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Isolation and structural characterisation of rhodium(III) η^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 η^2 -coordination of fluoroarenes \emph{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. Whilst well-defined examples can be found in the literature they are almost exclusively limited to half sandwich formulations, where the arene adopts an n⁶-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 η^2 -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 = C_6H_6 , 1a; FC_6H_5 , 1b; 1,2- $F_2C_6H_4$, 1c; 1,3- $F_2C_6H_4$, 1d; $1,4-F_2C_6H_4,$ 1e) that corroborate this conclusion experimentally.

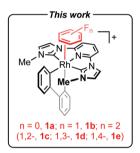
To enable systematic synthesis of the target complexes, $[Rh(CNC-Me)(biph)(\kappa^1-ClCH_2Cl)]^+$ 2 was ultimately identified

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Scheme 1 Intermediacy of η^2 -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 $[Rh(biph)Cl(tBu_2PCH_2PtBu_2)]$ 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 ± 1 kJ mol⁻¹, ΔS^{\ddagger} = +80 ± 5 J K⁻¹ mol⁻¹, $\Delta G_{298K}^{\ddagger}$ = 52 ± 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 η^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 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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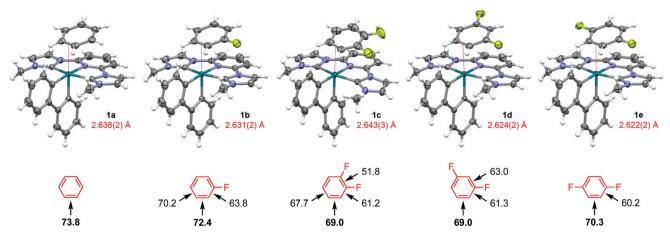


Fig. 1 Solid-state structures of η^2 -arene complexes 1a-e (top) and calculated binding energies (kJ mol⁻¹, bottom). Solid-state structures drawn with thermal ellipsoids at 50% probability, minor disordered components (local symmetry equivalent F atom in 1b) and $[B(3,5-(CF_3)_2C_6H_3)_4]^-$ anion omitted for clarity.

The rigid chelates of the biph and CNC pincer ligands provide a framework for pseudo-octahedral metal geometries in 1a-e, where η^2 -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 fragments⁶ 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 ν s. 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, 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 $\it trans$ -influence 2,2'-biphenyl ancillary to prepare an unprecedented homologous series of rhodium(m) complexes featuring η^2 -coordinated benzene and fluoroarenes. Supported by a DFT analysis, these complexes provide evidence for preferential η^2 -coordination of fluoroarenes $\it via$ 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.

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