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Steric effects on acetate-assisted cyclometallation of *meta*-substituted *N*-phenyl and *N*-benzyl imidazolium salts at $[MCl_2Cp^*]_2$ (M = Ir, Rh)†

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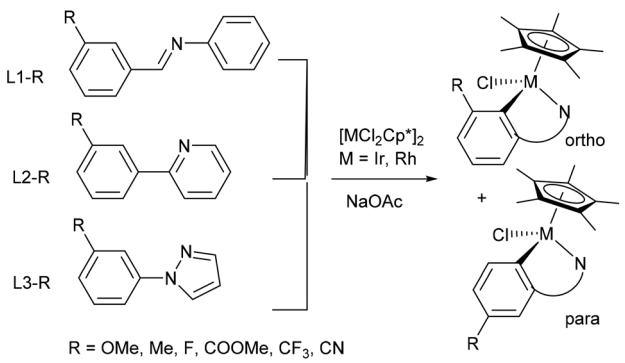
meta-Substituted *N*-phenyl,*N*′-methyl and *N*-benzyl,*N*′-methyl imidazolium salts undergo acetate-assisted cyclometallation to provide mixtures of *ortho* and *para* substituted cyclometallated complexes. The effect of the substituents on the isomer ratios is discussed; steric effects are more important in the 6-membered rings derived from the *N*-benzyl imidazolium salts than 5-membered rings from the *N*-phenyl salts. Comparisons are made to steric effects with some other common directing groups.

Introduction

Carboxylate-assisted cyclometallation is now a very well-established reaction both stoichiometrically and in catalysis.[1] Whilst there are now hundreds of examples in catalysis there are still relatively few publications that focus on a detailed understanding of the steric and electronic influences on the cyclometallation step. Acetate assisted cyclometallation at Cp*M (M = Ir, Rh) centres proceeds from $[M(OAc)_2Cp^*]$ which can be accessed by the reaction of $[MCl_2Cp^*]_2$ with NaOAc.[2] Cyclometallation consists of a number of steps (i) coordination of the directing group, (ii) possible anion loss, (iii) proton transfer to form coordinated carboxylic acid, (iv) substitution of carboxylic acid either by halide if stoichiometric, or by another substrate in catalysis. Recently, we described steric and electronic effects on acetate assisted cyclometallation of phenyl pyrazoles at Cp*M (M = Ir, Rh)[3] and (arene)Ru centres.[4] We showed that cyclometallation is kinetically favoured at electron rich phenyl groups but thermodynamically at electron poor ones. For *meta* substituted substrates steric factors were particularly important in controlling the *ortho*/*para* selectivity with *para* isomers being favoured thermodynamically for all substituents studied except fluorine. DFT studies surprisingly showed that initial proton transfer to form *ortho* isomers could actually be favoured over the *para* isomers, even for sterically bulky substituents. However, in those cases loss of coordinated acetic acid from the *ortho* isomer was significantly more endergonic leading to fast reverse proton transfer, which could only be detected by H/D exchange. The only exceptions to this were *meta*-fluorinated phenyl rings which always favoured the *ortho*-fluorine substituted products; a preference that is well precedented in other systems and is known as the "*ortho* effect".[5]

Jones *et al.* compared the effect of different directing groups phenylimines **L1-R** and phenylpyridines **L2-R** with $[MCl_2Cp^*]_2$ (M = Ir, Rh) on the regioselectivity of cyclometallation of differently *meta*-substituted phenyls (Scheme 1).[6] We have subsequently examined related reactions with phenylpyrazoles **L3-R**[3] and re-examined some phenylpyridines.[7] In making comparisons between different directing groups it is important to bear in mind that the *ortho* : *para* ratios of the products can vary over time. Therefore, ideally, final ratios corresponding to thermodynamic ratios should be compared. Jones *et al.* left their reactions a set amount of time and there is no mention of whether the ratios changed over time. It should be noted that reactions at Cp*Ir are faster and less easily reversible than those at Cp*Rh and those with electron



Scheme 1 *Meta*-substituted phenylimines **L1-R**,[6] phenylpyridines **L2-R**,[6,7] and phenylpyrazoles **L3-R**,[3] and their products from acetate assisted cyclometallation with $[MCl_2Cp^*]_2$ (M = Ir, Rh).[6]

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donating substituents equilibrate faster than those with electron withdrawing substituents.[3,6,8]

The *ortho* : *para* ratio of products for **L1-3** are shown in Table 1. As can be seen for the larger substituents CF_3 and Me the *para* isomer is heavily favoured. With less bulky substituents (R = OMe) two isomers were formed but the *para*-isomer was still preferred. However, for the F-substituted ligands the *ortho* isomer was favoured in all cases. Jones *et al.* suggested that the selectivity of *meta*-substituted phenylpyridines **L2-R** was slightly less than with the imines because the phenyl imines are more bulky than the corresponding pyridines. However, this seems to be mainly based on the selectivity with **L2-CF$_3$**, results which we were unable to reproduce. In our study **L2-CF$_3$** gave only the *para* isomer for both metals.

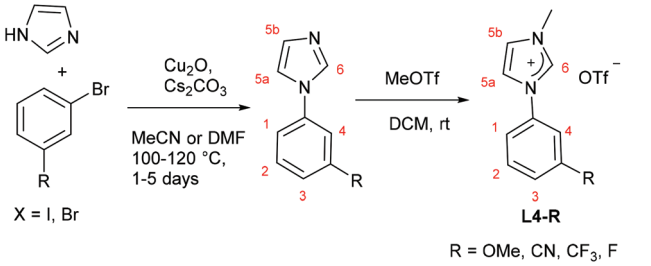
All the ligands mentioned above cyclometallate to form five membered rings. Formation of six-membered rings by acetate assisted cyclometallation is known, though it is less facile than for five-membered rings. For example, cyclometallation of 2-phenylpyridine with $[IrCl_2Cp^*]_2$ is complete within 4 hours,[9] whilst the corresponding reaction of 2-benzylpyridine takes 20 hours.[10] In addition, 2-phenylpyridines react with both Ir and Rh,[6,9] whilst 2-benzylpyridine was only shown to give a complex with Ir and not Rh.[6]

Both five and six-membered cyclometallated ring complexes with NHCs are well known[11] however in nearly all cases the phenyl that is activated has a *para*-substituent so only one product can be formed with the substituent *meta* to the metal. Here we examine acetate assisted cyclometallation of *meta*-substituted *N*-phenyl and *N*-benzyl imidazolium salts to consider the effect of directing group and ring size on steric effects on the cyclometallation.

Results and discussion

To examine NHCs as donor ligands we studied cyclometallation of *meta*-substituted *N*-phenyl, *N*′-methyl imidazolium salts **L4-R** (R = OMe, F, CF_3, CN) which were prepared as shown in Scheme 2 in high yields (72–98%). **L4-OMe**, **L4-F** and **L4-CN** are new compounds, whilst **L4-CF$_3$** is known as the iodide salt.[12]

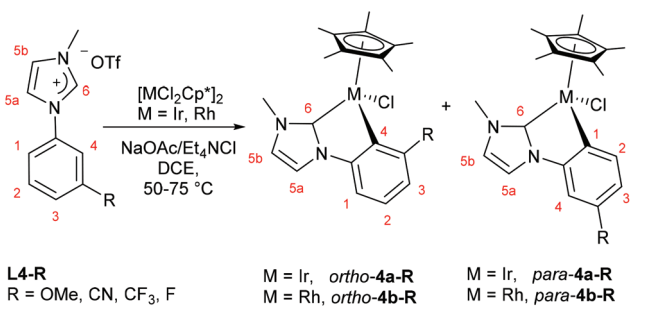
The reactions of **L4-R** with $[MCl_2Cp^*]_2$ (M = Ir, Rh) were carried out in the presence of NaOAc at 75 °C in dichloroethane; however very low conversions were observed after heating overnight.[13] The reactions were repeated in the presence of Et_4NCl[14] and proceeded slowly even at room temperature and gave high conversions (Scheme 3) and the products **4a/b-R** (R = OMe, CN, CF_3, F) were fully characterised.



Scheme 2 Preparation and NMR labelling scheme of *meta*-substituted *N*-phenyl,*N*′-methyl limidazolium salts **L4-R**.

Each isomer has a characteristic pattern in the ^{1}H NMR spectrum, for the *para* isomer H^4 is a very narrow doublet and H^2 shows an noe to the Cp* signal. The reactions were repeated and monitored at room temperature (*ca.* 20% conversion) and upon heating (50 °C overnight) to further investigate if the ratios change and so whether selectivity is kinetic or thermodynamic (see below).

All the reactions gave a mixture of two isomers and the ratios are shown in Table 2. In no case was an intermediate non-cyclometallated complex observed. This is consistent with activation of the imidazolium CH bond being relatively slow and the cyclometallation of the phenyl being much faster.[15]



Scheme 3 Reactions of **L4-R** with $[MCl_2Cp^*]_2$ (M = Ir, Rh) and NMR labelling scheme.

Table 1 *Ortho* : *para* ratios of acetate-assisted cyclometallation of *meta*-substituted ligands **L1-R**,[6] **L2-R**[6,7] and **L3-R**[3]

	L1-R		L2-R		L3-R	
R	Ir,	Rh	Ir	Rh	Ir	Rh
OMe	1 : 1.7	1 : 1.7	1 : 2.5[a]	1 : 3.0[a]	1 : 1.4	1 : 3.9
Me	*para* only	*para* only	*para* only	*para* only[b]	1 : 10	*para* only
CF_3	*para* only	*para* only	*para only*[c]	*para only*[c]	*para* only	*para* only
F	2.3 : 1	8.5 : 1	3.4 : 1	11 : 1	40 : 1	44 : 1

[a] Jones reported *ortho* : *para* ratios of 1 : 1.1 and 1 : 2.5 for Ir and Rh respectively but we found these changed with further heating. [b] Jones reported a small amounts of a second species presumed to be the *ortho* isomer,[6] however the selectivity with Rh is usually higher than with Ir hence it is likely that the minor species is a very small amount of an impurity. [c] Jones reported *ortho* : *para* ratios of 1 : 6.4 and 1 : 8.4 for Ir and Rh respectively. However, we found no evidence for *ortho* isomers in the ^{19}F or ^{1}H NMR spectra.

Table 2 *Ortho* : *para* ratios of acetate-assisted cyclometallation of *meta*-Substituted ligands **L4-R** in DCM/MeOH

Entry	R	Ir		Rh	
		r.t.	50 °C	r.t.	50 °C
1	OMe[a]	1 : 1.5[a]	1 : 3.0[a]	1 : 3.0	1 : 3.0
2	CN	1 : 1.3	1 : 2.2	1.2 : 1	1 : 2.0
3	CF_3	1 : 3[b]	1:>20[b]	1 : 6[b]	1:>40[b]
4	F	2.2 : 1	2.2 : 1	6.0 : 1	10 : 1

[a] In DCE at 50 °C after 1 hour and then after 6 hours. [b] Due to the small amount of minor species present it is not possible to unambiguously identify it as the *ortho* isomer.

The reactions of **L4-R** (R = OMe, CN, CF_3) with both Ir and Rh showed that a mixture of the *ortho* and *para*-isomers was formed initially with increasing fraction of the *para*-isomer after heating (entries 1–3 Table 2).

This indicates that the *para*-isomer is thermodynamically favoured, whilst kinetically there is no clear preference for either the *para* or the *ortho*-isomers, except for R = CF_3 which favours the *para* isomer kinetically and thermodynamically. For the reactions of **L4-F** both Ir and Rh favour the *ortho* isomer and with Rh the selectivity increases with heating indicating that the *ortho* isomer is favoured thermodynamically. This preference for *ortho* fluorine has been observed previously.[3,5,6]

Overall, the steric bulk mainly controls the regioselectivities in agreement with the results observed with phenylimines,[6] phenylpyridines[6,7] and phenylpyrazoles.[3] However, in those cases none of the *ortho*-isomer was observed for the reactions with R = CF_3, whilst it was present in substantial quantities for the reactions of **L4-CF_3** suggesting that there is less steric crowding at the metal centre in **4a/b-R** compared to phenylimine,[6] phenylpyridine,[6,7] and phenylpyrazole complexes.[3]

To examine the effect of ring size on regioselectivity we examined cyclometallation of *N*-benzyl,*N*′-methyl imidazolium salts **L5-R** (R = OMe, CF_3, F). These were prepared by reaction of *N*-methyl imidazole with an excess of appropriately *meta*-substituted benzyl chloride for 1–2 days. All three salts **L5-R** (R = OMe, CF_3, F) were obtained in moderate to good yields (55–87%) and have been reported previously.[16]

The cyclometallated complexes **6a/b-R** were prepared in a stepwise manner, transmetallation to form NHC bound complexes **5a/b-R** followed by cyclometallation (Scheme 4).[11a] Thus, **L5-R** (R = OMe, CF_3, F) was stirred with Ag_2O in the dark for 1 hour to give a silver NHC complex. The reactions were filtered through Celite to remove the excess of Ag salts, and the resulting filtrate was reacted with $[MCl_2Cp^*]_2$ (M = Ir, Rh) (Scheme 4) which after work up gave the new complexes **5a/b-R** (R = OMe, CF_3, F), in moderate to excellent yields (67–92%).

The ^{1}H NMR spectra of **5a/b-R** show two mutually coupled doublets at δ 5–6.5 due to the benzylic protons showing the chiral nature of the complexes with no mirror plane. Complex **5a-OMe** gave crystals suitable for X-ray diffraction and the structure is shown in Fig. 1. The orientation of the NHC ligand confirms that the benzyl protons are inequivalent and that the benzyl group has not cyclometallated.

The cyclometallated complexes **6a/b-R** were prepared in good to excellent yields (68–96%) by reaction of **5a/b-R** (R = OMe, CF_3, F) with NaOAc in DCM : MeOH (4 : 1) at room temperature (Scheme 4). The ^{1}H NMR spectra of **6a/b-R** show the mutually coupled benzylic proton doublets are closer together (between δ 4.5 and 5.0) than in complexes **5a/b-R.** For both the OMe and CF_3 substituted complexes only the *para*-isomer was

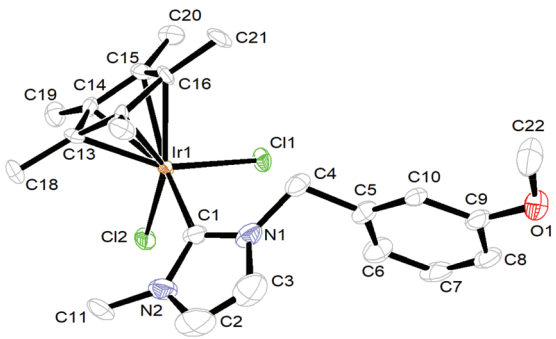
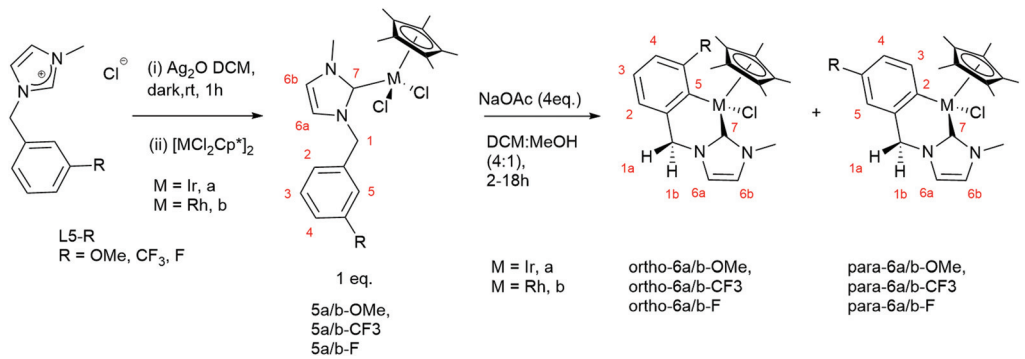


Fig. 1 The molecular structures of **5a-OMe** with 50% ellipsoids. H-atoms omitted for clarity. Selected bond distances Å; Ir–C(1), 2.047 (9), Ir–Cl(1) 2.417(2), Ir–Cl(2) 2.409(3).



Scheme 4 Synthesis and labelling of **6a/b-R**.

Table 3 *Ortho* : *para* ratios of acetate-assisted cyclometallation of complexes **5a/b-R**

Entry	R	Ir		Rh	
		1 day	10 days (conversion)	1 day	10 days (conversion)
1	OMe	1 : 1	1 : 10 (95%)	1 : 1	1 : >30(50%)
2	CF_3	*para*-only	*para*-only (33%)	*para*-only	*para*-only (15%)
3	F	10 : 1	10 : 1 (100)[a]	10 : 1	9 : 1 (100)[a]

[a] After heating in DCM/MeOH (4/1) at 50 °C for 2 days.

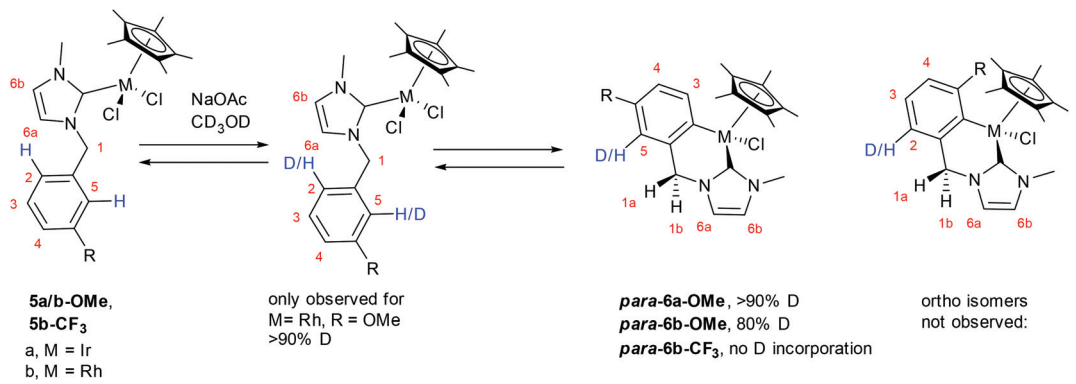
observed in each case; for the F-substituted products **6a/b-F** a mixture of both isomers (approximately 10 : 1) was formed favouring the *ortho* isomer in each case. The reactions were repeated in $CDCl_3$, in which they were considerably slower, to measure the initial product ratios and see if these changed over time and with heating (Table 3).

For the reactions of **5a/b-OMe** (entry 1 Table 3) at low conversions (<20%), the *ortho* and *para*-isomers **6a/b-OMe** were observed in 1 : 1 ratio. As the time and conversion increased the ratio between the two isomers changed significantly in favour of the *para*-isomer for both Ir (*ortho* : *para* 1 : 10) and Rh which showed only traces of the *ortho*-isomer. These results indicate that the *para*-isomer is favoured thermodynamically in this case, whilst there is almost no kinetic preference for either the *ortho* or *para* isomer.

This is consistent with the isolation of only the *para*-isomers **6a/b-OMe** from the preparative reactions in DCM : MeOH (4 : 1). In the case of **5a/b-CF_3** all the ^{1}H NMR spectra irrespective of conversion only showed the *para*-isomer (as in DCM : MeOH). Based on our related work with phenylpyrazoles it is likely that formation of the *ortho*-isomer is significantly endergonic so is not observed. The cyclometallations of **5a/b-F** led to the formation of **6a/b-F** in 10 : 1 *ortho* : *para* ratio for both Ir and Rh, (entries 5 and 6) irrespective of percentage conversion. Approximately the same ratios were formed in DCM : MeOH (4 : 1) after heating for 50 °C for two days. As the ratios did not change it is likely that the kinetic and thermodynamic selectivity are similar.

The reversibility of the cyclometallation of the benzyl complexes was probed by deuteration studies as in similar studies.[3–4,7,8b] Thus, **5a/b-OMe**, and **5b-CF_3** were reacted with NaOAc in CD_3OD and the percentage D-incorporation was determined by integration and the results are shown in Scheme 5.[17] For **5a/b-OMe**, a high D-incorporation (>80%) was observed in the *para* isomer products, *para*-**6a-OMe** and *para*-**6b-OMe**. The formation of the deuterated products shows that formation of the *ortho*-isomer had occurred but was easily reversible, ultimately leading to preferential formation of the thermodynamically favoured *para*-isomer (a more detailed scheme showing how D incorporation occurs is in the SI). This is consistent with entries 1 and 2 in Table 3 discussed above which show that the *ortho* : *para* ratio changes over time favouring the *para* isomer. Note, for Rh complex **5b-OMe** the reaction only reached about 55% conversion overnight and the starting complex was deuterated at sites 2 and 5 showing that formation of both isomers is reversible under these conditions. No D-incorporation was detected for the cyclometallation of **5b-CF_3**. This result shows that either the formation of the *ortho*-isomer has a significantly higher activation barrier than that of the *para*-isomer so the *para* isomer is kinetically preferred and/or formation of the *ortho*-isomer is so easily reversible that there is no time for H/D-exchange. In addition, the lack of observation of deuterated starting material means that formation of *para*-**6b-CF_3** is exergonic so not easily reversible.

Comparing the regioselectivity of the phenyl and benzyl complexes the phenyl-NHC complexes **4a/b-R** even for the largest substituent (R = CF_3) show some *ortho*-isomer (25 and 14% for Ir and Rh respectively) and about 30% *ortho*-isomer was seen for R = OMe with both metals after heating. Whereas, with the benzyl complexes **6a/b-R** for R = CF_3 only the *para*



Scheme 5 Deuterium incorporation experiments with **5a/b-OMe** and **5b-CF_3**.

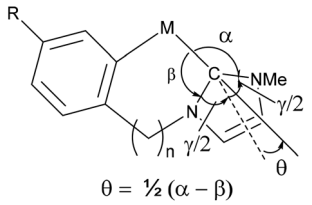


Fig. 2 Yaw distortion of chelating NHC complexes.

isomer is observed and for R = OMe less than 10% of the *ortho* isomer is observed after heating. These results suggest a more sterically hindered metal centre for the six-membered rings leading to less of the *ortho* isomer. Steric distortion of bidentate NHC containing ligands has been analysed previously in terms of a "yaw"-distortion (see Fig. 2).[18] A number of structures of Ir complexes have been reported for phenyl complexes (n = 0) the yaw angle varies from 9.2 to 10.2° whilst the benzyl complexes (n = 1) the yaw angles are much less at 2.1 to 3.4°.[18b] Interestingly the lower distortion in NHC coordination in the benzyl complexes leads the *ortho* H to be closer to the metal M···H distances 3.02 to 3.07 Å for benzyl complexes compared to 3.21 to 3.25 Å for the phenyl complexes. There are much smaller differences between 5-membered rings with different directing groups. The observation of a second species with **L4-CF$_3$** with an NHC directing group suggests the steric hindrance is slightly less in this case than with **L1-3** however it should be borne in mind that the NHC has an NMe substituent on the non-cyclometallated side, compared to a CH for the other ligands, and this may impact the overall geometry at the metal.

Conclusions

Steric effects on C–H activation were assessed using *meta*-substituted *N*-phenyl and *N*-benzylimidazolium salts **L4-R** and **L5-R** respectively. *N*-Phenyl limidazolium salts **L4-R** (R = OMe, CN, CF$_3$, F) underwent cyclometallation easily in the presence of NaOAc[14] and no intermediate non-cyclometallated NHC bound complexes were observed. The *para*-isomers were favoured thermodynamically over the *ortho* with both metals for R = OMe, CN, and particularly for the more bulky CF$_3$, whilst at shorter reaction times the selectivity was less. For **L4-F** cyclometallation at both metals favoured the *ortho* isomer as has been observed in other systems.

Cyclometallation to form 6-membered rings is less favourable than 5-membered ones hence for *N*-benzylimidazolium salts **L5-R (R = OMe, CF3, F)** intermediate non-cyclometallated NHC bound complexes **5a/b-OMe** could be prepared by transmetallation and the cyclometallation studied as a separate step. Treatment of **5a/b-OMe** with NaOAc resulted in formation of the *ortho* and *para* isomers of **6a/b-OMe** initially (<20% conversion) in equal quantities. At high conversions the proportion of the *ortho*-isomers diminished to <10% for Ir and none for Rh indicating a thermodynamic preference for the *para*-isomer. For cyclometallation of **5a/b-CF$_3$** none of the *ortho*-isomer could be detected even at low conversions likely due to the bulkier CF$_3$ group. Therefore, steric effects control regioselectivity with the *para*-isomer being the major one for cyclometallation of **5a/b-R** (R = OMe, CF$_3$). The selectivity for the *para*-isomer observed in six membered ring complexes **6a/b-R** is larger compared to the formation of the five-membered ring complexes **4a/b-R** consistent with a more sterically hindered metal centre for the six-membered rings.

Experimental

meta-Substituted N-phenylimidazoles were prepared according to a modified literature procedure.[19] *meta*-Substituted arylhalide (1 eq.), imidazole (1.5 eq.), Cs_2CO_3 (2 eq.), CuO_2 (10 mol%) and MeCN or DMF (5–10 mL) were added to a Schlenk flask, sealed with a screw-cap, placed under N_2 atmosphere, partially evacuated, transferred to an oil bath and stirred at 100–120 °C for 1–5 days behind a blast shield. Afterwards the reaction mixture was cooled to rt, followed by filtration through Celite. The solvent was removed by rotary evaporation and pure phenylimidazole was obtained by column chromatography. Data were in agreement with the literature.[20]

General procedure for preparation of *meta*-substituted phenylimidazolium salts L4-R

A nitrogen flushed Schlenk flask was charged with magnetic stirrer, *meta*-substituted phenylimidazole (1 eq.), dry DCM (4–6 mL), methyl trifluoromethanesulfonate (1.1 eq.), capped and stirred at rt for 2–4 h. The solvent was removed by rotary evaporation and the product was either precipitated from DCM/Et_2O mixture or washed with Et_2O to yield imidazolium salt **L4-R**.

Synthesis of L4-OMe. Following the general procedure, a mixture of 1-(3-methoxyphenyl)-1*H*-imidazole (174 mg, 1.002 mmol), dry DCM (4 mL), methyl trifluoromethanesulfonate (0.125 mL, 181 mg, 1.105 mmol), capped was stirred at rt for 4 h. The formed oil was washed with Et_2O (3 × 5 mL) to yield **L4-OMe** as a colourless oil (244 mg, 72%). ^{1}H NMR (400 MHz, CD_3CN): δ 3.88 (s, 3H, O*Me*), 3.97 (s, 3H, *Me*), 7.14 (m, 1H, *H*), 7.19–7.24 (m, 2H, H^1, H^4), 7.51 (t, J = 8.4 Hz, 1H, H^2), 7.57 (t, J = 1.9 Hz, 1H, H^{5b}), 7.80 (t, J = 2.0 Hz, 1H, H^{5a}), 9.23 (s, 1H, H^6), ^{13}C{^{1}H} NMR (126 MHz, CD_3CN): δ 37.3 (*Me*), 56.8 (O*Me*), 109.0 (C^4), 115.0 (C^1), 116.7 (C^3), 121.8 (d, J = 320.2 Hz, *OTf*), 122.3 (C^{5a}), 125.3 (C^{5b}), 132.2 (C^2), 136.6 (C^6), 136.8, 161.8. ^{19}F{^{1}H} NMR (376 MHz, CD_3CN): δ −79.3 (*OTf*). ESIMS: m/z 189 $[M]^+$. HRMS (ESI): Calcd for $C_{11}H_{13}N_2O$ $[M]^+$ 189.1028, found 189.1028.

Synthesis of L4-CN. Following the general procedure, a mixture of 3-(1*H*-imidazol-1-yl)benzonitrile (253 mg, 1.497 mmol), dry DCM (6 mL), methyl trifluoromethanesulfonate (0.19 mL, 278 mg, 1.680 mmol) was stirred at rt for 2.5 h. The product was precipitated from DCM/Et_2O to yield **L4-CN** as a white solid (412 mg, 1.237 mmol, 83%). ^{1}H NMR (400 MHz, CD_3OD): δ 4.08 (s, 3H, *Me*), 7.84 (m, 2H, H^4, H^{5b}),

7.97 (dt, J = 7.9, 1.3 Hz, 1H, H^1), 8.05 (ddd, J = 8.3, 2.4, 1.1 Hz, 1H, H^3), 8.12 (t, J = 1.8 Hz, 1H, H^{5b}), 8.20 (t, J = 1.7 Hz, 1H, H^4) 9.51 (s, 1H, H^6), $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD): δ 37.2 (*Me*), 115.6, 118.3, 121.9 (d, $^1J_{C-F}$ = 318.7 Hz, *OTf*), 123.0 (C^{5a}), 126.1 (C^{5b}), 127.3 (C^4), 128.2 (C^3), 132.9 (C^2), 134.9 (C^1), 137.2, 137.8 (C^6), $^{19}F\{^1H\}$ NMR (376 MHz, CD_3OD): δ −80.0 (*OTf*). ESIMS: m/z 227 $[M]^+$. HRMS (ESI): Calcd for $C_{11}H_{10}N_3$ $[M]^+$ 184.0875, found 184.0883.

Synthesis of L4-CF_3. Following the general procedure, a mixture of 1-(3-trifluoromethylphenyl)-1*H*-imidazole (213 mg, 1.007 mmol), dry DCM (4 mL), methyl trifluoromethanesulfonate (0.130 mL, 189 mg, 1.150 mmol) was stirred at rt for 3 h. The product was precipitated from a DCM/Et_2O to yield **L4-CF_3** as a white solid (306 mg, 81%). ^1H NMR (400 MHz, CD_3OD): δ 4.06 (s, 3H, *Me*), 7.81 (d, J = 2.2 Hz, 1H, H^{5b}), 7.88 (m, 1H, H^2), 7.94 (d, J = 7.8 Hz, 1H, H^3), 8.01 (d, J = 8.2 Hz, 1H, H^1), 8.11 (s, 1H, H^4), 8.15 (d, J = 1.2 Hz, 1H, H^{5a}), 9.55 (s, 1H, H^6), $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD): δ 37.1 (*Me*), 120.9 (q, $^3J_{C-F}$ = 4.2 Hz, C^4), 121.8 (q, $^1J_{C-F}$ = 319.2 Hz, *OTf*), 123.1 (C^{5a}), 124.8 (q, $^1J_{C-F}$ = 272.0 Hz, CF_3), 126.0 (C^{5b}), 127.5 (C^1), 128.1 (q, $^3J_{C-F}$ = 4.0 Hz, C^3), 132.8 (C^2) 133.8 (q, $^2J_{C-F}$ = 33.5 Hz, C-CF_3), 137.2 (q, $^4J_{C-F}$ = 3.0 Hz), 137.9 (C^6), $^{19}F\{^1H\}$ NMR (376 MHz, CD_3OD): δ −80.1 (*OTf*), −64.3 (CF_3). ESIMS: m/z 227 $[M]^+$. HRMS (ESI): Calcd for $C_{11}H_{10}N_2F_3$ $[M]^+$ 227.0796, found 227.0796.

Synthesis of L4-F. Following the general procedure, a mixture of 1-(3-fluorophenyl)-1*H*-imidazole (166 mg, 1.022 mmol), dry DCM (4 mL), methyl trifluoromethanesulfonate (0.130 mL, 189 mg, 1.150 mmol) was stirred at rt for 2.5 h. The formed oil was washed with Et_2O (3 × 5 mL) to yield **L4-F** as a colourless oil (325 mg, 98%). ^1H NMR (400 MHz, CD_3OD): δ 4.04 (s, 3H, *Me*), 7.34 (tdd, J = 8.4, 8.4, 2.4, 1.0 Hz, 1H, H^3), 7.57 (m, 2H, H^1, H^4), 7.65 (td, J = 8.3, 5.6 Hz, 1H, H^2), 7.76 (t, J = 1.8 Hz, 1H, H^{5b}), 8.05 (t, J = 2.0 Hz, 1H, H^{5a}), 9.47 (s, 1H, H^6), $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD): δ 37.1 (*Me*), 111.2 (d, $^2J_{C-F}$ = 27.1 Hz, C^4), 118.2 (d, $^2J_{C-F}$ = 21.1 Hz, C^3), 119.3 (d, $^4J_{C-F}$ = 3.0 Hz, C^1), 121.9 (d, $^1J_{C-F}$ = 318.2 Hz, *OTf*), 122.8 (C^{5a}), 125.9 (C^{5b}), 133.4 (d, ^3J = 9.0 Hz, C^2), 137.5 (C^6), 137.6 (d, $^3J_{C-F}$ = 10.0 Hz), 164.5 (d, $^1J_{C-F}$ = 249.0 Hz, *C*–F), $^{19}F\{^1H\}$ NMR (376 MHz, CD_3OD): δ −111.0 (*F*), −80.0 (*OTf*). ESIMS: m/z 177 $[M]^+$. HRMS (ESI): Calcd for $C_{10}H_{10}N_2F$ $[M]^+$ 177.0828, found 177.0832

General procedure for cyclometallation of *meta*-substituted phenylimidazolium salts L4-R with $[MCl_2Cp^*]_2$ (M = Ir, Rh) in DCE

$[MCl_2Cp^*]_2$ (M = Ir, Rh) (1 eq.), NaOAc (8 eq.) were placed in an oven-dried Schlenk flask, sealed with a screw-cap, evacuated for 15 min and placed under N_2 atmosphere. DCE (2 mL) was added and mixture stirred for another 15 min. The appropriate imidazolium salt **L4-R** (2.1 eq.) and Et_4NCl (2 eq.) was added, and the Schlenk flask transferred to a preheated oil bath and stirred at 50 °C for 1–2 h, then at 70 °C for 1–6 h. The reaction mixture was cooled to rt with continuous stirring, diluted with DCM (10 mL), filtered through Celite and solvent removed by rotary evaporation. The pure products were isolated by several precipitations from DCM/hexane.

General procedure for cyclometallation of *meta*-substituted phenylimidazolium salts L4-R with $[MCl_2Cp^*]_2$ (M = Ir, Rh) in DCM : MeOH

$[MCl_2Cp^*]_2$ (M = Ir, Rh) (1 eq., 0.0251 mmol), NaOAc (8 eq.) were placed in an oven-dried Schlenk flask, sealed with a screw-cap, evacuated for 15 min and placed under N_2 atmosphere. Dry DCM (1.6 mL) and MeOH (0.4 mL) were added and the mixture stirred for another 15 min. The appropriate imidazolium salt (2.1 eq.) and Et_4NCl (2 eq.) was added and the mixture stirred at rt overnight and then heated to 50 °C overnight. The reactions were monitored by ^1H NMR spectroscopy by comparing the relative integrations of the appropriate signals (H^3 of the *ortho*-isomers compared to the H^3 of the *para*-isomers).

Synthesis of 4a-OMe. Following the general procedure, a mixture of $[IrCl_2Cp^*]_2$ (20 mg, 0.0251 mmol), NaOAc (17 mg, 0.207 mmol), **L4-OMe** (18 mg, 0.0533 mmol), Et_4NCl (9 mg, 0.053 mmol), in DCE (2 mL) was heated to 50 °C for 2 h, then heated further at 70 °C for 6 h. The product was purified by crystallisation from DCM/hexane to yield **4a-OMe** (*ortho* : *para* ratio 1 : 2.2) as a yellow powder (29.9 mg, 94%). *ortho*-**4a-OMe**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.85 (s, 15H, C_5Me_5), 3.82 (s, 3H, O*Me*), 3.97 (s, 3H, *Me*), 6.54 (dd, J = 7.9, 1.1 Hz, 1H, H^3), 6.83 (dd, J = 7.7, 1.1 Hz, 1H, H^1), 6.93 (t, J = 8.3 Hz, 1H, H^2), 6.95 (d, J = 2.2 Hz, 1H, H^{5b}), 7.31 (d, J = 2.2 Hz, 1H, H^{5a}). ESIMS: m/z 513 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{193}Ir$ $[M - Cl]^+$ 515.1674, found 515.1675. *para*-**4a-OMe**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 15H, C_5Me_5), 3.80 (s, 3H, O*Me*), 3.98 (s, 3H, *Me*), 6.65 (dd, J = 8.2, 2.6 Hz, 1H, H^3), 6.76 (d, J = 2.4 Hz, 1H, H^4), 6.97 (d, J = 2.2 Hz, 1H, H^{5b}), 7.29 (d, J = 2.2 Hz, 1H, H^{5a}), 7.60 (d, J = 8.3 Hz, 1H, H^2), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.74 (C_5Me_5), 37.0 (*Me*), 55.5 (O*Me*), 90.6 (C_5Me_5), 98.6 (C^4), 110.8 (C^3), 114.8 (C^{5a}), 121.3 (C^{5b}), 131.2, 136.1 (C^2), 146.9 (C^1), 156.3, 166.6 (C^6). ESIMS: m/z 513 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{193}Ir$ $[M - Cl]^+$ 515.1674, found 515.1675.

Synthesis of 4b-OMe. Following the general procedure, a mixture of $[RhCl_2Cp^*]_2$ (15 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), **L4-OMe** (18 mg, 0.053 mmol), Et_4NCl (9 mg, 0.054 mmol), in DCE (2 mL) was stirred at 50 °C for 1 h, then at 70 °C for 6 h. The product was purified by precipitation from DCM/hexane to yield **4b-OMe** (*ortho* : *para* 1 : 1.9 ratio) as an orange-yellow powder (14 mg, 61%). *ortho*-**4b-OMe**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.68 (s, 15H, C_5Me_5), 3.83 (s, 3H, O*Me*), 3.97 (s, 3 H, *Me*), 6.58 (dd, J = 8.0, 0.9 Hz, 1H, H^3), 6.78 (dd, J = 7.7, 1.0 Hz, 1H, H^1), 6.98 (d, J = 2.0 Hz, 1H, H^{5b}), 6.99 (t, J = 7.8 Hz, 1H, H^2), 7.37 (d, J = 2.0 Hz, 1H, H^{5a}), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.9 (C_5Me_5), 37.0 (*Me*), 56.3 (O*Me*), 97.9 (d, $^1J_{C-Rh}$ = 5.2 Hz, C_5Me_5), 104.9 (C^1), 108.9 (C^3), 115.9 (C^{5a}), 121.9 (C^{5b}), 124.0 (C^2), 146.1, 145.6 (d, $^1J_{C-Rh}$ = 42.1 Hz, C^4), 156.7, 184.2 (d, $^1J_{C-Rh}$ = 55.5 Hz, C^6). ESIMS: m/z 425 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{103}Rh$ $[M - Cl]^+$ 425.1100, found 425.1100. *para*-**4b-OMe**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.70 (s, 15H, C_5Me_5), 3.78 (s, 3H, O*Me*), 4.01 (s, 3H, *Me*), 6.66 (dd, J = 8.3, 2.6 Hz, 1H, H^3), 6.71 (d, J = 2.5 Hz, 1H, H^4), 6.98 (d, J = 2.1 Hz, 1H, H^{5b}), 7.35 (d, J = 2.0 Hz, 1H, H^{5a}),

7.63 (d, J = 8.3 Hz, 1H, H^2), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.9 (C_5Me_5), 37.0 (*Me*), 55.5 (O*Me*), 97.2 (d, $^1J_{C-Rh}$ = 5.0 Hz, C_5Me_5), 99.0 (C^4), 110.5 (C^3), 115.1 (C^{5a}), 122.2 (C^{5b}), 137.2 (C^2), 146.1, 146.6 (d, $^1J_{C-Rh}$ = 35.7 Hz, C^1), 165.0, 184.2 (d, J_{C-Rh} = 55.5 Hz, C^6). ESIMS: m/z 425 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{26}N_2O^{103}Rh$ $[M-Cl]^+$ 425.1100, found 425.1100.

Synthesis of 4a-CN. Following the general procedure, a mixture of $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), NaOAc (16 mg, 0.196 mmol), **L4-CN** (18 mg, 0.0526 mmol), Et_4NCl (9 mg, 0.053 mmol), in DCE (2 mL) was stirred at 50 °C for 1.5 h, then heated further to 70 °C for 1 h. The product was purified by crystallisation from DCM/hexane to yield **4a-CN** (*ortho* : *para* ratio 1 : 2.0) as an orange-yellow powder (24 mg, 90%). *ortho*-**4a-CN**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.83 (s, 15H, C_5Me_5), 3.98 (s, 3H, *Me*), 7.00 (t, J = 7.8 Hz, 1H, H^2), 7.01 (d, J = 2.6 Hz, 1H, H^{5b}), 7.21 (dd, J = 7.8, 1.2 Hz, 1H, H^1), 7.33 (d, J = 2.2 Hz, 1H, H^{5a}), 7.37 (dd, J = 7.7, 1.2 Hz, 1H, H^3), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.6 (C_5Me_5), 36.8 (*Me*), 92.6 (C_5Me_5), 94.8, 112.5 (C^1), 115.6 (C^{5a}), 120.3, 121.6 (C^2), 122.0 (C^{5b}), 131.2 (C^3), 148.0, 151.1 (C^4), 167.9 (C^6). ESIMS: m/z 510 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{23}{}^{193}IrN_3$ $[M-Cl]^+$ 510.1521, found 510.1523. ESIMS: m/z 551 $[M-Cl+MeCN]^+$. HRMS (ESI): Calcd for $C_{23}H_{26}N_4{}^{193}Ir$ $[M-Cl+MeCN]^+$ 551.1787, found 551.1790. *para*-**4a-CN**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 15H, C_5Me_5), 3.99 (s, 3H, *Me*), 7.03 (d, J = 2.2 Hz, 1H, H^{5b}), 7.21 (dd, J = 7.7 Hz, 1.7, 1H, H^3), 7.32 (d, J = 1.7 Hz, 1H, H^4), 7.34 (d, J = 2.1 Hz, 1H, H^{5a}), 7.88 (d, J = 7.7 Hz, 1H, H^2), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.7 (C_5Me_5), 37.0 (*Me*), 91.8 (C_5Me_5), 104.6, 112.6 (C^4), 114.9 (C^{5a}), 122.2 (C^{5b}), 122.6, 129.0 (C^3), 137.2 (C^2), 147.3, 153.4 (C^1), 166.2 (C^6). ESIMS: m/z 510 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{23}{}^{193}IrN_3$ $[M-Cl]^+$ 510.1521, found 510.1523. ESIMS: m/z 551 $[M-Cl+MeCN]^+$. HRMS (ESI): Calcd for $C_{23}H_{26}N_4{}^{193}Ir$ $[M-Cl+MeCN]^+$ 551.1787, found 551.1790.

Synthesis of 4b-CN. Following the general procedure, a mixture of $[RhCl_2Cp^*]_2$ (15 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), **L4-CN** (18 mg, 0.054 mmol), Et_4NCl (9 mg, 0.054 mmol), in DCE (2 mL) was stirred at 50 °C for 1.5 h, then heated to 70 °C for 1 h. The product was purified by precipitation from DCM/hexane to yield **4b-CN** (*ortho* : *para* ratio 1 : 1.9) as an orange-yellow powder (13 mg, 58%). *ortho*-**4b-CN**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 15H, C_5Me_5), 3.99 (s, 3H, *Me*), 7.01 (d, J = 2.2 Hz, 1H, H^{5b}), 7.05 (t, J = 7.7 Hz, 1H, H^2), 7.17 (dd, J = 7.8, 1.3 Hz, 1H, H^1), 7.40 (m, 1H, H^3), 7.41 (d, J = 2.0 Hz, 1H, H^{5a}), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.7 (C_5Me_5), 37.1 (*Me*), 94.0, 98.8 (d, $^1J_{C-Rh}$ = 4.8 Hz, C_5Me_5), 113.1 (C^1), 116.1 (C^{5a}), 122.0, 123.1 (C^2), 123.3 (C^{5b}), 130.7 (C^3), 147.3, 167.4 (d, $^1J_{C-Rh}$ = 38.2 Hz, C^4), 185.1 (d, $^1J_{C-Rh}$ = 54.8 Hz, C^6). ESIMS: m/z 420 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{23}N_3{}^{103}Rh$ $[M-Cl]^+$ 420.0947, found 420.0947. ESIMS: m/z 461 $[M-Cl+MeCN]^+$. HRMS (ESI): Calcd for $C_{23}H_{26}N_4{}^{103}Rh$ $[M-Cl+MeCN]^+$ 461.1213, found 461.1213. *para*-**4b-CN**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 15H, C_5Me_5), 4.00 (s, 3H, *Me*), 7.03 (d, J = 2.2 Hz, 1H, H^{5b}), 7.27 (m, 1H, H^3), 7.27 (br.s, 1H, H^4), 7.41 (d, J = 2.1 Hz, 1H, H^{5a}), 7.94 (dd, J = 8.1, 0.9 Hz, 1H, H^2), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.8 (C_5Me_5), 37.1 (*Me*), 98.2 (d, $^1J_{C-Rh}$ = 5.6 Hz, C_5Me_5), 105.5, 112.8 (C^4), 115.4 (C^{5a}), 120.1, 123.1 (C^{5b}), 128.0 (C^3), 138.4 (C^2), 146.6, 170.3 (d, $^1J_{C-Rh}$ = 35.8 Hz, C^1), 183.7 (d, $^1J_{C-Rh}$ = 55.6 Hz, C^6). Calcd for $C_{21}H_{23}N_3$ ^{103}Rh $[M-Cl]^+$ 420.0947, found 420.0947. ESIMS: m/z 461 $[M-Cl+MeCN]^+$. HRMS (ESI): Calcd for $C_{23}H_{26}N_4{}^{103}Rh$ $[M-Cl+MeCN]^+$ 461.1213, found 461.1213.

Synthesis of 4a-CF_3. Following the general procedure, a mixture of $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), **L4-CF_3** (20 mg, 0.0532 mmol), Et_4NCl (9 mg, 0.055 mmol), in DCE (2 mL) was stirred first at rt for 24 h, then heated to 50 °C for 1 h and then at 70 °C for a further 1 h. The product was purified by crystallisation from DCM/hexane to yield single regioisomer *para*-**4-CF_3** as orange crystals (19 mg, 64%). *para*-**4a-CF_3**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.80 (s, 15H, C_5Me_5), 3.97 (s, 3H, *Me*), 7.02 (d, J = 2.2 Hz, 1H, H^{5b}), 7.22 (br. d, J = 7.8 Hz, 1H, H^3), 7.30 (d, J = 1.2 Hz, 1H, H^4), 7.38 (d, J = 2.2 Hz, 1H, H^{5a}), 7.87 (d, J = 7.8 Hz, 1H, H^2), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.7 (C_5Me_5), 37.0 (*Me*), 91.4 (C_5Me_5), 106.8 (q, $^3J_{C-F}$ = 4.0 Hz, C^4), 114.9 (C^{5a}), 121.8 (C^{5b}), 122.1 (q, $^3J_{C-F}$ = 3.2 Hz, C^3), 124.4 (q, $^2J_{C-F}$ = 31.2 Hz, *C*-CF_3), 125.0 (q, $^1J_{C-F}$ = 271.0, *C*F_3), 136.6 (C^2), 146.9, 148.9 (C^1), 166.3 (C^6), $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −61.5 (CF_3). ESIMS: m/z 553 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{23}N_2F_3{}^{193}Ir$ $[M-Cl]^+$ 553.1643, found 553.1645.

Synthesis of 4b-CF_3. Following the general procedure, a mixture of $[RhCl_2Cp^*]_2$ (20 mg, 0.032 mmol), NaOAc (21 mg, 0.259 mmol), **L4-CF_3** (25 mg, 0.066 mmol), in DCE (2.5 mL) was stirred first at rt for 24 h, then heated to 50 °C for 1 h and then at 70 °C for a further 1 h. The product was purified by crystallisation from DCM/hexane to yield *para*-**4b-CF_3** as yellow crystals (25 mg, 78%).

***Para*-4b-CF_3.** ^1H NMR (400 MHz, CD_2Cl_2): δ 1.71 (s, 15H, C_5Me_5), 4.00 (s, 3H, *Me*), 7.10 (d, J = 2.2 Hz, 1H, H^{5b}), 7.28 (d, J = 7.8 Hz, 1H, H^3), 7.33 (d, J = 1.5 Hz, 1H, H^4), 7.49 (d, J = 2.0 Hz, 1H, H^{5a}), 7.92 (d, J = 7.8 Hz, 1H, H^2), $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2): δ 10.2 (C_5Me_5), 37.6 (*Me*), 98.5 (d, $^1J_{C-Rh}$ = 4.8 Hz, C_5Me_5), 107.5 (q, $^3J_{C-F}$ = 4.0 Hz, C^4), 115.7 (C^{5a}), 121.5 (q, $^4J_{C-F}$ = 2.4 Hz, C^3), 123.6 (C^{5b}), 125.4 (q, $^2J_{C-F}$ = 31.8 Hz, *C*-CF_3), 125.6 (q, $^1J_{C-F}$ = 271.0, *C*F_3), 138.5 (C^2), 147.1, 167.1 (d, $^1J_{C-Rh}$ = 36.6 Hz, C^1), 184.7 (d, $^1J_{C-Rh}$ = 55.6 Hz, C^6), $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2): δ −61.8 (CF_3). ESIMS: m/z 463 $[M-Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{23}N_2F_3{}^{103}Rh$ $[M-Cl]^+$ 463.0868, found 463.0862. Anal Calcd for $C_{21}H_{23}N_2F_3ClRh$ [M]: C, 50.57; H, 4.65; N, 5.62; found C, 50.44; H, 4.77; N, 5.47%.

Synthesis of 4a-F. Following the general procedure, a mixture of $[IrCl_2Cp^*]_2$ (20 mg, 0.025 mmol), NaOAc (16 mg, 0.200 mmol), **L4-F** (18 mg, 0.055 mmol), Et_4NCl (9 mg, 0.055 mmol), DCE (2 mL) was heated to 70 °C for 3 h. The product was purified by crystallisation from DCM/hexane to yield **4a-F** (*ortho* : *para* ratio 2.1 : 1) as a yellow powder (18 mg, 67%). *ortho*-**4a-F**. ^1H NMR (400 MHz, $CDCl_3$): δ 1.80 (d, 15 H, C_5Me_5), 3.97 (s, 3H, *Me*), 6.72 (m, 1H, H^3), 6.94 (m, 2H, H^1,H^2), 6.97 (d, J = 2.1 Hz, 1H, H^{5b}), 7.32 (d, J = 2.1 Hz, 1H, H^{5a}), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.9 (d, J_{C-F} = 2.7 Hz, C_5Me_5), 36.9 (*Me*), 91.6 (C_5Me_5), 106.6 (d, $^4J_{C-F}$ = 2.7 Hz, C^1), 112.1 (d,

$^{2}J_{C-F}$ = 29.4 Hz, C^{3}), 115.5 (C^{5a}), 121.4 (C^{5b}), 123.8 (d, $^{3}J_{C-F}$ = 8.2 Hz, C^{2}), 126.3 (d, $^{2}J_{C-F}$ = 44.6 Hz, C^{4}), 148.5 (d, $^{3}J_{C-F}$ = 18.3 Hz), 166.5 (C^{6}), 167.8 (d, $^{1}J_{C-F}$ = 235.0 Hz, *C*–F), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ −94.9 (*F*). ESIMS: *m*/*z* 503 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{20}H_{23}N_2F^{193}Ir$ $[M - Cl]^+$ 503.1674, found 503.1676. ESIMS: *m*/*z* 544 $[M - Cl + MeCN]^+$. HRMS (ESI): Calcd for $C_{22}H_{26}N_3F^{193}Ir$ $[M - Cl + MeCN]^+$ 544.1740, found 544.1744. *para*-**4a-F**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79 (s, 15H, C_5Me_5), 3.99 (s, 3H, *Me*), 6.78 (ddd, *J* = 9.8, 8.3, 2.7 Hz, 1H, H^{3}), 6.87 (dd, *J* = 9.5, 2.6 Hz, 1H, H^{4}), 6.97 (d, *J* = 2.1 Hz, 1H, H^{5b}), 7.27 (d, *J* = 2.1 Hz, 1H, H^{5a}), 7.64 (dd, *J* = 8.3, 6.5 Hz, 1H, H^{2}), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ −122.9 (*F*). ESIMS: *m*/*z* 503 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{20}H_{23}{}^{193}IrN_2F$ $[M - Cl]^+$ 503.1674, found 503.1676. ESIMS: *m*/*z* 544 $[M - Cl + MeCN]^+$. HRMS (ESI): Calcd for $C_{22}H_{26}N_3F^{193}Ir$ $[M - Cl + MeCN]^+$ 544.1740, found 544.1744.

Synthesis of 4b-F. Following the general procedure, a mixture of $[RhCl_2Cp^*]_2$ (15 mg, 0.025 mmol), NaOAc (17 mg, 0.207 mmol), **L4-F** (17 mg, 0.052 mmol), Et_4NCl (9 mg, 0.053 mmol), DCE (2 mL) was heated to 70 °C for 3 h. The product was purified by precipitation from DCM/hexane to yield **4b-F** (*ortho* : *para* ratio 10 : 1) as an orange-yellow powder (13 mg, 59%).

***Ortho*-4b-F.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.75 (s, 15H, C_5Me_5), 3.98 (s, 3H, *Me*), 6.72 (td, *J* = 8.0, 1.0 Hz, 1H, H^{3}), 6.92 (dd, *J* = 7.6, 1.0 Hz, 1H, H^{1}), 6.98 (td, *J* = 7.8, 5.4 Hz, 1H, H^{2}), 6.98 (d, *J* = 2.1 Hz, 1H, H^{5b}), 7.39 (d, *J* = 2.1 Hz, 1H, H^{5a}), $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 10.0 (d, $^{1}J_{C-F}$ = 1.6 Hz, C_5Me_5), 37.1 (*Me*), 98.2 (d, $^{1}J_{C-Rh}$ = 5.6 Hz, C_5Me_5), 107.1 (C^{1}), 112.3 (d, $^{2}J_{C-F}$ = 29.4 Hz, C^{3}), 115.9 (C^{5a}), 122.3 (C^{5b}), 124.4 (d, $^{3}J_{C-F}$ = 7.9 Hz, C^{2}) 141.1 (dd, $^{2}J_{C-Rh,C-F}$ = 39.7, 10.3 Hz, C^{4}), 147.9 (d, $^{3}J_{C-F}$ = 19.1 Hz), 168.3 (d, $^{1}J_{C-F}$ = 232.9 Hz, *C*–F), 183.9 (d, $^{1}J_{C-Rh}$ = 54.8 Hz, C^{6}), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ −93.9 (*F*). ESIMS: *m*/*z* 413 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{20}H_{23}N_2FRh$ $[M - Cl]^+$ 413.0900, found 413.0902.

General procedure for preparation of *meta*-substituted benzylimidazolium salts L5-R

A Schlenk flask was charged with *N*-methylimidazole (1 eq.), *meta*-substituted benzyl chloride (1–2 eq.) and MeCN (5 mL) and stirred at 55 °C for 1 day. The resulting mixture was concentrated *in vacuo*, the residue dissolved in DCM and washed with hexane, then the solvent removed by rotary evaporation giving pure imidazolium salt as an oil or a sticky solid.

Synthesis of L5-OMe. Following the general procedure, *N*-methylimidazole (250 mg, 3.049 mmol), 3-methoxybenzyl chloride (373 mg, 2.382 mmol) and MeCN (5 mL) were added to a Schlenk flask and stirred at 55 °C for 20 h. **L5-OMe** was obtained as a white sticky solid (480 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.65 (s, 3H, O*Me*), 3.93 (s, 3H, *Me*), 5.41 (s, 2H, H^{1}), 6.72 (dd, *J* = 8.2, 2.3 Hz, 1H, H^{4}), 6.87 (d, *J* = 7.6 Hz, 1H, H^{2}), 6.93 (br. s, 1H, H^{5}), 7.12 (t, *J* = 7.9 Hz, 1H, H^{3}), 7.41 (s, 1H, H^{6b}), 7.56 (s, 1H, H^{6a}), 10.46 (s, 1H, H^{7}), $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 36.1 (*Me*), 52.6 (C^{1}), 55.1 (O*Me*), 114.0 (C^{5}), 114.4 (C^{4}), 120.5 (C^{2}), 121.6 (C^{6a}), 123.4 (C^{6b}), 130.0 (C^{3}), 134.4 (CCH_2), 137.1 (C^{7}), 159.7 (*C*-OMe). ESIMS: *m*/*z* 203 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{12}H_{15}N_2O$ $[M]^+$ 203.1184, found 203.1186.

Synthesis of L5-CF_3. Following the general procedure, *N*-methylimidazole (159 mg, 1.939 mmol), 3-trifluoromethylbenzyl chloride (563 mg, 2.893 mmol) and MeCN (5 mL) were added to a Schlenk flask and stirred at 55 °C for 1 day. Additional portion of 3-trifluoromethylbenzyl chloride (188 mg, 0.965 mmol) was added and mixture stirred at 65 °C for 1 day. **L5-CF_3** was obtained as a white sticky solid (294 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H, *Me*), 5.59 (s, 2H, H^{1}), 7.30 (m, 1H, H^{3}), 7.38 (m, 1H, H^{4}), 7.49 (br s, 1H, H^{6b}), 7.58 (br s, 1H, H^{ab}), 7.67 (m, 2H, H^{2}, H^{5}), 10.37 (m, 1H, H^{7}), $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 36.0 (*Me*), 51.6 (C^{1}), 122.0 (C^{6a}), 123.2 (q, $^{1}J_{C-F}$ = 273.1 Hz, CF_3), 123.5 (C^{6b}), 125.2 (C^{5}), 125.6 (C^{4}), 129.5 (C^{3}), 130.6 (q, $^{2}J_{C-F}$ = 33.1 Hz, *C*-CF_3), 132.2 (C^{2}), 134.3 (CCH_2), 137.0 (C^{7}), $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$): δ −62.4 (CF_3). ESIMS: *m*/*z* 241 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{12}H_{12}F_3N_2$ $[M]^+$ 241.0953, found 241.0960.

Synthesis of L5-F. Following the general procedure, *N*-methylimidazole (165 mg, 2.010 mmol), 3-fluorobenzyl chloride (404 mg, 2.793 mmol) and MeCN (5 mL) were added to a Schlenk flask and stirred at 60 °C for 24 h. **L5-F** was obtained as a pale yellow oil (396 mg, 87%). ^{1}H NMR (400 MHz, CD_3OD): δ 3.96 (s, 3H, *Me*), 5.48 (s, 2H, H^{1}), 7.16 (tdd, *J* = 8.7, 2.2, 0.7 Hz, 1H, H^{4}), 7.25 (dt, *J* = 9.5, 2.0 Hz, 1H, H^{5}), 7.30 (br. d, *J* = 8.3, 1H, H^{3}), 7.47 (td, *J* = 8.0, 5.7 Hz, 1H, H^{2}), 7.63 (d, *J* = 2.0 Hz, 1H, H^{6b}), 7.67 (d, *J* = 2.0 Hz, 1H, H^{6a}), 9.13 (s, 1H, H^{7}), $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_3OD): δ 36.8 (*Me*), 53.4 (C^{1}), 116.7 (d, $^{2}J_{C-F}$ = 23.0 Hz, C^{5}), 117.2 (d, $^{2}J_{C-F}$ = 20.7 Hz, C^{4}), 123.8 (C^{6a}), 125.5 (C^{6b}), 125.7 (d, $^{4}J_{C-F}$ = 3.2 Hz, C^{2}), 132.5 (d, $^{3}J_{C-F}$ = 7.9 Hz, C^{3}), 138.0 (d, $^{3}J_{C-F}$ = 7.2 Hz, CCH_2), 138.1 (C^{7}), 164.6 (d, $^{1}J_{C-F}$ = 246.4 Hz, *C*–F). $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3OD): δ −113.7 (*F*). ESIMS: *m*/*z* 191 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{11}H_{12}FN_2$ $[M]^+$ 191.0985, found 191.0982.

General procedure for complexation of *meta*-substituted benzylimidazolium salts L5-R with $[MCl_2Cp^*]_2$ (M = Ir, Rh)

An aluminium foil wrapped Schlenk flask was charged with a magnetic stirrer bar, the appropriate *meta*-substituted benzylimidazolium salt **L5-R** (2.1 eq.) and Ag_2O (2.2 eq.), capped, purged with N_2. Dry DCM (2.5 mL) was added and the mixture stirred at rt for 1–2 h. Then the reaction mixture was filtered through Celite and the solvent removed by rotary evaporation. The residue was re-dissolved in dry DCM (2.5 mL) and added to an N_2 purged Schlenk flask wrapped in aluminium foil, followed by addition of $[MCl_2Cp^*]_2$ (M = Ir, Rh) (1 eq.). The reaction mixture was stirred at rt for 1–2 h, filtered through Celite, the solvent removed by rotary evaporation and the final product **5a/b-R** obtained by precipitation/crystallisation from DCM/Et_2O or DCM/hexane.

Synthesis of 5a-OMe. Following the general procedure, a mixture of **L5-OMe** (58 mg, 0.243 mmol), Ag_2O (59 mg, 0.254 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[IrCl_2Cp^*]_2$ (91 mg, 0.114 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from

DCM/hexane yielded **5a-OMe** as yellow crystals (99 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.62 (s, 15H, C_5Me_5), 3.78 (s, 3H, O*Me*), 4.00 (s, 3H, *Me*), 5.22 (d, J = 14.9 Hz, 1H, H^1), 5.93 (d, J = 14.9 Hz, 1H, H^1), 6.72 (d, J = 2.2 Hz, 1H, H^{6a}), 6.84 (dd, J = 7.9, 2.2 Hz, 1H, H^4), 6.88 (d, J = 7.6 Hz, 1H, H^2), 6.90 (d, J = 2.2 Hz, 1H, H^{6b}), 6.95 (d, J = 2.2 Hz, 1H, H^5), 7.25 (t, J = 7.9 Hz, 1H, H^3), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 9.3 (C_5Me_5), 38.7 (*Me*), 54.5 (C^1), 55.4 (O*Me*), 88.9 (C_5Me_5), 113.7 (C^5), 113.9 (C^4), 120.7 (C^2), 121.9 (C^{6a}), 123.3 (C^{6b}), 129.7 (C^3), 138.3, 156.9 (C^7), 159.9. ESIMS: m/z 565 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{29}N_2OCl^{193}Ir$ $[M - Cl]^+$ 565.1598, found 565.1591.

Synthesis of 5b-OMe. Following the general procedure, a mixture of **L5-OMe** (51 mg, 0.214 mmol), Ag_2O (52 mg, 0.224 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[RhCl_2Cp^*]_2$ (62 mg, 0.100 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded **5b-OMe** as yellow/orange crystals (94 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (s, 15H, C_5Me_5), 3.78 (s, 3H, O*Me*), 4.05 (s, 3 H, *Me*), 5.27 (br d, J = 14.7 Hz, 1H, H^1), 6.03 (br d, J = 14.5 Hz, 1H, H^1), 6.80 (d, J = 2.0 Hz, 1H, H^{6a}), 6.84 (dd, J = 8.2, 2.3 Hz, 1H, H^4), 6.89 (br d, J = 7.5 Hz, 1H, H^2), 6.97 (m, 2 H, H^5, H^{6b}), 7.24 (t, J = 7.8 Hz, 1H, H^3), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 9.5 (C_5Me_5), 39.2 (*Me*), 54.6 (C^1), 55.3 (O*Me*), 96.2 (d, $^1J_{C-Rh}$ = 6.0 Hz, C_5Me_5), 113.7 (C^5), 113.9 (C^4), 120.6 (C^2), 122.7 (C^{6a}), 124.1 (C^{6b}), 129.6 (C^3), 138.2, 159.9, 170.3 (d, $^1J_{C-Rh}$ = 56.2 Hz, C^7). ESIMS: m/z 475 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{29}N_2OCl^{103}Rh$ $[M - Cl]^+$ 475.1023, found 475.1016.

Synthesis of 5a-CF$_3$. Following the general procedure, a mixture of **L5-CF$_3$** (52 mg, 0.188 mmol), Ag_2O (46 mg, 0.211 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[IrCl_2Cp^*]_2$ (71 mg, 0.089 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded **5a-CF$_3$** as yellow crystals (81 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 15H, C_5Me_5), 4.01(s, 3H, *Me*), 5.14 (br d, J = 14.7 Hz, 1H, H^1), 6.23 (br d, J = 14.9 Hz, 1H, H^1), 6.66 (d, J = 2.2 Hz, 1H, H^{6a}), 6.94 (d, J = 2.0 Hz, 1H, H^{6b}), 7.46 (t, J = 7.7 Hz, 1H, H^3), 7.55 (br. s, 1H, H^5), 7.56 (br. d, J = 7.8 Hz, 1H, H^4), 7.71 (br. d, J = 7.6 Hz, 1H, H^2), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 9.1 (C_5Me_5), 38.7 (*Me*), 53.9 (C^1), 88.9 (C_5Me_5), 121.6 (C^{6b}), 123.7 (C^{6a}), 124.0 (q, $^1J_{C-F}$ = 245.0 Hz, CF_3), 124.8 (q, $^3J_{C-F}$ = 3.0 Hz, $C^{4/5}$), 124.9 (q, $^3J_{C-F}$ = 4.0 Hz, $C^{4/5}$), 129.4 (C^2), 130.7 (q, $^2J_{C-F}$ = 33.1 Hz, C-CF_3), 132.4 (C^3), 137.8, 157.3 (C^7), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −62.5 (CF_3).ESIMS: m/z 603 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{26}N_2F_3Cl^{193}Ir$ $[M - Cl]^+$ 603.1366, found 603.1360.

Synthesis of 5b-CF$_3$. Following the general procedure, a mixture of **L5-CF$_3$** (53 mg, 0.191 mmol), Ag_2O (57 mg, 0.245 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[RhCl_2Cp^*]_2$ (69 mg, 0.112 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded **5b-CF$_3$** as yellow/orange crystals (89 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 15H, C_5Me_5), 4.05 (s, 3H, *Me*), 5.17 (br d, J = 14.5 Hz, 1H, H^1), 6.36 (br d, J = 14.5 Hz, 1H, H^1), 6.73 (d, J = 2.0 Hz, 1H, H^{6a}), 7.02 (d, J = 2.0 Hz, 1H, H^{6b}), 7.44 (t, J = 8.0 Hz, 1H, H^3), 7.55 (m, 2H, H^4, H^5), 7.70 (d, J = 7.6 Hz, 1H, H^2), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 9.5 (C_5Me_5), 39.3 (*Me*), 54.1 (C^1), 96.3 (d, $^1J_{C-Rh}$ = 6.0 Hz, C_5Me_5), 125.5 (C^{6a}), 123.8 (q, $^1J_{C-F}$ = 246.0 Hz, CF_3), 124.7 (C^{6b}), 124.8 (q, $^3J_{C-F}$ = 4.0 Hz, $C^{4/}C^5$), 125.0 (q, $^3J_{C-F}$ = 4.0 Hz $C^{4/}C^5$), 129.5 (C^3), 130.7 (q, $^2J_{C-F}$ = 32.1 Hz, C-CF_3), 132.6 (C^2), 137.7, 171.0 (d, $^1J_{C-Rh}$ = 56.2 Hz, C^7), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −62.5 (CF_3). m/z 513 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{26}N_2F_3Cl^{103}Rh$ $[M - Cl]^+$ 513.0792, found: 513.0786.

Synthesis of 5a-F. Following the general procedure, a mixture of **L5-F** (50 mg, 0.218 mmol), Ag_2O (50 mg, 0.216 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[IrCl_2Cp^*]_2$ (79 mg, 0.099 mmol) and dry DCM (2.5 mL) was added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded **5a-F** as yellow crystals (86 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 15H, C_5Me_5), 4.00 (s, 3H, *Me*), 5.16 (d, J = 14.8 Hz, 1H, H^1), 5.93 (d, J = 14.8 Hz, 1H, H^1), 6.69 (d, J = 2.0 Hz, 1H, H^{6a}), 6.94 (d, J = 2.1 Hz, 1H, H^{6b}), 6.99 (td, J = 8.3, 2.3 Hz, 1H, H^4), 7.08 (td, J = 9.6, 2.1 Hz, 1H, H^5), 7.16 (d, J = 7.8 Hz, 1H, H^2), 7.31 (m, 1H, H^3), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 9.1 (C_5Me_5), 38.7 (*Me*), 53.9 (C^1), 88.8 (C_5Me_5), 114.9 (d, $^2J_{C-F}$ = 21.1 Hz, C^4), 115.3 (d, $^2J_{C-F}$ = 23.1 Hz, C^5), 121.7 (C^{6a}), 123.5 (C^{6b}), 124.2 (d, $^4J_{C-F}$ = 2.0 Hz, C^2), 130.2 (d, $^3J_{C-F}$ = 8.0 Hz, C^3), 139.3 (d, $^3J_{C-F}$ = 7.0 Hz, C), 157.1 (C^7), 162.9 (d, $^1J_{C-F}$ = 247.0 Hz, C–F), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −112.4 (F). ESIMS: m/z 553 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{26}N_2Cl^{193}Ir$ $[M - Cl]^+$ 553.1398, found 553.1394.

Synthesis of 5b-F. Following the general procedure, a mixture of **L5-F** (50 mg, 0.221 mmol), Ag_2O (52 mg, 0.223 mmol), dry DCM (2.5 mL), stirred at rt for 1 h, then $[RhCl_2Cp^*]_2$ (62 mg, 0.101 mmol) and dry DCM (2.5 mL) were added and the mixture was stirred for 1 h. Crystallisation from DCM/hexane yielded **5b-F** as yellow crystals (67 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.63 (s, 15H, C_5Me_5), 4.06 (s, 3H, *Me*), 5.22 (d, J = 14.1 Hz, 1H, H^1), 6.19 (d, J = 14.1 Hz, 1H, H^1), 6.78 (d, J = 2.0 Hz, 1H, H^{6a}), 7.00 (m, 2H, H^3, H^{6b}), 7.09 (td, J = 9.6, 1.9 Hz, 1H, H^5), 7.17 (dd, J = 7.6, 0.6 Hz, 1H, H^2), 7.31 (td, J = 7.9, 5.9 Hz, 1H, H^3), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 9.5 (C_5Me_5), 39.2 (*Me*), 54.1 (C^1), 96.3 (d, J_{C-Rh} = 6.0 Hz, C_5Me_5), 115.0 (d, $^2J_{C-F}$ = 20.1 Hz, C^4), 115.4 (d, $^2J_{C-F}$ = 22.1 Hz, C^5), 122.6 (C^{6a}), 124.3 (d, $^4J_{C-F}$ = 2.0 Hz, C^2), 124.5 (C^{6b}), 130.3 (d, $^3J_{C-F}$ = 8.0 Hz, C^3), 139.3 (d, $^3J_{C-F}$ = 8.0 Hz, C), 162.9 (d, $^1J_{C-F}$ = 250.0 Hz, C–F), 170.8 (d, J_{C-Rh} = 56.2 Hz, C^7), ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$): δ −112.3 (F). ESIMS: m/z 463 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{103}Rh$ $[M - HCl_2]^+$ 427.1057, found 427.1052.

General procedure for cyclometallation of 5a/b-R

An oven-dried and N_2 purged Schlenk flask was charged with a magnetic stirrer bar, **5a/b-R** (1 eq.), NaOAc (5 eq.) and dry DCM (2 mL) and MeOH (0.5 mL) and stirred at rt for indicated time. The reaction mixture was filtered through Celite, which was washed with additional DCM (5–10 mL), the solvent removed by rotary evaporation and the residue purified by precipitation from DCM/hexane.

Synthesis of 6a-OMe. Following the general procedure, a mixture of **5a-OMe** (15 mg, 0.025 mmol), NaOAc (8 mg, 0.098 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was

stirred at rt overnight. Precipitation from DCM/hexane yielded regioisomer *para*-**6a-OMe** as a yellow powder (12 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (s, 15H, C_5Me_5), 3.75 (s, 3H, O*Me*), 3.92 (s, 3H, *Me*), 4.60 (d, J = 13.9 Hz, 1H, H^{1b}), 4.84 (d, J = 13.9 Hz, 1H, H^{1a}), 6.61 (d, J = 2.7 Hz, 1H, H^5), 6.67 (dd, J = 8.3, 2.6 Hz 1H, H^4), 6.89 (d, J = 1.4 Hz, 1H, H^{6b}), 6.94 (d, J = 1.4 Hz, 1H, H^{6a}), 7.47 (br d, J = 8.2 Hz, 1H, H^3), $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 9.4 (C_5Me_5), 36.9 (*Me*), 55.3 (C^1), 57.1 (O*Me*), 90.0 (C_5Me_5), 111.1 (C^5), 113.6 (C^4), 120.3 (C^{6a}), 121.1 (C^{6a}), 132.5 (C^2), 138.5, 141.4 (C^3), 155.8, 157.3 (C^7). ESIMS: m/z 529 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{28}N_2O^{191}Ir$ $[M - Cl]^+$ 527.1808, found 527.1804.

Synthesis of 6b-OMe. Following the general procedure, a mixture of **5b-OMe** (19 mg, 0.037 mmol), NaOAc (12 mg, 0.146 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was stirred at rt overnight. Precipitation from DCM/hexane yielded *para*-**6b-OMe** as a yellow/orange powder (12 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.60 (s, 15H, C_5Me_5), 3.74 (s, 3H, O*Me*), 4.00 (s, 3H, *Me*), 4.68 (d, J = 14.3 Hz, 1H, H^{1b}), 4.94 (d, J = 14.3 Hz, 1H, H^{1a}), 6.61 (d, J = 2.5 Hz, 1H, H^5), 6.71 (dd, J = 8.4, 2.7 Hz, 1H, H^4), 6.95 (d, J = 1.8 Hz, 1H, H^{6b}), 7.02 (d, J = 1.6 Hz, 1H, H^{6a}), 7.56 (d, J = 8.4 Hz, 1H, H^3), $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 9.6 (C_5Me_5), 37.5(*Me*), 55.3 (C^1), 56.3 (O*Me*), 97.0 (d, $^1J_{C-Rh}$ = 5.0 Hz, C_5Me_5), 111.6 (C^5), 113.3 (C^4), 121.4 (C^{6a}), 122.0 (C^{6b}), 139.1, 141.0 (C^3), 147.8 (d, $^1J_{C-Rh}$ = 32.1 Hz, C^2), 156.1, 175.0 (d, $^1J_{C-Rh}$ = 55.2 Hz, C^7). ESIMS: m/z 439 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{28}N_2O^{103}Rh$ $[M - Cl]^+$ 439.1257, found 439.1246.

Synthesis of 6a-CF$_3$. Following the general procedure, a mixture of **5a-CF$_3$** (27 mg, 0.042 mmol), NaOAc (14 mg, 0.171 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was stirred at rt overnight. Precipitation from DCM/hexane yielded *para*-**6a-CF$_3$** as a yellow powder (21 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68 (s, 15H, C_5Me_5), 3.90 (s, 3H, *Me*), 4.72 (br d, J = 13.7 Hz, 1H, H^{1b}), 4.86 (br d, J = 14.1 Hz, 1H, H^{1a}), 6.92 (br s, 1H, H^{6b}), 6.98 (br s, 1H, H^{6a}), 7.18 (m, 2H, H^4, H^5), 7.75 (m, 1H, H^3), $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 9.4 (C_5Me_5), 36.9 (*Me*), 55.3 (C^1), 90.5 (C_5Me_5), 120.3 (q, $^3J_{C-F}$ = 3.0 Hz, $C^{4/5}$), 120.4 (C^{6a}), 121.4 (C^{6b}), 123.6 (q, $^3J_{C-F}$ = 3.0 Hz, $C^{4/5}$), 124.1 (q, $^2J_{C-F}$ = 31.1 Hz, *C*-CF$_3$), 125.2 (q, $^1J_{C-F}$ = 271.1 Hz, *C*F$_3$), 138.9, 141.8 (C^3), 152.1 (C^2), 156.6 (C^7). $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −61.4 (*C*F$_3$). ESIMS: m/z 567 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{25}N_2F_3{}^{191}Ir$ $[M - Cl]^+$ 565.1574, found 565.1576.

Synthesis of 6b-CF$_3$. Following the general procedure, a mixture of **5b-CF$_3$** (50 mg, 0.091 mmol), NaOAc (30 mg, 0.366 mmol), dry DCM (2 mL) and dry MeOH (0.5 mL) was stirred at rt overnight. Precipitation from DCM/hexane yielded *para*-**6b-CF$_3$** as a yellow/orange powder (40 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (s, 15H, C_5Me_5), 3.97 (s, 3H, *Me*), 4.80 (d, J = 14.3 Hz, 1H, H^{1b}), 4.97 (d, J = 14.3 Hz, 1H, H^{1a}), 6.95 (d, J = 1.8 Hz, 1H, H^{6b}), 7.03 (d, J = 1.8 Hz, 1H, H^{6a}), 7.16 (br s, 1H, H^5), 7.21 (br d, J = 8.0 Hz, 1H, H^4), 7.86 (br d, J = 7.8 Hz, 1H, H^3), $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 9.6 (C_5Me_5), 37.4 (*Me*), 56.1 (C^1), 97.4 (d, $^1J_{C-Rh}$ = 5.0 Hz, C_5Me_5), 120.6 (q, $^3J_{C-F}$ = 3.0 Hz, C^5), 121.5 (q, $^3J_{C-F}$ = 3.0 Hz, C^4), 122.4 (C^{6a}), 122.8 (C^{6b}), 124.4 (q, $^2J_{C-F}$ = 31.1 Hz, *C*-CF$_3$), 125.1 (q, $^1J_{C-F}$ = 271.0 Hz, *C*F$_3$), 139.5, 141.3 (q, $^4J_{C-F}$ = 2.0 Hz, C^3), 169.0 (d, $^1J_{C-Rh}$ = 32.1 Hz, C^2), 174.3 (d, $^1J_{C-Rh}$ = 56.2 Hz, C^7), $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −61.5 (*C*F$_3$). ESIMS: m/z 477 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{22}H_{25}N_2F_3{}^{103}Rh$ $[M - Cl]^+$ 477.1025, found 477.10250.

Synthesis of 6a-F. Following the general procedure, a mixture of **5a-F** (30.0 mg, 0.051 mmol), NaOAc (16.5 mg, 0.201 mmol), dry DCM (2.4 mL) and dry MeOH (0.6 mL) was stirred at rt for 2 h. Precipitation from DCM/hexane yielded **6a-F** (*ortho* : *para* ratio 10 : 1) as a yellow powder (27 mg, 96%). *ortho*-**6a-F**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.73 (s, 15H, C_5Me_5), 3.89 (s, 3H, *Me*), 4.71 (dd, J = 13.9, 1.3 Hz, 1H, H^{1b}), 4.88 (d, J = 13.9 Hz, 1H, H^{1a}), 6.76 (m, 3H, H^2, H^3, H^4), 6.90 (d, J = 1.9 Hz, 1H, H^{6b}), 6.94 (d, J = 2.0 Hz, 1H, H^{6a}), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.4 (C_5Me_5), 37.0 (*Me*), 57.0 (C^1), 90.04 (C_5Me_5), 114.2 (d, $^2J_{C-F}$ = 31.0 Hz, C^4), 120.3 (C^{6a}), 120.6 (d, $^4J_{C-F}$ = 1.6 Hz, C^2), 121.6 (C^{6b}), 123.8 (d, $^3J_{C-F}$ = 8.7 Hz, C^3), 128.0 (d, $^2J_{C-F}$ = 38.9 Hz, C^5), 141.0 (d, $^3J_{C-F}$ = 14.3 Hz, *C*), 156.4 (C^7), 167.2 (d, $^1J_{C-F}$ = 232.9 Hz, *C*–F), $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −87.8 (*F*). ESIMS: m/z 517 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{193}Ir$ $[M - Cl]^+$ 517.1631, found 517.1631. *para*-**6a-F**.^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (s, 15H, C_5Me_5), 3.91 (s, 3H, *Me*), 4.6 (d, J = 14.1 Hz, 1H, H^{1a}), 4.81 (d, J = 13.9 Hz, 1H, H^{1b}), 6.71–6.74 (m, 2H, H^4, H^5), 6.89 (d, J = 1.9 Hz, 1H, H^{6b}), 6.93 (d, J = 1.9 Hz, 1H, H^{6a}), 7.51 (dd, J = 8.3, 7.0 Hz, 1H, H^3), $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −125.3 (*F*). ESIMS: m/z 427 $[M - Cl]^+$. HRMS (ESI): ESIMS: m/z 517 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{193}Ir$ $[M - Cl]^+$ 517.1631, found 517.1631.

Synthesis of 6b-F. Following the general procedure, a mixture of **5b-F** (25.5 mg, 0.051 mmol), NaOAc (16.7 mg, 0.204 mmol), dry DCM (2.4 mL) and dry MeOH (0.6 mL) was stirred at rt for 2 h. Precipitation from DCM/hexane yielded regioisomers **6b-F** (*ortho* : *para* ratio 10 : 1) as a yellow powder (22.5 mg, 96%). *ortho*-**6b-F**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (s, 15H, C_5Me_5), 3.99 (s, 3H, *Me*), 4.71 (dd, J = 14.2, 1.0 Hz, 1H, H^{1a}), 4.97 (d, J = 14.2 Hz, 1H, H^{1b}), 6.76 (m, 2 H, H^2, H^4), 6.82 (m, 1H, H^3), 6.97 (d, J = 1.9 Hz, 1H, H^{6b}), 7.02 (d, J = 1.9 Hz, 1H, H^{6a}), $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 9.7 (C_5Me_5), 37.8 (*Me*), 56.4 (C^1), 97.5 (d, $^1J_{C-Rh}$ = 5.6 Hz, C_5Me_5), 114.4 (d, $^2J_{C-F}$ = 31.0 Hz, C^4), 120.9 (C^{6a}), 121.3 (C^2), 122.6 (C^{6b}), 124.1 (d, $^3J_{C-F}$ = 8.7 Hz, C^3), 141.60 (d, $^3J_{C-F}$ = 15.1 Hz, *C*), 142.8 (m, C^5), 166.9 (d, $^1J_{C-F}$ = 232.1 Hz, *C*–F), 174.2 (d, $^1J_{C-Rh}$ = 54.8 Hz, C^7), $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −84.7 (*F*). m/z 427 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{103}Rh$ $[M - Cl]^+$ 427.1057, found 427.1049. *para*-**6b-F**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.73 (s, 15H, C_5Me_5), 3.99 (s, 3H, *Me*), 4.68 (d, J = 14.2, 1.0 Hz, 1H, H^{1a}), 4.92 (d, J = 14.2 Hz, 1H, H^{1b}), 6.73 (dd, J = 10.0, 3.0 Hz, 1H, H^5), 6.76 (td, J = 9.0, 2.8 Hz, 1H, H^4), 6.97 (d, J = 1.9 Hz, 1H, H^{6b}), 7.02 (d, J = 1.9 Hz, 1H, H^{6a}), 7.61 (dd, J = 8.3, 7.0 Hz, 1H, H^3), $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −125.0 (*F*). ESIMS: m/z 427 $[M - Cl]^+$. HRMS (ESI): Calcd for $C_{21}H_{25}N_2F^{103}Rh$ $[M - Cl]^+$ 427.1057, found 427.1049.

Deuteration studies

An NMR tube was charged with **5a/b-R** (5 mg) and CD_3OD (0.5 mL). The ^{1}H NMR spectrum was recorded and then NaOAc (4 eq.) was added. The reactions were allowed to sit at

rt overnight. The spectra in CD_3OD were broad so the samples were evaporated and redissolved in $CDCl_3$. The percentage deuteration was determined by ^{1}H NMR spectroscopy by comparing the relative integrations for H^3 and H^5 for the *para*-isomers in the ^{1}H NMR spectra.

Conflicts of interest

There are no conflicts to declare.

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