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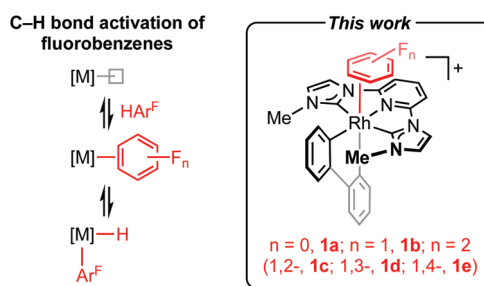
Isolation and structural characterisation of rhodium(III) η²-fluoroarene complexes: experimental verification of predicted regioselectivity†

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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 η²-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 π-complexes.[1] Whilst well-defined examples can be found in the literature they are almost exclusively limited to half sandwich formulations, where the arene adopts an η⁶-coordination mode.[1,2] The formation of η²-arene complexes is notably invoked in C–H bond oxidative addition of partially fluorinated benzenes to late transition metals (Scheme 1),[3,4] but to the best of our knowledge isolation of mononuclear species of this nature is limited to coinage metal examples.[5] Computational studies indicate a coordination site preference in the order HC=CH > HC=CF > FC=CF, with the strongest η²-arene complexes formed at the HC=CH positions adjacent to a fluorine substituent.[6] Building on our work employing the high *trans*-influence 2,2′-biphenyl (biph) ancillary ligand,[7,8] we herein present the synthesis and solid-state characterisation of rhodium(III) pincer complexes [Rh(CNC-Me)(biph)(η²-arene)]⁺ (Scheme 1; arene = C₆H₆, **1a**; FC₆H₅, **1b**; 1,2-F₂C₆H₄, **1c**; 1,3-F₂C₆H₄, **1d**; 1,4-F₂C₆H₄, **1e**) that corroborate this conclusion experimentally.

To enable systematic synthesis of the target complexes, [Rh(CNC-Me)(biph)(κ¹-ClCH₂Cl)]⁺ **2** was ultimately identified

Scheme 1 Intermediacy of η²-adducts in the C–H bond activation of fluoroarenes. [B(3,5-(CF₃)₂C₆H₃)₄]⁻ anion omitted for clarity.

as the most convenient well-defined precursor and prepared using a silver-based transmetallation procedure involving reaction of [Ag(CNC-Me)]⁺ with [Rh(biph)Cl(*t*Bu₂PCH₂P*t*Bu₂)] and halide abstraction in CH₂Cl₂ (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 CD₂Cl₂ or neat fluoroarene, with the organometallic displaying time averaged C_{2v} 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⁻¹, $\Delta S^{\ddagger} = +80 \pm 5$ J K⁻¹ mol⁻¹, $\Delta G^{\ddagger}_{298K} = 52 \pm 3$ kJ mol⁻¹ in CD₂Cl₂).[6] In the latter case, selective removal of CH₂Cl₂ *in vacuo* and subsequent recrystallisation from the neat fluoroarene enabled isolation of the corresponding η²-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 ¹⁹F MAS NMR spectroscopy and dissolution in CD₂Cl₂; with one equivalent of the respective free arene observed by ¹H and ¹⁹F NMR spectroscopy (see ESI).†

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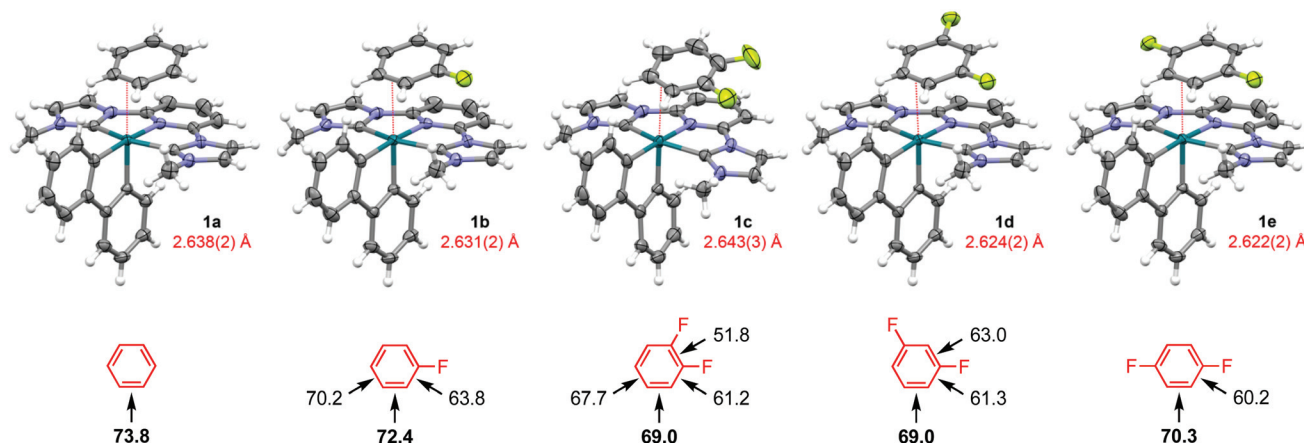
Fig. 1 Solid-state structures of η²-arene complexes **1a–e** (top) and calculated binding energies (kJ mol⁻¹, bottom). Solid-state structures drawn with thermal ellipsoids at 50% probability, minor disordered components (local symmetry equivalent F atom in **1b**) and [B(3,5-(CF₃)₂C₆H₃)₄]⁻ anion omitted for clarity.

The rigid chelates of the biph and CNC pincer ligands provide a framework for pseudo-octahedral metal geometries in **1a–e**, where η²-arene coordination [Rh–(C≡C) = 2.622(2)–2.643(2) Å] completes the coordination sphere and enables attainment of 18 VE configurations. The observed selectivity for coordination of the fluoroarenes *via* the HC=CH sites adjacent to a fluorine substituent, notably vindicates computational trends in binding energy previously established for neutral rhenium cyclopentadienyl fragments[6] and those determined as part of this study for **1a–e** at the ωB97X-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 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,[9] suggests these interactions are dominated by arene to metal σ-donation with only minor metal to arene π-backbonding contributions (see ESI).† The former are sufficient to explain the observed regioselectivity for all but **1c**, where subtle differences in π-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 η²-coordinated benzene and fluoroarenes. Supported by a DFT analysis, these complexes provide evidence for preferential η²-coordination of fluoroarenes *via* the HC=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.

Acknowledgements

Notes and references

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