





**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  $[\text{B}(\text{3,5}-(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]^-$  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 [ $\text{Rh}-(\text{C}=\text{C}) = 2.622(2)–2.643(2) \text{ \AA}$ ] 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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