Dalton Transactions

COMMUNICATION

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Cite this: *Dalton Trans.*, 2020, **49**, 5791

Received 4th March 2020,
Accepted 2nd April 2020

DOI: 10.1039/d0dt01137a

rsc.li/dalton

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

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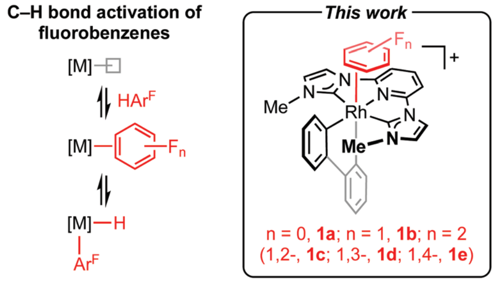
**The isolation and solid-state characterisation of complexes featuring partially coordinated benzene, fluorobenzene and all three isomers of difluorobenzene are described. Supported by a DFT analysis, this well-defined homologous series demonstrates the preference for $\eta^2$-coordination of fluoroarenes *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 $\eta^6$-coordination mode.[1,2] The formation of $\eta^2$-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 $\eta^2$-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.



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

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 $\eta^2$-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 $^1$H and $^{19}$F NMR spectroscopy (see ESI).†

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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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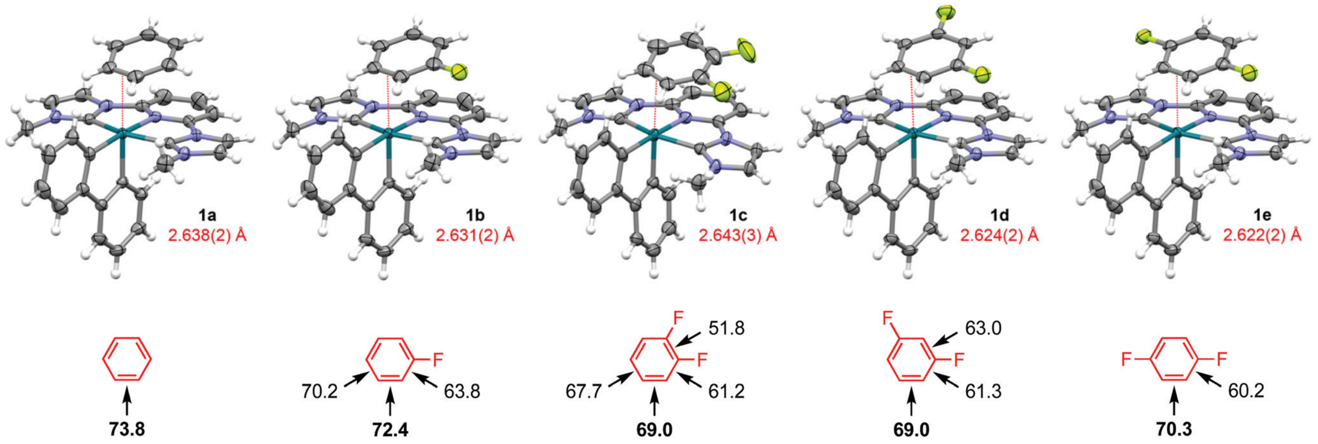

**Fig. 1** Solid-state structures of η$^2$-arene complexes **1a–e** (top) and calculated binding energies (kJ mol$^{-1}$, bottom). Solid-state structures drawn with thermal ellipsoids at 50% probability, minor disordered components (local symmetry equivalent F atom in **1b**) and $[B(3,5-(CF_3)_2C_6H_3)_4]^-$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

## Acknowledgements

This work was supported by European Research Council (ERC, grant agreements 637313 and 639907) and Royal Society (UF100592, UF150675). Computing facilities were provided by the Scientific Computing Research Technology Platform of the University of Warwick.

## 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.