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

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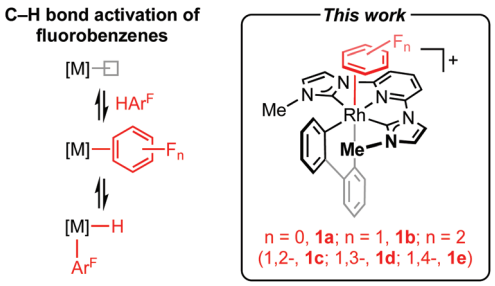
The isolation and solid-state characterisation of complexes featuring partially coordinated benzene, fluorobenzene and all three isomers of difluorobenzene are described. Supported by a DFT analysis, this well-defined homologous series demonstrates the preference for η^2-coordination of fluoroarenes *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 η^6-coordination mode.[1,2] The formation of η^2-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 $[Rh(CNC\text{-}Me)(biph)(\eta^2\text{-arene})]^+$ (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, $[Rh(CNC\text{-}Me)(biph)(\kappa^1\text{-}ClCH_2Cl)]^+$ **2** was ultimately identified as the most convenient well-defined precursor and prepared using a silver-based transmetallation procedure involving reaction of $[Ag(CNC\text{-}Me)]^+$ with $[Rh(biph)Cl(tBu_2PCH_2PtBu_2)]$ and halide abstraction in CH_2Cl_2 (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_2Cl_2 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}, $\Delta S^{\ddagger}$ = +80 ± 5 J K^{-1} mol^{-1}, $\Delta G^{\ddagger}_{298K}$ = 52 ± 3 kJ mol^{-1} in CD_2Cl_2).[6] In the latter case, selective removal of CH_2Cl_2 *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 ^{19}F MAS NMR spectroscopy and dissolution in CD_2Cl_2; with one equivalent of the respective free arene observed by ^1H and ^{19}F NMR spectroscopy (see ESI).†



Scheme 1 Intermediacy of η^2-adducts in the C–H bond activation of fluoroarenes. $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ anion omitted for clarity.

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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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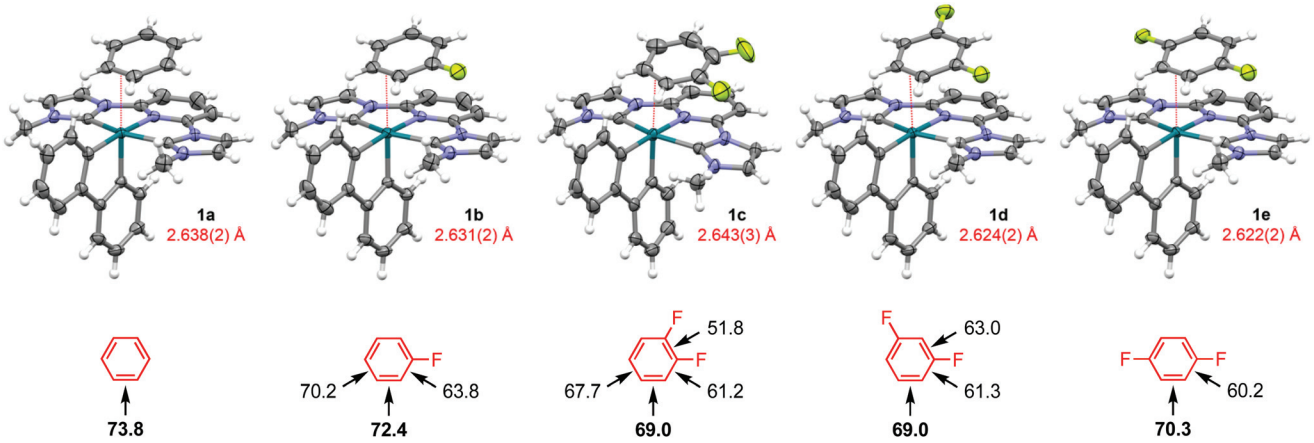

Fig. 1 Solid-state structures of η^2-arene complexes **1a–e** (top) and calculated binding energies (kJ mol^{-1}, bottom). Solid-state structures drawn with thermal ellipsoids at 50% probability, minor disordered components (local symmetry equivalent F atom in **1b**) and $[B(3,5\text{-}(CF_3)_2C_6H_3)_4]^-$ 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 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 η^2-coordinated benzene and fluoroarenes. Supported by a DFT analysis, these complexes provide evidence for preferential η^2-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.

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Notes and references

1 S. D. Pike, M. R. Crimmin and A. B. Chaplin, *Chem. Commun.*, 2017, **53**, 3615–3633.
2 For recent rhodium examples see: (*a*) A. I. McKay, J. Barwick-Silk, M. Savage, M. C. Willis and A. S. Weller, *Chem. – Eur. J.*, 2020, **26**, 2883–2889; (*b*) A. L. Colebatch, A. I. McKay, N. A. Beattie, S. A. Macgregor and A. S. Weller, *Eur. J. Inorg. Chem.*, 2017, 4533–4540; (*c*) S. D. Pike, I. Pernik, R. Theron, J. S. McIndoe and A. S. Weller, *J. Organomet. Chem.*, 2015, **784**, 75–83; (*d*) I. Pernik, J. F. Hooper, A. B. Chaplin, A. S. Weller and M. C. Willis, *ACS Catal.*, 2012, **2**, 2779–2786; (*e*) A. B. Chaplin, J. F. Hooper, A. S. Weller and M. C. Willis, *J. Am. Chem. Soc.*, 2012, **134**, 4885–4897.
3 O. Eisenstein, J. Milani and R. N. Perutz, *Chem. Rev.*, 2017, **117**, 8710–8753.
4 For spectroscopic evidence see: J. J. Carbó, O. Eisenstein, C. L. Higgitt, A. H. Klahn, F. Maseras, B. Oelckers and R. N. Perutz, *Dalton Trans.*, 2001, 1452–1461.
5 For representative examples see: (*a*) A. Martens, P. Weis, M. C. Krummer, M. Kreuzer, A. Meierhöfer, S. C. Meier,

J. Bohnenberger, H. Scherer, I. Riddlestone and I. Krossing, *Chem. Sci.*, 2018, **9**, 7058–7068; (*b*) M. M. D. Roy, M. J. Ferguson, R. McDonald and E. Rivard, *Chem. Commun.*, 2018, **54**, 483–486; (*c*) R. Ramírez-Contreras and O. V. Ozerov, *Dalton Trans.*, 2012, **41**, 7842–7844; (*d*) G. Santiso-Quinones, A. Higelin, J. Schaefer, R. Brückner, C. Knapp and I. Krossing, *Chem. – Eur. J.*, 2009, **15**, 6663–6677.

6 E. Clot, B. Oelckers, A. H. Klahn, O. Eisenstein and R. N. Perutz, *Dalton Trans.*, 2003, 4065–4074.

7 T. M. Hood, B. Leforestier, M. R. Gyton and A. B. Chaplin, *Inorg. Chem.*, 2019, **58**, 7593–7601.

8 (*a*) T. M. Hood, M. R. Gyton and A. B. Chaplin, *Dalton Trans.*, 2020, **49**, 2077–2086; (*b*) J. Emerson-King, I. Prokes and A. B. Chaplin, *Chem. – Eur. J.*, 2019, **25**, 6317–6319; (*c*) M. R. Gyton, B. Leforestier and A. B. Chaplin, *Organometallics*, 2018, **37**, 3963–3971; (*d*) R. C. Knighton, J. Emerson-King, J. P. Rourke, C. A. Ohlin and A. B. Chaplin, *Chem. – Eur. J.*, 2018, **24**, 4927–4938.

9 (*a*) A. Altun, F. Neese and G. Bistoni, *J. Chem. Theory Comput.*, 2019, **15**, 215–228; (*b*) M. P. Mitoraj, A. Michalak and T. Ziegler, *J. Chem. Theory Comput.*, 2009, **5**, 962–975; (*c*) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2018, **8**, e1327; (*d*) F. Neese, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2012, **2**, 73–77.