



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 $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$ 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 η^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 fragments⁶ 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 ($69.0\text{--}73.8$ vs. $87.0\text{--}99.3\text{ kJ mol}^{-1}$ 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 4.1.2,⁹ 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 η^2 -coordinated benzene and fluoroarenes. Supported by a DFT analysis, these complexes provide evidence for preferential η^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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