31}$P($^1$H) NMR spectra of [Rh(biph)(acac)(PPh$_2$Ar$_F$)$_3$] 3 (162 MHz, CD$_2$Cl$_2$, 298 K).

**Figure S20:** VT $^{19}$F($^1$H) NMR spectra of [Rh(biph)(acac)(PPh$_2$Ar$_F$)$_3$] 3 (376 MHz, CD$_2$Cl$_2$, 298 K).
Figure S21: HR ESI-MS spectrum of [Rh(biph)(acac)(PPh₂Ar)] 3.
5. Preparation of $[\text{Rh(biph)}(\text{PPh}_2\text{Ar})_2][\text{BAR}_4]^4$

A suspension of 1 (62.1 mg, 50.0 μmol), Na[B(3,5-(CF_3)_2C_6H_3)a] (97.5 mg, 110 μmol), and PPh_2Ar (36.3 mg, 110 μmol) in CH_2Cl_2 (5 mL) was stirred at ambient temperature for 18 h. The resulting pale-yellow solution was filtered, and the product crystallised by the addition of excess hexane (ca. 20 mL). Yield: 153.9 mg (87%, pale yellow solid).

$^1$H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.13 (d, $^3J_{HH} = 7.8$, 2H, 6-Ar), 7.87 (t, $^3J_{HH} = 7.8$, 2H, 5-Ar), 7.75 – 7.70 (m, 8H, [B(3,5-(CF_3)_2C_6H_3)_a]^−), 7.69 (t, $^3J_{HH} = 7.8$, 2H, 4-Ar), 7.55 (br, 4H, [B(3,5-(CF_3)_2C_6H_3)_a]^−), 7.49 (dt, $^3J_{HH} = 7.8$, $^3J_{HF} = 5.0$, 2H, 5-Ar), 7.36 (t, $^3J_{HH} = 7.5$, 4H, p-Ph), 7.10 (t, $^3J_{HH} = 7.8$, 8H, m-Ph), 7.03 (d, $^3J_{HH} = 8.0$, 2H, 6-biph), 6.78 (t, $^3J_{HH} = 7.4$, 2H, 4-biph), 6.66 (t, $^3J_{HH} = 7.6$, 2H, 5-biph), 6.56 (vbr, fwhm = 22.5 Hz, 8H, o-Ph), 6.50 (d, $^3J_{HH} = 7.4$, 3-biph).

$^{13}$C($^1$H) NMR (126 MHz, CD_2Cl_2, 298 K): δ 162.3 (q, $^1J_{CB} = 50$, [B(3,5-(CF_3)_2C_6H_3)_a]^−), 152.5 (br d, $^1J_{RC} = 42$, 1-biph), 150.0 (s, 2-biph), 137.4 (s, 3-Ar), 135.3 (s, [B(3,5-(CF_3)_2C_6H_3)_a]^−), 134.1 (t, $^3J_{RC} = 3$, 4-Ar), 133.5 (t, $^1J_{PC} = 6$, o-Ph), 133.1 (s, 5-Ar), 131.9 (s, p-Ph), 131.7 (obscured, 2-Ar), 129.9 (s, 6-biph), 129.4 (qq, $^1J_{RC} = 32$, $^3J_{CB} = 3$, [B(3,5-(CF_3)_2C_6H_3)_a]^−), 129.1 (obscured, m, 6-Ar), 128.9 (t, $^1J_{PC} = 5$, m-Ph), 126.7 (t, $^1J_{PC} = 19$, 1-Ar), 126.1 (s, 5-biph), 125.9 (q, $^1J_{PC} = 276$, CF_3), 125.2 (q, $^1J_{PC} = 272$, [B(3,5-(CF_3)_2C_6H_3)_a]^−), 125.0 (obscured, m-Ph), 124.9 (s, 4-biph), 123.7 (s, 3-biph), 118.0 (sept, $^3J_{RC} = 4$, [B(3,5-(CF_3)_2C_6H_3)_a]^−). $^{31}$P($^1$H) NMR (162 MHz, CD_2Cl_2, 298 K): δ 20.1 (dh, $^1J_{HP} = 124$, $^2J_{PF} = 5$).

$^{19}$F($^1$H) NMR (376 MHz, CD_2Cl_2, 298 K): δ -62.89 (s, [B(3,5-(CF_3)_2C_6H_3)_a]^−), -66.39 (app. q, $^1J_{HP} = 2^1J_{HP} = 5$, Ar).

HR ESI-MS (positive ion, 4 kV): 915.1222 ([M]^+, calcld 915.1246) m/z.

Anal. calcd for C_{82}H_{48}BF_{30}P_{2}Rh (1778.90 g·mol⁻¹): C, 55.37; H, 2.72; N, 0.00. Found: C, 55.56; H, 2.62; N, 0.0.

Figure S22: $^1$H NMR spectrum of $[\text{Rh(biph)}(\text{PPh}_2\text{Ar})_2][\text{BAR}_4]^4$ (500 MHz, CD_2Cl_2, 298 K).
Figure 23: $^{13}\text{C}^{(1)}\text{H}$ APT NMR spectrum of $[\text{Rh(biph)}(\text{PPh}_2\text{Ar}_F)_2][\text{BARF}_4]$ 4 (126 MHz, CD$_2$Cl$_2$, 298 K).

Figure S24: $^{31}\text{P}^{(1)}\text{H}$ NMR spectrum of $[\text{Rh(biph)}(\text{PPh}_2\text{Ar}_F)_2][\text{BARF}_4]$ 4 (162 MHz, CD$_2$Cl$_2$, 298 K).

Figure S25: $^{19}\text{F}^{(1)}\text{H}$ NMR spectrum of $[\text{Rh(biph)}(\text{PPh}_2\text{Ar}_F)_2][\text{BARF}_4]$ 4 (376 MHz, CD$_2$Cl$_2$, 298 K).
Figure S26: VT $^1$H NMR spectra of [Rh(biph)(PPh$_2$Ar$^t$)$_2$][BAr$_4$] 4 (400 MHz, CD$_2$Cl$_2$, 298 K).

Figure S27: VT $^{31}$P($^1$H) NMR spectra of [Rh(biph)(PPh$_2$Ar$^t$)$_2$][BAr$_4$] 4 (162 MHz, CD$_2$Cl$_2$, 298 K).

Figure S28: VT $^{19}$F($^1$H) NMR spectra of [Rh(biph)(PPh$_2$Ar$^t$)$_2$][BAr$_4$] 4 (376 MHz, CD$_2$Cl$_2$, 298 K).
Figure S29: HR ESI-MS spectrum of [Rh(biph)(PPh$_2$Ar$_F$)$_2$][BAR$_F$$_4$] 4.
6. Preparation of \([\text{Rh(biph)(Cp)}(\text{PPh}_2\text{Ar}^\text{F})]_5\)

A suspension of 1 (62.1 mg, 50.0 \(\mu\)mol), Na[Cp] (9.7 mg, 110 \(\mu\)mol) in \(\text{CH}_2\text{Cl}_2\) (5 mL) was stirred at ambient temperature for 18 h. The resulting pale-yellow solution was filtered, and the product crystallised by the addition of excess hexane (ca. 20 mL). Yield: 9.1 mg (13%, yellow solid).

\(^1\text{H NMR}\) (500 MHz, \(\text{CD}_2\text{Cl}_2\), 298 K): \(\delta\) 9.09 (dd, \(^3J_{\text{PH}} = 16.3, \(^3J_{\text{HH}} = 7.8, 1\text{H, 6-Ar}\)), 7.89 (t, \(^3J_{\text{HH}} = 7.7, 1\text{H, 5-Ar}\)), 7.71 (t, \(^3J_{\text{HH}} = 7.8, 1\text{H, 4-Ar}\)), 7.64 (d, \(^3J_{\text{HH}} = 8.0, 1\text{H, 3-Ar}\)), 7.59 (d, \(^3J_{\text{HH}} = 7.5, 2\text{H, 6-biph}\)), 7.19 (td, \(^3J_{\text{HH}} = 7.5, \(^2J_{\text{PH}} = 1.8, 2\text{H, p-Ph}\)), 7.02 (td, \(^3J_{\text{HH}} = 7.8, \(^2J_{\text{PH}} = 2.5, 4\text{H, m-Ph}\)), 6.95 (dd, \(^3J_{\text{HH}} = 7.4, 4\text{H, o-Ph}\)), 6.86 (dd, \(^3J_{\text{HH}} = 8.0, \(^3J_{\text{PH}} = 11.2, 4\text{H, o-Ph}\)), 6.77 (t, \(^3J_{\text{HH}} = 7.4, 2\text{H, 4-biph}\)), 6.67 (td, \(^3J_{\text{HH}} = 7.8, \(^3J_{\text{PH}} = 2.5, 2\text{H, 5-biph}\)), 5.22 (s, 5H, Cp).

\(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (126 MHz, \(\text{CD}_2\text{Cl}_2\), 298 K): \(\delta\) 162.8 (dd, \(^1J_{\text{HC}} = 35, \(^2J_{\text{HC}} = 17, \text{1-biph}\)), 155.3 (s, \text{1-biph}), 144.2 (d, \(^2J_{\text{PC}} = 25, \text{6-Ar}\)), 141.3 (d, \(^3J_{\text{HC}} = 2, \text{6-biph}\)), 134.9 (d, \(^1J_{\text{PC}} = 50, \text{i-Ph}\)), 132.7 (q, \(^2J_{\text{PC}} = 33, \text{2-Ar}\)), 132.0 (d, \(^3J_{\text{PC}} = 2, \text{4-Ar}\)), 131.6 (d, \(^2J_{\text{PC}} = 10, \text{o-Ph}\)), 131.3 (d, \(^3J_{\text{PC}} = 14, \text{5-Ar}\)), 130.3 (d, \(^1J_{\text{PC}} = 38, \text{1-Ar}\)), 129.4 (obscurred, \text{3-Ar}), 129.4 (d, \(^2J_{\text{PC}} = 3, \text{p-Ph}\)), 127.4 (d, \(^3J_{\text{PC}} = 10, \text{m-Ph}\)), 124.0 (s, \text{5-biph}), 123.8 (q, \(^1J_{\text{PC}} = 274, \text{CF}_3\)), 122.7 (s, \text{4-biph}), 121.9 (s, \text{3-biph}), 93.1 (app. t, \(J = 3, \text{Cp}\)).

\(^{31}\text{P}\{^1\text{H}\} \text{NMR}\) (162 MHz, \(\text{CD}_2\text{Cl}_2\), 298 K): \(\delta\) 55.9 (d, \(^1J_{\text{PBP}} = 167\)).

\(^{19}\text{F}\{^1\text{H}\} \text{NMR}\) (376 MHz, \(\text{CD}_2\text{Cl}_2\), 298 K): \(\delta -55.12\) (s).

\text{HR ESI-MS}\) (positive ion, 4 kV): 650.0847 ([M]⁺, calcd 684.0852) \(m/z\).

**Figure S30**: \(^1\text{H NMR spectrum of \([\text{Rh(biph)(Cp)}(\text{PPh}_2\text{Ar}^\text{F})]_5\) (500 MHz, \(\text{CD}_2\text{Cl}_2\), 298 K).**
Figure S31: $^{13}$C\(\text{H}^1\) NMR spectrum of $[\text{Rh}(\text{biph})(\text{Cp})(\text{PPh}_2\text{Ar}^F)] \ 5$ (126 MHz, $\text{CD}_2\text{Cl}_2$, 298 K).

Figure S32: $^{31}$P\(\text{H}^1\) NMR spectrum of $[\text{Rh}(\text{biph})(\text{Cp})(\text{PPh}_2\text{Ar}^F)] \ 5$ (162 MHz, $\text{CD}_2\text{Cl}_2$, 298 K).

Figure S33: $^{19}$F\(\text{H}^1\) NMR spectrum of $[\text{Rh}(\text{biph})(\text{Cp})(\text{PPh}_2\text{Ar}^F)] \ 5$ (376 MHz, $\text{CD}_2\text{Cl}_2$, 298 K).
Figure S34: HR ESI-MS spectrum of [Rh(biph)(Cp)(PPh$_2$Ar)]$_5$.  

7. References

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