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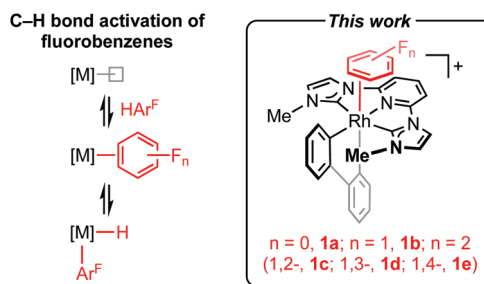
## Isolation and structural characterisation of rhodium(III) $\eta^2$ -fluoroarene complexes: experimental verification of predicted regioselectivity†

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The isolation and solid-state characterisation of complexes featuring partially coordinated benzene, fluorobenzene and all three isomers of difluorobenzene are described. Supported by a DFT analysis, this well-defined homologous series demonstrates the preference for  $\eta^2$ -coordination of fluoroarenes *via* the HC=CH sites adjacent to a fluorine substituent.

Partially fluorinated benzenes are chemically robust and weakly coordinating substrates, for which there is a paucity of late transition metal  $\pi$ -complexes.<sup>1</sup> Whilst well-defined examples can be found in the literature they are almost exclusively limited to half sandwich formulations, where the arene adopts an  $\eta^6$ -coordination mode.<sup>1,2</sup> The formation of  $\eta^2$ -arene complexes is notably invoked in C–H bond oxidative addition of partially fluorinated benzenes to late transition metals (Scheme 1),<sup>3,4</sup> but to the best of our knowledge isolation of mononuclear species of this nature is limited to coinage metal examples.<sup>5</sup> Computational studies indicate a coordination site preference in the order HC=CH > HC=CF > FC=CF, with the strongest  $\eta^2$ -arene complexes formed at the HC=CH positions adjacent to a fluorine substituent.<sup>6</sup> Building on our work employing the high *trans*-influence 2,2'-biphenyl (biph) ancillary ligand,<sup>7,8</sup> we herein present the synthesis and solid-state characterisation of rhodium(III) pincer complexes [Rh(CNC-Me)(biph)( $\eta^2$ -arene)]<sup>+</sup> (Scheme 1; arene = C<sub>6</sub>H<sub>6</sub>, **1a**; FC<sub>6</sub>H<sub>5</sub>, **1b**; 1,2-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, **1c**; 1,3-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, **1d**; 1,4-F<sub>2</sub>C<sub>6</sub>H<sub>4</sub>, **1e**) that corroborate this conclusion experimentally.

To enable systematic synthesis of the target complexes, [Rh(CNC-Me)(biph)( $\kappa^1$ -ClCH<sub>2</sub>Cl)]<sup>+</sup> **2** was ultimately identified



**Scheme 1** Intermediacy of  $\eta^2$ -adducts in the C–H bond activation of fluoroarenes. [B(3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>4</sub>]<sup>−</sup> anion omitted for clarity.

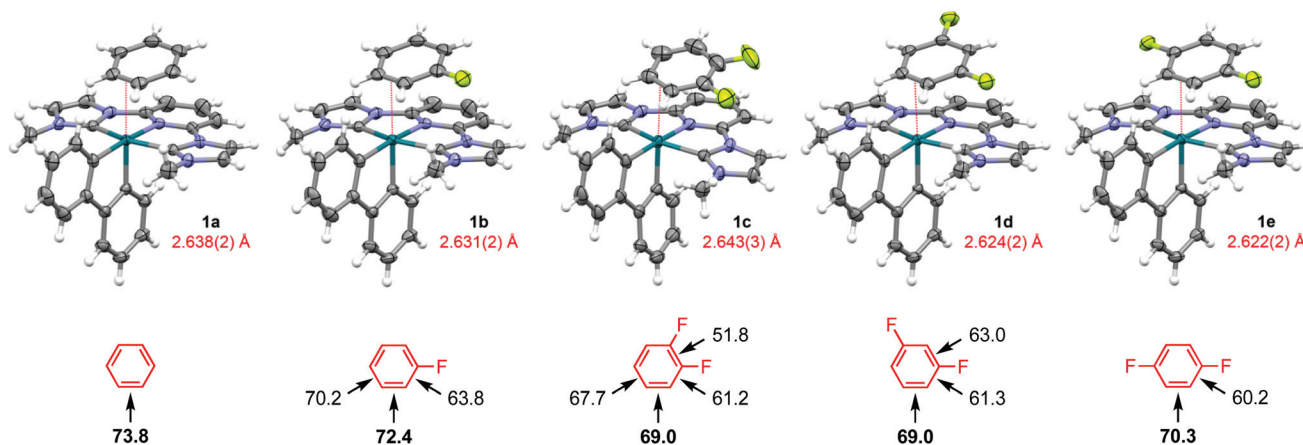
as the most convenient well-defined precursor and prepared using a silver-based transmetalation procedure involving reaction of [Ag(CNC-Me)]<sup>+</sup> with [Rh(biph)Cl(*t*Bu<sub>2</sub>PCH<sub>2</sub>P*t*Bu<sub>2</sub>)] and halide abstraction in CH<sub>2</sub>Cl<sub>2</sub> (80% yield; see ESI† for solid-state structure, Rh–Cl = 2.5932(7) Å).† Dichloromethane is labile and not retained on dissolution of **2** in CD<sub>2</sub>Cl<sub>2</sub> or neat fluoroarene, with the organometallic displaying time averaged C<sub>2v</sub> symmetry at 298 K consistent with formulation as a five-coordinate complex in solution and rapid pseudorotation of the biphenyl ligand on the NMR time scale ( $\Delta H^\ddagger = 75 \pm 1$  kJ mol<sup>−1</sup>,  $\Delta S^\ddagger = +80 \pm 5$  J K<sup>−1</sup> mol<sup>−1</sup>,  $\Delta G_{298K}^\ddagger = 52 \pm 3$  kJ mol<sup>−1</sup> in CD<sub>2</sub>Cl<sub>2</sub>).<sup>6</sup> In the latter case, selective removal of CH<sub>2</sub>Cl<sub>2</sub> *in vacuo* and subsequent recrystallisation from the neat fluoroarene enabled isolation of the corresponding  $\eta^2$ -arene complexes **1b–e** in 61–81% yield. Benzene is a poor solvent for cationic species of this nature, but **1a** was prepared in a similar manner using a 1:1 molar mixture of benzene – 1,2-difluorobenzene in 77% yield. Crystals suitable for analysis by X-ray diffraction were obtained in all cases (Fig. 1), with bulk purity confirmed using a combination of combustion analysis, solid-state <sup>19</sup>F MAS NMR spectroscopy and dissolution in CD<sub>2</sub>Cl<sub>2</sub>; with one equivalent of the respective free arene observed by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy (see ESI).†

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† Electronic supplementary information (ESI) available: Full experimental and computational details, including NMR and IR spectra and ETS-NOCV deformation density plots (PDF), and optimised geometries (XYZ). CCDC 1988128–1988133. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt01137a

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**Fig. 1** Solid-state structures of  $\eta^2$ -arene complexes **1a–e** (top) and calculated binding energies ( $\text{kJ mol}^{-1}$ , bottom). Solid-state structures drawn with thermal ellipsoids at 50% probability, minor disordered components (local symmetry equivalent F atom in **1b**) and  $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$  anion omitted for clarity.

The rigid chelates of the biph and CNC pincer ligands provide a framework for pseudo-octahedral metal geometries in **1a–e**, where  $\eta^2$ -arene coordination [ $\text{Rh}-(\text{C}=\text{C}) = 2.622(2)\text{--}2.643(2)\text{ \AA}$ ] completes the coordination sphere and enables attainment of 18 VE configurations. The observed selectivity for coordination of the fluoroarenes *via* the  $\text{HC}=\text{CH}$  sites adjacent to a fluorine substituent, notably vindicates computational trends in binding energy previously established for neutral rhenium cyclopentadienyl fragments<sup>6</sup> and those determined as part of this study for **1a–e** at the  $\omega\text{B97X-D3/def2-TZVP(f)}$  level of theory (Fig. 1). The absolute magnitudes of the calculated arene binding energies are considerably lower than the corresponding rhenium systems (69.0–73.8 vs. 87.0–99.3  $\text{kJ mol}^{-1}$  for the lowest energy regioisomers), consistent with the cationic nature of **1** and reconciling the entropically unfavourable coordination inferred in solution. Moreover, the relative binding energies of **1a/c** are supported by the aforementioned (competition) experiment involving dissolution of **2** in a 1 : 1 molar mixture of benzene – 1,2-difluorobenzene, yielding exclusively **1a**. DFT-based energy decomposition analysis of the metal-arene bonding interactions using the ETS-NOCV method, as implemented in ORCA 4.1.2,<sup>9</sup> suggests these interactions are dominated by arene to metal  $\sigma$ -donation with only minor metal to arene  $\pi$ -backbonding contributions (see ESI).<sup>†</sup> The former are sufficient to explain the observed regioselectivity for all but **1c**, where subtle differences in  $\pi$ -backbonding are decisive.

In summary, we have exploited a planar NHC-based pincer ligand and the high *trans*-influence 2,2'-biphenyl ancillary to prepare an unprecedented homologous series of rhodium(III) complexes featuring  $\eta^2$ -coordinated benzene and fluoroarenes. Supported by a DFT analysis, these complexes provide evidence for preferential  $\eta^2$ -coordination of fluoroarenes *via* the  $\text{HC}=\text{CH}$  sites adjacent to a fluorine substituent; an important finding relevant to the selective C–H activation of these valuable fluoroaryl synthons.

## Conflicts of interest

There are no conflicts to declare.

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