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Simple NMR predictors of catalytic hydrogenation activity for Rh(cod)Cl(NHC) complexes featuring fluorinated NHC ligands.

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A series of imidazolium salts precursors for *N*-heterocyclic carbenes (NHCs) featuring fluoroaryl substituents have been prepared along with their selenides and rhodium complexes. Tests of the catalytic activity of the [Rh(cod)Cl(NHC)] complexes in the transfer hydrogenation of acetophenone with *i*PrOH shows that the activities of the rhodium complexes bearing fluorinated NHCs are better than their non-fluorinated counterparts. The order of activity being 4-F-C₆H₄ < 2,4-F₂-C₆H₃ < 2,4,5-F₃-C₆H₂ < 2,6-F₂-C₆H₄ < 2,4,6-F₃-C₆H₂. This order of reactivity is consistent with a number of simple NMR measures of the electronic properties of these systems, including ¹J_{CH} of the NHC.HBF₄ salts, δ(⁷⁷Se) of the NHC selenides and ¹J_{Rh-C} and δ(¹³C_{carbene}) of the [Rh(cod)Cl(NHC)] complexes.

Introduction

Two of the key tenets of green chemistry are to develop chemical transformations that operate with high efficiency using environmentally benign reagents in as few steps as possible.¹ One reaction that falls into this category is catalytic transfer hydrogenation in which cheap, readily-available and easily handled hydrogen donors, such as isopropanol, are used instead of pressurised H₂ for hydrogenation reactions under catalytic conditions.²

NHC-containing complexes of the type [M(cod)Cl(NHC)] (M = Ir, Rh; cod = 1,5-cyclooctadiene) have been shown to act as effective catalysts for transfer hydrogenation reactions.³ A number of studies of these systems have demonstrated that both the steric and donor properties of the NHC and ancillary ligands influence the catalyst efficiency. In one such study it was shown that lower donor strength carbenes in the iridium systems tended to give higher overall yields and shorter induction times.⁴

Based on the generic catalytic cycle for transfer hydrogenation (Figure 1)⁵ it is expected that a change in the Lewis acidity of the metal centre will influence the coordination of both the substrate and the hydrogen transfer reagent. This being the case it would appear that less donating NHC ligands would be advantageous. Surprisingly, given the very large number of different NHCs that have been prepared, one variation that has been less systematically studied (unlike in the case of phosphines⁶) is the introduction of fluorine into NHC ligands.

Figure 1 Generalised catalytic cycle for transfer hydrogenation of carbonyl compounds. Modified from reference 5.

Only a relatively small number of metal complexes involving 1,3-fluoroaryl-substituted NHCs have been reported, and fewer still have been used in catalytic systems. Those that have been studied include work on fluorinated symmetric⁷ and asymmetric^{8,9} Grubbs II and Hoveyda-Grubbs catalysts, and a gold(I) complex prepared from 1,3-bis(2,4-difluorophenyl)imidazolium chloride (IPh^{24F2}.HCl) used in an A³ coupling reaction.¹⁰ In the case of transfer hydrogenation, there is only one report of the application of fluorinated NHC-containing complexes. In 2009 Herrmann *et al.* reported that for a series of [Ir(cod)X(NHC)] complexes, including the 1,3-bis(4-fluorophenyl)imidazolium (IPh^{4F}) derived complex, although the fluoro-substituted NHC ligand system did not perform particularly well against other systems.⁴

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The introduction of fluorine is expected to reduce the σ -donation of an NHC and enhance its π -accepting ability by lowering the energy of the LUMO, and so reduce the electron density on the metal centre. Traditionally measurements of the donating ability of ligands (L) have been based on the Tolman electronic parameter (TEP) derived from the CO stretching frequencies of carbonyl-containing complexes such as $[\text{Ni}(\text{CO})_3\text{L}]$ or $[\text{MCl}(\text{CO})_2\text{L}]$ ($\text{M} = \text{Rh}, \text{Ir}$).¹¹ Using these methods NHCs are found to be more donating than some of the most basic phosphine ligands. However, NMR spectroscopy has the potential to act as a more sensitive probe than IR because of the wide range of chemical shift values compared with $\nu(\text{CO})$ stretching frequencies, combined with the narrow linewidths of signals and the existence of both chemical shift and coupling constant information. For this reason a number of NMR studies of NHC-containing systems have been investigated using a variety of different nuclei.^{12–15} However, as Nelson and Nolan point out in an extensive review of such data,¹⁶ the information obtained from IR and NMR techniques do not necessarily correlate well, as one is dominated by the effects of π -backbonding from the metal to carbonyl ligands, while the other is more closely associated with the electron density around the nucleus under investigation.

Huynh and colleagues used the ^{13}C NMR resonance of the carbene nucleus of $\text{iPr}_2\text{-bimy}$ (1,3-diisopropylbenzimidazolin-2-ylidene) in *trans*- $[\text{PbBr}_2(\text{iPr}_2\text{-bimy})\text{L}]$ complexes as a reporter of the σ -donating strength of a wide range of carbene and phosphine ligands on a common scale.¹² While $\delta(^{195}\text{Pt})$ and $^1\text{J}_{\text{PtC}}$ coupling constants obtained from *cis*- $[\text{Pt}(\text{NHC})(\text{DMSO})\text{Cl}_2]$ complexes were interpreted as a measure of the amount of backbonding from the platinum centre to an empty π -orbital of the carbene.¹³ Bertrand and colleagues focussed on the ^{31}P NMR chemical shift of NHC phosphinidene adducts,¹⁴ while corresponding studies of the ^{77}Se NMR chemical shift of NHC selenide adducts were reported by Ganter and co-workers.¹⁵ In both cases if an NHC is a better π -acceptor then electron density is removed from the phosphorus or selenium centre, resulting in that nucleus becoming more deshielded and so its resonance is observed at higher chemical shift values. Ganter *et al* further demonstrated that $^1\text{J}_{\text{CSe}}$ coupling constants, which are related to Fermi contact and thus s-electron density between the two coupling nuclei, could provide an estimate of the σ -donating ability of NHCs. However, due to the low natural abundance of both ^{13}C and ^{77}Se and long T_1 relaxation times, data collection within a reasonable time proved to be problematic. They further reported that a trend similar to that found for $^1\text{J}_{\text{CSe}}$ of the NHC selenide adducts was observed in $^1\text{J}_{\text{CH}}$ coupling constants of the cationic NHC precursor salts. Whilst our study was underway a further report on the use of $^1\text{J}_{\text{CH}}$ coupling constant information derived from NHC ligand precursors was reported,¹⁷ and very recently Eisenstein and co-workers have used the ^{13}C chemical shift tensors obtained from solid-state NMR studies to provide a profile which can be used to distinguish Fischer and Schrock-type carbenes.¹⁸

Here we report a study of the systematic inclusion of fluorine in the aryl substituents of imidazolium-based NHC systems. From these NHCs we prepared the first series fluoro-aryl NHC selenide adducts and $[\text{Rh}(\text{cod})\text{Cl}(\text{NHC})]$. These have been used to probe the electronic properties of the NHC ligands by multinuclear NMR studies and to investigate their use as catalysts for transfer hydrogenation, a system in which the reduced donating ability of the NHCs are expected to result in enhanced catalytic activity.

Results and Discussion.

A series of *N,N'*-fluoroaryl NHC precursors were prepared as their fluorinated imidazolium chloride salts *via* a one-pot condensation reaction of the appropriate fluoroaniline with glyoxal and *para*-formaldehyde in the presence of hydrochloric acid, as illustrated in Scheme 1.¹⁹ The chloride salts were not isolated, but directly converted to the tetrafluoroborate analogues (as it has been reported that the application of tetrafluoroborate salts in metal complex formation is more efficient in terms of time and yield than using the chloride analogues²⁰) by addition of aqueous HBF_4 to afford the white crystalline salts, **1–5**, in good yields and high purity. Using this method we were able to readily obtain NHCs possessing one, two or three fluorine substituents around the phenyl ring. However, attempts to prepare the pentafluorophenyl-containing NHC salt were repeatedly unsuccessful, resulting only in small amounts of impure product, presumably due to the reduced nucleophilicity of the starting pentafluoroaniline as suggested previously.²¹ For comparison purposes we also prepared the known, non-fluorinated IMes.HBF_4 and IPh.HBF_4 NHC salts in a similar way.

The NHC salts were characterised in all cases by satisfactory elemental analyses and by ^1H , ^{13}C and ^{19}F NMR spectroscopy. In deuterated DMSO all of the salts gave rise to a carbenic proton signal between 10.2 and 10.3 ppm, with associated $^1\text{J}_{\text{CH}}$ coupling constants that range from 226.1 to 231.1 Hz. The order of the coupling constant values were observed to increase in the sequence **1** < **2** < **4** < **3** < **5**. The non-fluorinated imidazolium salts IPr.HBF_4 and IMes.HBF_4 have $^1\text{J}_{\text{CH}}$ coupling constant values of 223.7 and 225.2 Hz respectively, while their saturated analogues SIPr and SIMes display much smaller values (206.1 and 207.4 Hz respectively). Indeed of the data presented by Szostak *et al.*¹⁷, only the salts of NQ-Imes (*N,N'*-dimesitylnaphthoquinimidazol-2-ylidene) and IPr^{Cl} (*N,N'*-bis(2,6-diisopropylphenyl)-4,5-dichloro-imidazol-2-ylidene) systems have coupling constant values (both 229.0 Hz) within the range determined for our fluorinated NHCs. Thus based on the $^1\text{J}_{\text{CH}}$ coupling constant values the fluorinated NHCs **1 – 5** possess electronic properties quite distinct from more common NHCs.

Scheme 1 Synthetic route used for the synthesis of fluorinated NHC tetrafluoroborate salts **1-5**.

Preparation and Characterisation of fluoroaryl imidazolium selenides

As described above ^{77}Se NMR chemical shift values of the selenium adducts of NHCs have been correlated with the π -acceptor strength of NHCs¹⁵ and as such is complementary to information provided by coupling constant data, which is related primarily to the σ -donor strength. There have been only two previous reports of fluoro-aryl substituted NHC selenium adducts, and both of these are saturated imidazolidine NHCs^{15,22}, there are to date no reports of fluoroaryl imidazolium selenides. We therefore attempted the reaction of the fluorinated NHC salts with elemental selenium in the presence of K_2CO_3 (scheme 2), which we were pleased to find successfully generated the selenide adducts (**8 - 12**) of the fluorinated NHCs from which the ^{77}Se NMR chemical shifts were obtained and these are listed in Table 1.

Scheme 2 – The preparation of fluoroaryl imidazolium selenides **8 - 12**.

The ^{77}Se NMR chemical shifts for the selenium adducts **8-12** are found to be in the range 60 – 73 ppm. These values lie between those observed for the imidazolium systems, such as IPh, IMes, (**13** and **14**) which are < 50 ppm, suggesting that these NHCs are more π -acidic, but not to the extent of imidazolidine systems, where chemical shift values above 100 ppm are observed.¹⁵ This suggests that the inclusion of fluorine on the nitrogen-bound aryl substituents has significantly influenced the electronic properties of the imidazolium π -system. It is also interesting to note that the same order of $\delta(\text{Se})$ chemical shifts and $^1J_{\text{CH}}$

coupling constants is observed for **1-5**, i.e. the fluorinated NHCs that give rise to the larger C-H coupling values display higher selenium chemical shifts. Based on these data it suggests that NHCs **1-5** are poorer σ -donors than most currently characterised NHC ligands, with π -accepting properties that lie between those of the traditional two classes of NHC ligands.

Preparation and characterisation of Rh-complexes

Having generated a series of NHC salts with electronic properties that according to NMR measurements are distinct from the more commonly used, non-fluorinated, NHC ligands we were interested to see what influence this might have on their metal complexes and subsequent application to transfer hydrogenation catalysis. Although iridium complexes have been shown to be more catalytically active in transfer hydrogenation than the rhodium analogues, rhodium is NMR-active (^{103}Rh , 100%, $I = 1/2$) and so offers additional spectroscopic data so we chose to synthesise a series of rhodium complexes.

The most common methods of preparing NHC metal complexes is either by reaction of a suitable metal complex with the pre-generated free carbene, metathesis via a pre-prepared silver carbene compound or from the *in situ* deprotonation of an azolium salt in the presence of a suitable metal precursor. The last method is operationally more straight-forward and has been used by Savka and Plenio,²³ to generate $[\text{Rh}(\text{cod})\text{Cl}(\text{IMes})]$ from the one-pot reaction of $[\text{Rh}(\text{cod})\text{Cl}]_2$ with IMes.HCl in the presence of K_2CO_3 . We therefore tested a similar approach, by reacting the fluorinated NHC tetrafluoroborate salts, **1-5**, with $[\text{Rh}(\text{cod})\text{Cl}]_2$ and K_2CO_3 in acetone under standard atmospheric conditions (scheme 3). These reactions resulted in the first

examples of rhodium complexes containing nitrogen-bound fluoroaryl imidazol-2-ylidene ligand systems, $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh}^{4\text{F}})]$ (**15**), $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh}^{24\text{F}2})]$ (**16**), $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh}^{26\text{F}2})]$ (**17**), $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh}^{245\text{F}3})]$ (**18**) and $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh}^{246\text{F}3})]$ (**19**) as air- and moisture stable yellow crystalline solids in 75 – 85% yield. The corresponding IPh, **20**, and IMes, **21**, complexes were also prepared in a similar way.

Scheme 3 – The preparation of fluoroaryl-substituted NHC-containing complexes **15 - 19**.

Table 1 Selected NMR data for the NHC salts, their selenide adducts and [Rh(cod)Cl(NHC)] complexes.View Article Online
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NHC	NHC.HB F ₄	NHC=Se	Rh(cod)Cl(NHC)							
	¹ J _{C-H} (Hz)		δ ⁷⁷ Se (ppm)		δ ¹³ C _{carbene}	¹ J _{Rh-C} (Hz)	δ ¹³ C _{cod} (ppm)	¹ J _{Rh-C} (Hz)	δ ¹³ C _{cod} (ppm)	¹ J _{Rh-C} (Hz)
IPh ^{4F} , 1	226.1	8	60.7	15	185.1	51.7	97.8	7.1	68.4	14.6
IPh ^{24F2} , 2	228.3	9	66.6	16	187.6	51.8	98.8	7.1	68.4	14.5
IPh ^{26F2} , 3	230.9	10	68.3	17	191.5	53.4	98.7	7.2	68.7	14.0
IPh ^{245F3} , 4	229.0	11	67.4	18	189.5	51.9	99.3	6.9	68.7	14.5
IPh ^{246F3} , 5	231.1	12	73.0	19	194.9	59.7	99.4	7.0	68.8	14.1
IPh, 6	225.7	13	24.1	20	181.5	48.6	96.1	7.2	67.4	13.3
IMes, 7	225.2 ²¹	14	35 ¹⁵	21	183.5	50.8	96.2	7.6	68.1	14.3

Figure 2 ORTEP representations of **15** – **17**, **19** and **20**, at 50% probability. **Table 2** Selected bond lengths (Å) for **15**, **16**, **17**, **19**, **20** and [Rh(cod)Cl(IMes)] (**21**).²⁵

Complex	d(Rh-C _{carbene})	d(Rh-Cl)	d(C-N _{av})	C=C _{av} trans ^b	C=C _{av} cis ^b	d(Rh-C _{cod}) _{av} trans ^b	d(Rh-C _{cod}) _{av} cis ^b	%V _{bur} ^c
15 ^a	2.021(11)	2.414(3)	1.365(17)	1.360(20)	1.425(20)	2.192(13)	2.108(13)	14.5
16	2.000(8)	2.402(2)	1.387(9)	1.391(12)	1.415(12)	2.200(9)	2.114(9)	35.0
17	2.029(5)	2.389(2)	1.370(7)	1.385(8)	1.402(8)	2.197(6)	2.117(6)	38.2
19	2.006(4)	2.357(1)	1.381(6)	1.367(7)	1.401(6)	2.207(4)	2.104(4)	46.2
20	2.016(3)	2.408(1)	1.376(4)	1.368(5)	1.396(5)	2.198(3)	2.107(3)	9.3
21 ²⁵	2.049(2)	2.337(4)	1.364(2)	1.384(3)	1.408(3)	2.197(2)	2.108(2)	2.3

^a Average of the four unique molecules in the unit cell.^b *trans*- or *cis*- with respect to the carbene.^c %V_{bur} determined using SambVca.²⁷

Confirmation of NHC coordination comes from the ^{13}C NMR signals for the carbenic carbon which are observed as doublets, due to coupling with rhodium, between 181 and 195 ppm; these data are listed in Table 1. The ^{13}C NMR signals for the rhodium-bound carbenic carbon of complexes **15** – **19** are all observed at higher chemical shift values than for the non-fluorinated counterparts, $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh})]$, **20**, and $[\text{Rh}(\text{cod})\text{Cl}(\text{IMes})]$, **21**. This suggests that introducing fluorine to the NHC ligands results in a considerably more deshielded ^{13}C carbene environment than is found in the corresponding IPh and IMes complexes. The observed order of the carbenic carbon resonances increase in the order **20** < **21** < **15** < **16** < **18** < **17** < **19**, with the highest chemical shifts being observed for the rhodium complexes of the NHC ligands derived from **5** and **3**. Similarly the two largest magnitude $^1J_{\text{RhC}}$ coupling constants are also observed for the same two complexes.

The electronic properties of the NHC ligands are expected to affect the bonding between the rhodium centre and the C=C bonds of the cod ligand. A less σ -donating, or more π -accepting, NHC ligand will reduce the electron density at the metal centre so decreasing the amount of backbonding into the π^* C=C molecular orbital, leading to the carbon atoms of the cod alkenes being more sp^2 than sp^3 hybridised and hence being observed at higher ^{13}C chemical shift values and with larger Rh-C coupling constants. The observed data are presented in Table 1, and shows that the ^{13}C chemical shifts increase in the order **20** < **21** < **15** < **17** < **16** < **18** < **19**. That is for the fluorinated, and hence less donating, NHC ligands higher chemical shift values are indeed observed and these values generally decrease as the degree of fluorinated of the NHC decreases. However, apart from complex **21**, that contains IMes, which has a significantly larger $^1J_{\text{RhC}}$ value than the others, there is no obvious trend in the Rh-C coupling constants, due to the very small range of values observed.

Significantly, the trend in chemical shifts of the carbenic carbon and $^1J_{\text{RhC}}$ coupling constants of the rhodium complexes is the same as that observed for the $\delta(^{77}\text{Se})$ NMR data of the NHC selenides and the $^1J_{\text{HC}}$ coupling constants of the NHC tetrafluoroborate salts. Thus, each of these NMR probes place the NHC ligands in the same order. It is perhaps noteworthy that the two NHC ligands that possess two *ortho* fluorine substituents on the aryl rings (ie **3** and **5**) exhibit the most extreme values of all four of these measures. In some NHC complexes of other transition metals, fluorine substitution in the *ortho* position of the nitrogen-bound aryl ring has given rise to M...F interactions^{9,24} and hence we were interested to obtain the solid state structures of our rhodium complexes to see if such interactions were also present. We were able to grow successfully single crystals suitable for X-ray diffraction studies of **15**, **16**, **17**, **19** and **20** by slow diffusion of hexane into saturated dichloromethane solutions of the complexes. Figure 2 shows representations of the complexes, while Table 2 lists selected bond lengths. For complexes **16**, **17**, **19** and **20** the unit

cell contains a single molecule; while for complex **15** four molecules are present, although there are no significant differences between the geometric parameters of the four molecules. In the case of complex **16** one of the *ortho*-fluorines of one ring was found to be disordered.

In every complex the rhodium centre is four coordinate with bonds to the carbene, chloride and two olefinic bonds of the cyclooctadiene ligand giving distorted square planar structures. However, none of the structures displayed any significant Rh...F interactions. Instead, in the extended structures intramolecular hydrogen bonds are observed between the chloride and *ortho*-hydrogens of the aryl rings in complexes **15**, **16** and **20**. These interactions are not possible for complexes **17** and **19** where the aryl *ortho* positions are occupied by fluorine. Intermolecular interactions involving the chloride and hydrogens in the *meta*-position of the aryl ring are observed in all of the structures, while intermolecular distances less than the sum of the relevant van der Waals radii are observed between the chlorine, and where present, fluorine, centres and the backbone protons of the heterocyclic unit.

Bielawski has previously reported that for a series of non-fluorine containing $\text{Rh}(\text{cod})\text{Cl}(\text{NHC})$ complexes the Rh-C bond length contracts as the π -back bonding ability of the NHC increases. Conversely the average length of the C-N bonds and the C=C distance of the cod double bond *trans* to the NHC increase, as do the corresponding Rh-C_{cod} bond lengths.²⁶ It is apparent from the metrical data (Table 2) that the rhodium-carbene distances of the complexes containing fluorinated NHC ligands (complexes **15** – **17** and **19**) are all significantly shorter than those of the non-fluorinated analogue **21**, $[\text{Rh}(\text{cod})\text{Cl}(\text{IMes})]$, they are comparable to those of **20**, $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh})]$. This may be evidence to suggest that NHCs **1**–**5** are better π -donors than IMes. However, there are no particularly obvious trends in the C-N_{av} and C=C_{av} bond length metrics. Similarly it is not possible to discern any pattern in the observed C=C and Rh-C bond lengths of the cod ligand with respect to the particular NHC ligands. However, the average Rh-C_{cod} distances are shorter and C=C bondlength longer for that *trans* to the NHC compared with that *trans* to chloride, consistent with better π -bonding from the chloride ligand. Interestingly the torsion angle between the two aromatic rings of the NHC ligand vary considerably from 2.34° in the previously reported structure of complex **21**,²⁵ through to 46.21° in **19** with intermediate values of 9.25 , 14.46 , 34.97 and 38.17° for complexes **20**, **15**, **16** and **17**.

Having the X-ray structures of the complexes meant that it was possible to obtain an estimate of the steric demand of the NHCs. This was achieved using the SambVca web application²⁷ from which the percentage buried volume, $\%V_{\text{bur}}$ was calculated. The values obtained for **20**, **15**, **16**, **17** and **19** were 31.9 , 32.1 , 32.8 , 33.8 and 34.8% , and these can be compared with 32.9% for IMes measured in a similar way based on previously reported data.²⁵

Catalytic hydrogen transfer testing

As described earlier, one application of rhodium complexes of this type is as catalysts for transfer hydrogenation using isopropanol as a convenient source of hydrogen. Herrmann *et. al* have studied the use of $[\text{Ir}(\text{cod})\text{Cl}(\text{NHC})]$ complexes in a transfer hydrogenation reaction and found that the donor strength of NHC ligands affected the catalytic activity of these complexes.⁴ A weaker donor strength NHC ligand was found to increase the complex activity by reducing the initiation time and accelerating the rate of reaction. We have extended this work by applying it to the rhodium complexes **15** to **19** which contain NHC ligands possessing different degrees of fluorination, and hence differing donor properties, as well as **20** and **21** in the conversion of acetophenone to 1-phenylethanol, as shown in Scheme 4.

Scheme 4 $[\text{Rh}(\text{cod})\text{Cl}(\text{NHC})]$ catalysed transfer hydrogenation of acetophenone

The reactivity of complexes **15** to **21** in transfer hydrogenation was investigated using 1.0 mmol of acetophenone, 0.01 mmol (1% mol) of rhodium complex in 5 mL of 2-propanol, with a catalyst: substrate ratio of 1 : 100. The percentage conversion was measured by integration of the methyl proton signals of acetophenone (s, δ 2.60 ppm) and 1-phenylethanol (d, δ 1.50 ppm) in the ^1H NMR spectrum of the crude product recorded in deuterated chloroform. Tests using the non-fluorinated analogues, $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh})]$, **20**, and $[\text{Rh}(\text{cod})\text{Cl}(\text{IMes})]$, **21**, were conducted in an identical manner in order to compare the effectiveness of the fluorinated NHC rhodium complexes against commonly used non-fluorinated NHC ligand analogues.

Figure 3 Time dependence of the catalytic transfer hydrogenation of acetophenone with i-PrOH and $[\text{Rh}(\text{cod})\text{Cl}(\text{NHC})]$ complexes

Figure 3 shows the average time dependent conversions for the catalytic transfer hydrogenation reactions. From this it can

be seen that the fluorinated NHC rhodium complexes, **15** to **19** are more competent catalysts than those of the non-fluorinated analogues, $[\text{Rh}(\text{cod})\text{Cl}(\text{IMes})]$, **21**, and $[\text{Rh}(\text{cod})\text{Cl}(\text{IPh})]$, **20**. For example, **19** achieved 70% conversion after just 10 minutes whilst **20** achieved only 15% conversion within the same period. It has previously been reported that imidazolium salts alone can catalyse hydrogen transfer reactions, albeit significantly less effectively,²⁸ so experiments were also undertaken in which the metal catalysts were replaced with the NHC.HBF₄ salts. In this case after one hour the maximum yield of 1-phenylethanol was 20%, with the greatest conversion being found for **5**, followed by **3**, **4**, **2** and **1**. Importantly, when no catalyst was present 0% conversion was observed after 60 minutes.

As described by in previous studies of transfer hydrogenation, weaker donor strength NHC ligands increased the catalytic activity of the $[\text{Ir}(\text{cod})\text{Cl}(\text{NHC})]$ complexes.⁴ If the rhodium complexes operate in a similar way then based on the electronic properties of NHCs **1** – **5**, as measured by the various NMR parameters described above, then the rhodium complex of **5**, ie **19**, should be the most active, followed by the complexes of **3**, **4**, **2** and finally **1**, ie **19** > **17** > **18** > **16** > **15**, with the non-fluorinated NHC-containing complexes being the least active. Referring to Figure 3, it can be seen that this is indeed the order observed, suggesting not only that the electronic properties of the NHC ligand are a significant factor in determining the conversion, and that NMR studies of the precursor imidazolium salts provides a good guide to the activity of the derived complexes in this case.

A possible explanation for the enhanced catalytic properties of the fluorinated-NHC-containing complexes comes from the proposed catalytic cycle for transfer hydrogenation of a ketone with 2-propanol, shown in figure 1. The presence of a more poorly donating ligand will render the metal centre more acidic so enhancing the initiation and coordination of both iPrOH and incoming ketone. While the steric properties of the ligand are expected to influence the rate of the migratory insertion step and the exchange of the bulky, newly-formed alcohol and isopropanol.

In a number of different NHC catalytic systems the steric bulk that the NHC imparts on the metal centre is determined as having a very significant influence on the efficiency of the catalyst.²⁹ Indeed, in some catalytic systems a considerably amount of effort has been used to generate very sterically demanding ligands for this purpose.³⁰ We therefore investigated these effects in this system, by plotting the one hour conversion against the %V_{bur} steric parameter of the NHCs, and this is depicted in Fig. 4. A general trend is observed that rhodium complexes bearing more bulky NHC ligands typically give rise to higher catalytic activities than those containing less bulky NHC ligands. However while this is true within the series of fluorinated NHC ligands, $[\text{Rh}(\text{cod})\text{Cl}(\text{IMes})]$ that contains the IMes ligand which is bulkier than either **15**, IPh^{4F}, or **16**, IPh^{24F2}, has a lower catalytic performance than those rhodium complexes.

Figure 4 Plot of percentage conversion in transfer hydrogenation of acetophenone against the percent buried volume $\%V_{bur}$.

This suggests that in this system the electronic properties of the NHC ligands are probably more significant in determining the behaviour of the activity of the rhodium catalyst. In order to test this we investigated links between the percentage conversion after one hour and the following NMR parameters $^1J(\text{CH})$ coupling constant of the NHC.HBF₄ salts, $\delta(^{77}\text{Se})$ for the NHC selenides, $\delta(^{13}\text{C})$ and $^1J(\text{C-Rh})$ for the rhodium NHC complexes as a measure of the electronic properties of the NHC ligands. Of these the best correlations were observed with the ^{77}Se NMR chemical shift and then the ^{13}C carbenic resonance of the rhodium complex, and these are shown in Figure 5. (Plots against the other measures are given in the supplementary information.) However, even though a less good correlation exists with the other NMR parameters in each case the order of the efficiency of each of the catalysts is reproduced.

Figure 5 Plot of percentage conversion in transfer hydrogenation of acetophenone against ^{77}Se chemical shifts of the NHC selenides (top line, right hand axis) and ^{13}C chemical shifts of the NHC-containing rhodium complexes (lower line, left hand axis).

The observation of the best fit between conversion and ^{77}Se chemical shift values, suggests that there may be a link between the π -accepting properties (to which selenium chemical values are most sensitive) of the NHC ligands and the catalytic activity of the corresponding complexes. NHC ligands with greater π -accepting ability, such as those in **15** to **19** give rise to complexes that have higher catalytic performances than those NHC ligands

with weaker π -acceptor strengths [Rh(cod)Cl(IMes)] and [Rh(cod)Cl(IPh)]. The inclusion of fluorine substituents on the aryl rings of the NHC ligands increases the π -accepting ability of the ligands and so influences the catalytic activity of the corresponding complexes. These findings are consistent with those of other studies and suggest that π -interaction can also play a significant role in the bonding of these classical σ -donor NHC ligands to transition metals.³¹ Thus, amongst the NHCs investigated the inclusion of fluorine substituents in the 2,4 and 6-positions results in an NHC ligand with the largest steric impact, based on the $\%V_{bur}$ steric parameter and the largest electronic influence, as judged by a range of NMR measurements, and this combination results in its rhodium complex being the most catalytically active in the transfer hydrogenation reaction under investigation.

Conclusions

The tetrafluoroborate salts of five NHCs possessing a systematic variation in fluorine content of the nitrogen-bound aryl rings were successfully synthesised as were their selenide derivatives. NMR measurements show that the electronic properties of these NHC ligands are distinct from the more commonly used NHC ligands in the imidazolium and imidazolidine families. Direct reaction of the NHC salts with [Rh(cod)Cl]₂ in the presence of K₂CO₃ resulted in the formation of the first examples of fluoraryl substituted imidazolium rhodium complexes. The catalytic activities of these fluorinated NHC-containing rhodium complexes in the transfer hydrogenation of acetophenone using iso-propanol as the hydrogen source were found to be greater than those of the non-fluorinated NHCs counterparts, [Rh(cod)Cl(IMes)] and [Rh(cod)Cl(IPh)]. This shows that even remote inclusion of fluorine on the aryl substituents of an NHC has an influence on the properties of the rhodium centre. Furthermore the efficiency of the conversion was found to correspond to the electronic properties of the NHCs as determined by $\delta(^{77}\text{Se})$ of the NHC selenides and $\delta(^{13}\text{C})$ of the precursor NHC.HBF₄ salts, potentially providing an easy and very readily accessible method to screen future NHCs in catalyst systems.

Experimental

General considerations

Unless otherwise stated all reactions were carried out in air. 4-fluoroaniline, 2,4-difluoroaniline, 2,6-difluoroaniline, 2,4,5-trifluoroaniline and 2,4,6-trifluoroaniline were purchased from Fluorochem; paraformaldehyde and glyoxal were purchased from Aldrich Chemical Co. and used without further purification. [Rh(cod)Cl]₂ and [Rh(cod)Cl(IMes)] were prepared according to the published procedures.²³ All other chemicals were obtained commercially from Sigma Aldrich or Alfa Aesar and were of analytical grade or higher and were used without further purification. ^1H , ^{13}C , ^{19}F and ^{77}Se NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer, and were referenced to external TMS (^1H , ^{13}C) and CFCl₃ (^{19}F) and Me₂Se (^{77}Se). Chemical

shifts (δ) are reported in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). Elemental analyses for carbon, hydrogen and nitrogen were performed on Thermo Scientific Flash 2000 Organic Elemental Analyser whilst rhodium metal was analysed using Thermo Scientific iCAP DUO 6300 inductively coupled plasma optical emission spectroscopy (ICP-OES) instrument.

Synthetic procedures

1,3-Bis(4-fluorophenyl)imidazolium tetrafluoroborate, IPH^{4F}.HBF₄ (1) To a stirred solution of 4-fluoroaniline (4.3 g, 38.7 mmol) in toluene (17 mL) was added paraformaldehyde (0.58 g, 19.3 mmol). The resulting mixture was heated to 100°C and then cooled to 40°C before glyoxal (2.20 mL of a 40% aqueous solution, 19.3 mmol) was added. The mixture was stirred for 5 min, and then HCl (6.45 mL, 3M) was added dropwise. The mixture was heated to 100°C for 12 hours. After cooling to room temperature, the solvent was removed by vacuum rotary evaporator. Subsequently, the resulting mixture was then dissolved in water (20 mL), followed by the addition of tetrafluoroboric acid HBF₄ (1.2 mL of a 40 wt.% in water, 19.3 mmol). The mixture was stirred for one hour and transferred into a separating funnel. The aqueous phase was extracted with CH₂Cl₂ (3 x 50 mL). The combined organic phases were dried with MgSO₄ for 1 hour and all volatiles were removed *in vacuo*. Repeated recrystallization from dichloromethane/diethyl ether gave **1** as a white solid (5.45 g, 82%). ¹H NMR (DMSO) δ (ppm): 10.30 (s, 1H, NCHN), 8.54 (s, 2H, NCHCHN), 7.97 (m, 4H, ³J_{HH} = 4.61 Hz, ArH), 7.62 (m, 4H, ³J_{HH} = 8.92 Hz, ArH). ¹³C{¹H} NMR (DMSO) δ (ppm): 164.12, 135.53, 131.60, 125.10, 122.60, 117.60. ¹⁹F{¹H} NMR (DMSO) δ (ppm): -111.00 (s, 2F, ArF), -148.00 (s, 4F, BF₄). Anal. Calcd for C₁₅H₁₁BF₆N₂ (%): C, 52.44, H, 3.22, N, 8.14, B, 3.20. Found: C, 52.76, H, 3.16, N, 7.95, B, 3.10.

1,3-Bis(2,4-difluorophenyl)imidazolium tetrafluoroborate, IPH^{2F2}.HBF₄ (2) Using a method similar to that used for compound **1** gave **2** as a white solid (6.23 g, 85%). The characterisation data are in good agreement with the chloride analogue that has been reported in the literature.³² ¹H NMR (DMSO) δ (ppm): 10.20 (s, 1H, NCHN), 8.45 (s, 2H, NCHCHN), 8.00 (m, 2H, ArH), 7.84 (m, 2H, ArH), 7.52 (m, 2H, ArH). ¹³C{¹H} NMR (DMSO) δ (ppm): 164.70, 154.52, 139.20, 129.18, 124.42, 119.81, 113.35, 106.21. ¹⁹F{¹H} NMR (DMSO) δ (ppm): -105.00 (d, 2F, ⁴J_{FF} = 8.6 Hz, ArF), -118.00 (d, 2F, ⁴J_{FF} = 8.6 Hz, ArF), -148.00 (s, 4F, BF₄). Anal. Calcd for C₁₅H₉BF₈N₂ (%): C, 47.38, H, 2.39, N, 7.37, B, 2.89. Found: C, 47.77, H, 2.17, N, 7.37, B, 2.60.

1,3-Bis(2,6-difluorophenyl)imidazolium tetrafluoroborate, IPH^{2F2}.HBF₄ (3) Using a similar method to that described for compound **1** gave **3** as a white solid (5.50 g, 75%). ¹H NMR (DMSO) δ (ppm): 10.33 (s, 1H, NCHN), 8.54 (s, 2H, NCHCHN), 7.84 (tt, 2H, ArH), 7.60 (t, 4H, ³J_{HH} = 8.8 Hz, ArH). ¹³C{¹H} NMR (DMSO) δ (ppm): 165.66, 155.11, 141.61, 133.90, 125.44, 113.53. ¹⁹F{¹H} NMR (DMSO) δ (ppm): -120.75 (s, 4F, ArF), -148.27 (s, 4F, BF₄). Anal. Calcd for C₁₅H₉BF₈N₂ (%): C, 47.38, H, 2.39, N, 7.37, B, 2.89. Found: C, 47.34, H, 2.47, N, 7.08, B, 3.30.

1,3-Bis(2,4,5-trifluorophenyl)imidazolium tetrafluoroborate, IPH^{2F3}.HBF₄ (4) Using a method similar to that used for **1** gave compound **5** as a white solid of **5** (6.02 g, 75%). ¹H NMR (DMSO) δ (ppm): 10.23 (s, 1H, NCHN), 8.46 (s, 2H, NCHCHN), 8.25 (m, 2H, ArH),

8.17 (m, 2H, ArH). ¹³C{¹H} NMR (DMSO) δ (ppm): 162.10, 152.75, 150.46, 147.50, 139.57, 124.36, 119.54, 116.59, 108.41, 107.41. ¹⁹F{¹H} NMR (DMSO) δ (ppm): -123.10 (dd, 2F, ⁴J_{FF} = 14.6 Hz, ⁵J_{FF} = 5.7 Hz, ArF), -129.57 (dd, 2F, ³J_{FF} = 22.9 Hz, ⁵J_{FF} = 5.7 Hz, ArF), -139.86 (dd, 2F, ³J_{FF} = 22.9 Hz, ⁴J_{FF} = 14.6 Hz, ArF), -148.00 (s, 4F, BF₄). Anal. Calcd for C₁₅H₇BF₁₀N₂ (%): C, 43.29, H, 1.69, N, 6.73, B, 2.64. Found: C, 43.93, H, 1.43, N, 6.76, B, 2.50.

1,3-Bis(2,4,6-trifluorophenyl)imidazolium tetrafluoroborate, IPH^{2F3}.HBF₄ (5) A preparation method similar to that used for compound **1** gave **5** as a white solid (6.34 g, 79%). The characterisation data are in good agreement with the chloride analogue that has been reported in the literature.³² ¹H NMR (DMSO) δ (ppm): 10.27 (s, 1H, NCHN), 8.49 (s, 2H, NCHCHN), 7.80 (m, 4H, ArH). ¹³C{¹H} NMR (DMSO) δ (ppm): 164.71, 158.43, 141.83, 125.52, 110.10, 103.07. ¹⁹F{¹H} NMR (DMSO) δ (ppm): -101.87 (t, 2F, ⁴J_{FF} = 7.7 Hz, ArF), -117.17 (d, 4F, ⁴J_{FF} = 7.7 Hz, ArF), -148.20 (s, 4F, BF₄). Anal. Calcd for C₁₅H₇BF₁₀N₂ (%): C, 43.29, H, 1.69, N, 6.73, B, 2.64. Found: C, 43.48, H, 1.43, N, 6.69, B, 2.64.

1,3-Bis(phenyl)imidazolium tetrafluoroborate, IPH.HBF₄ (6) A preparation method similar to that used for compound **1** gave **6** as a white solid of (4.64 g, 78%). ¹H NMR (DMSO) δ (ppm): 10.34 (s, 1H, NCHN), 8.55 (s, 2H, NCHCHN), 7.90 (d, 4H, ³J_{HH} = 7.6 Hz, ArH), 7.72 (t, 4H, ³J_{HH} = 7.8 Hz, ArH), 7.60 (t, 2H, ³J_{HH} = 7.4 Hz, ArH). ¹³C{¹H} NMR (DMSO) δ (ppm): 135.10, 134.55, 130.22, 130.10, 122.52, 121.95. ¹⁹F{¹H} NMR (DMSO) δ (ppm): -148.12 (s, 4F, BF₄). Anal. Calcd for C₁₅H₁₃BF₄N₂ (%): C, 58.42, H, 4.25, N, 9.09, B, 3.57. Found: C, 58.58, H, 4.23, N, 9.19, B, 3.64. Data were consistent with those reported previously.

1,3-Bis(4-fluorophenyl)imidazol-2-selenone, IPH^{4F}Se (8) In a 250 mL single neck round bottom flask, a mixture of **1** (0.580 g, 1.70 mmol), selenium powder (0.135 g, 1.70 mmol) and potassium carbonate (0.290 g, 2.10 mmol) in methanol (50 mL) was heated at reflux for 24 hours after which the mixture was concentrated on a rotary evaporator. The remaining solid was dissolved in dichloromethane (30 mL), then the solution was filtered through celite and the solvent was evaporated. The resulting compound was recrystallized from dichloromethane (5 mL) and pentane (20 mL) mixture and filtered, to afford an off-white solid (0.450 g, 79%). ¹H NMR (CDCl₃) δ (ppm): 7.60 (s, 2H, NCHCHN), 7.20 (m, 4H, ³J_{HH} = 4.6 Hz, ArH), 7.12 (m, 4H, ³J_{HH} = 8.9 Hz, ArH). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 163.39, 134.87, 128.70, 123.90, 120.99, 116.30. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -111.60 (s, 2F, F). ⁷⁷Se{¹H} NMR (CDCl₃) δ (ppm): 60.7. Anal. Calcd for C₁₅H₁₀F₂N₂Se (%): C, 53.72, H, 3.01, N, 8.36. Found: C, 53.48, H, 3.43, N, 8.69.

1,3-Bis(2,4-difluorophenyl)imidazol-2-selenone, IPH^{2F2}Se (9) A preparation method similar to that used for compound **8** afforded **9** as an off-white solid (0.511 g, 81%). ¹H NMR (CDCl₃) δ (ppm): 8.19 (s, 2H, NCHCHN), 7.71 (m, 2H, ArH), 7.28 (s, 2H, ArH), 7.20 (m, 2H, ArH). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 163.39, 155.81, 149.91, 131.14, 129.85, 121.22, 112.19, 105.16. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -106.05 (d, 2F, ⁴J_{FF} = 8.6 Hz, Ar-4-F), -115.29 (d, 2F, ⁴J_{FF} = 8.6 Hz, Ar-2-F). ⁷⁷Se{¹H} NMR (CDCl₃) δ (ppm): 66.7. Anal. Calcd for C₁₅H₈F₄N₂Se (%): C, 48.51, H, 2.17, N, 7.55. Found: C, 48.48, H, 2.43, N, 7.69.

1,3-Bis(2,6-difluorophenyl)imidazol-2-selenone, IPH^{26F2}Se (10) A preparation method similar to that used for compound **8** afforded **9** as an off-white solid (0.536 g, 85%). ¹H NMR (CDCl₃) δ (ppm): 8.32 (s, 2H, NCHCHN), 7.55 (s, 2H, ArH), 7.20 (t, 4H, ³J_{HH} = 8.8 Hz, ArH). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 163.68, 153.26, 140.19, 131.62, 122.26, 112.30. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -118.75 (s, 4F, ArF). ⁷⁷Se{¹H} NMR (CDCl₃) δ (ppm): 68.3. Anal. Calcd for C₁₅H₈F₄N₂Se (%): C, 48.51, H, 2.17, N, 7.55. Found: C, 48.71, H, 2.03, N, 7.39.

1,3-Bis(2,4,5-trifluorophenyl)imidazol-2-selenone, IPH^{245F3}Se (11) Using a similar preparation method to that used for compound **8** afforded **11** as an off-white solid (0.567 g, 82%). ¹H NMR (CDCl₃) δ (ppm): 8.19 (s, 2H, NCHCHN), 7.81 (m, 2H, ArH), 7.68 (s, 2H, ArH). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 151.68, 149.26, 146.19, 137.62, 122.26, 117.57, 114.59, 106.31. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -125.10 (dd, 2F, ⁴J_{FF} = 14.7 Hz, ⁵J_{FF} = 5.2 Hz, Ar-2-F), -127.30 (dd, 2F, ³J_{FF} = 23.3 Hz, ⁵J_{FF} = 5.2 Hz, Ar-5-F), -137.66 (dd, 2F, ³J_{FF} = 23.2 Hz, ⁴J_{FF} = 14.7 Hz, Ar-4-F). ⁷⁷Se{¹H} NMR (CDCl₃) δ (ppm): 67.4. Anal. Calcd for C₁₅H₆F₆N₂Se (%): C, 44.23, H, 1.49, N, 6.88. Found: C, 44.25, H, 1.60, N, 6.85.

1,3-Bis(2,4,6-trifluorophenyl)imidazol-2-selenone, IPH^{246F3}Se (12) A preparation method similar to that used for compound **8** afforded **12** as an off-white solid (0.574 g, 83%). ¹H NMR (CDCl₃) δ (ppm): 8.13 (s, 2H, NCHCHN), 6.92 (m, 4H, ArH). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 164.52, 161.90, 157.50, 121.33, 112.64, 101.79. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -102.84 (t, 2F, ⁴J_{FF} = 7.5 Hz, Ar-4-F), -112.68 (d, 4F, ⁴J_{FF} = 7.5 Hz, Ar-2,6-F). ⁷⁷Se{¹H} NMR (CDCl₃) δ (ppm): 73.0. Anal. Calcd for C₁₅H₆F₆N₂Se (%): C, 44.23, H, 1.49, N, 6.88. Found: C, 44.71, H, 1.33, N, 6.89.

1,3-Bis(phenyl)imidazol-2-selenone, IPHSe (13) Using a preparation method similar to that used for compound **8** gave compound **13** as a white solid (0.346 g, 68%). ¹H NMR (CDCl₃) δ (ppm): 8.05 (s, 2H, NCHCHN), 7.80 (d, 4H, ³J_{HH} = 7.6 Hz, ArH), 7.62 (t, 4H, ³J_{HH} = 7.8 Hz, ArH), 7.55 (t, 2H, ³J_{HH} = 7.4 Hz, ArH). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 154.60, 134.45, 130.22, 130.10, 122.12, 121.92. ⁷⁷Se{¹H} NMR (CDCl₃) δ (ppm): 24.1. Anal. Calcd for C₁₅H₁₂N₂Se (%): C, 60.19, H, 4.04, N, 9.36. Found: C, 60.31, H, 4.03, N, 9.29.

[Rh(cod)Cl(IPH^{4F})] (15) This complex was prepared from **1** (69.5 mg, 0.202 mmol), [Rh(cod)Cl]₂ (50.0 mg, 0.101 mmol) and K₂CO₃ (83.6 mg, 0.606 mmol) in acetone (6.0 mL). The resulting mixture was refluxed for 20 hours at 60°C. Subsequently, the solvent was removed on a rotary evaporator and dichloromethane was added (6.0 mL). The mixture was filtered through silica gel and washed with dichloromethane until the filtrate was colourless. The solvent was removed affording a yellow crystalline solid (76.1 mg, 75%). ¹H NMR (CDCl₃) δ (ppm): 8.26 (s, 2H, NCHCHN), 7.28 (m, 4H, ArH), 7.24 (m, 4H, ArH), 4.92 (s, 2H, Hcod), 2.64 (s, 2H, Hcod), 1.96 (m, 4H, Hcod), 1.61 (m, 4H, Hcod). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 184.82 (d, J_{C-Rh} = 51.7 Hz, Ccarbene), 162.15 (d, J_{C-F} = 245.3 Hz, CF), 160.89, 136.23, 129.07, 123.45, 97.80 (d, J_{C-Rh} = 15.1 Hz, Ccod), 68.30 (d, J_{C-Rh} = 22.1 Hz, Ccod), 32.41, 29.05. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -113.11 (s, 2F, Ar-4-F). Anal. Calcd for C₂₃H₂₂F₂N₂ClRh (%): C, 54.92, H, 4.41, N, 5.57, Rh, 20.48. Found: C, 54.09, H, 4.32, N, 5.43, Rh, 20.45.

[Rh(cod)Cl(IPH^{24F2})] (16) A preparation method similar to that used for complex **15** gave **16** as a yellow crystalline solid (84.8 mg, 78%). ¹H NMR (CDCl₃) δ (ppm): 8.88 (m, 2H, ArH), 7.19 (s, 2H, NCHCHN),

7.11 (m, 2H, ArH), 6.98 (m, 2H, ArH), 4.80 (br, 2H, Hcod), 2.69 (br, 2H, Hcod), 1.83 (m, 4H, Hcod), 1.58 (m, 4H, Hcod). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 187.60 (d, J_{C-Rh} = 51.8 Hz, Ccarbene), 161.31 (d, J_{C-F} = 249.3 Hz, CF), 154.96 (d, J_{C-F} = 250.9 Hz, CF), 132.20, 123.97, 123.27, 111.48, 104.18, 98.82 (d, J_{C-Rh} = 15.5 Hz, Ccod), 68.35 (d, J_{C-Rh} = 22.7 Hz, Ccod), 32.36, 28.49. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -107.52 (d, 2F, ⁴J_{FF} = 8.6 Hz, Ar-4-F), -119.67 (d, 2F, ⁴J_{FF} = 8.6 Hz, Ar-2-F). Anal. Calcd for C₂₃H₂₀F₄N₂ClRh (%): C, 51.25, H, 3.74, N, 5.20, Rh, 19.11. Found: C, 51.16, H, 3.59, N, 5.04, Rh, 19.14.

[Rh(cod)Cl(IPH^{26F2})] (17) A preparation method similar to that used for complex **15** afforded a yellow crystalline solid of **17** (91.5 mg, 85%). ¹H NMR (CDCl₃) δ (ppm): 7.72 (s, 2H, NCHCHN), 7.56 (m, 2H, ArH), 7.22 (m, 4H, ArH), 4.72 (br, 2H, Hcod), 3.29 (br, 2H, Hcod), 2.15 (m, 4H, Hcod), 1.60 (m, 4H, Hcod). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 191.52 (d, J_{C-Rh} = 53.4 Hz, Ccarbene), 167.81 (d, J_{C-F} = 252.3 Hz, CF), 159.61, 128.71, 123.59, 111.04, 98.09 (d, J_{C-Rh} = 16.5 Hz, Ccod), 68.14 (d, J_{Rh-C} = 22.7 Hz, Ccod), 32.71, 28.38. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -118.93 (s, 2F, Ar-2F). Anal. Calcd for C₂₃H₂₀F₄N₂ClRh (%): C, 51.25, H, 3.74, N, 5.20, Rh, 19.11. Found: C, 50.99, H, 3.78, N, 5.05, Rh, 19.37.

[Rh(cod)Cl(IPH^{245F3})] (18) A preparation method similar to that used for complex **15** afforded complex **18** as a yellow crystalline solid (91.7 mg, 79%). ¹H NMR (CDCl₃) δ (ppm): 8.90 (s, 2H, NCHCHN), 7.51 (m, 2H, ArH), 7.32 (m, 2H, ArH), 4.72 (br, 2H, Hcod), 2.56 (br, 2H, Hcod), 1.76 (m, 4H, Hcod), 1.50 (m, 4H, Hcod). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 189.54 (d, J_{C-Rh} = 51.9 Hz, Ccarbene), 167.81 (d, J_{C-F} = 249.3 Hz, CF), 152.41 (d, J_{C-F} = 247.1 Hz, CF), 144.11 (d, J_{C-F} = 245.2 Hz, CF), 139.89, 136.54, 123.33, 111.91, 98.28 (d, J_{C-Rh} = 15.8 Hz, Ccod), 71.14 (d, J_{C-Rh} = 21.4 Hz, Ccod), 31.40, 27.48. ¹⁹F{¹H} NMR (CDCl₃) δ (ppm): -123.06 (dd, 2F, ⁴J_{FF} = 14.7 Hz, ⁵J_{FF} = 5.2 Hz, Ar-2-F), -129.46 (dd, 2F, ³J_{FF} = 23.3 Hz, ⁵J_{FF} = 5.2 Hz, Ar-5-F), -139.73 (dd, 2F, ³J_{FF} = 23.2 Hz, ⁴J_{FF} = 14.7 Hz, Ar-4-F). Anal. Calcd for C₂₃H₁₈F₆N₂ClRh (%): C, 48.08, H, 3.16, N, 4.87, Rh, 17.91. Found: C, 48.68, H, 3.11, N, 4.71, Rh, 17.97.

[Rh(cod)Cl(IPH^{246F3})] (19) A preparation method similar to that used for complex **15** afforded a yellow crystalline solid for **19** (88.2 mg, 76%). ¹H NMR (CDCl₃) δ (ppm): 7.14 (s, 2H, NCHCHN), 6.98 (br, 4H, ArH), 4.80 (s, 2H, Hcod), 3.27 (s, 2H, Hcod), 1.98 (br, 4H, Hcod), 1.76 (br, 4H, Hcod). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ (ppm): 194.95 (d, J_{Rh-C} = 59.75 Hz, Ccarbene), 162.41, 148.82, 144.23, 139.51, 136.54, 125.33, 99.10 (d, J_{Rh-C} = 16.8 Hz, Ccod), 72.14 (d, J_{Rh-C} = 23.4 Hz, Ccod), 55.50, 33.42, 27.53. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ (ppm): -103.65 (s, 2F, Ar F), -106.03 (s, 2F, ArF), -115.58 (s, 2F, ArF). ¹⁹F NMR (376 MHz, CDCl₃) δ (ppm): -115.39 (s, 2F, FAR), -122.93 (m, 2F, FAR), -132.93 (m, 2F, FAR). Anal. Calcd for C₂₃H₂₂ClN₂F₄Rh (%): C, 48.04, H, 3.16, N, 4.87, Rh, 17.91. Found: C, 48.01, H, 3.22, N, 4.91, Rh, 17.93.

[Rh(cod)Cl(IPH)] (20) A preparation method similar to that used for complex **14** gave complex **20** as a white solid [Rh(cod)Cl(IPH)] (58.4 g, 62%). ¹H NMR (CDCl₃) δ (ppm): 7.73 (s, 2H, NCHCHN), 7.51 (d, 4H, ³J_{HH} = 7.6 Hz, ArH), 7.45 (t, 4H, ³J_{HH} = 7.8 Hz, ArH), 7.32 (t, 2H, ³J_{HH} = 7.4 Hz, ArH), 4.65 (br, 2H, Hcod), 2.31 (br, 2H, Hcod), 1.95 – 1.75 (m, 4H, Hcod), 1.65 – 1.45 (m, 4H, Hcod). ¹³C{¹H} NMR (CDCl₃) δ (ppm): 181.52 (d, J_{C-Rh} = 48.6 Hz, Ccarbene), 153.10, 150.65, 145.39, 143.55, 139.21, 96.11 (d, J_{C-Rh} = 7.2 Hz, Ccod), 67.44 (d, J_{C-Rh} = 13.3 Hz, Ccod), 32.21, 28.89. Anal. Calcd for C₂₃H₂₄N₂ClRh (%): C, 59.16, H, 5.18, N, 6.00, Rh, 22.06. Found: C, 59.01, H, 5.22, N, 5.91, Rh, 22.23.

Transfer hydrogenation catalytic tests.

The catalyst (0.01 mmol, 1 mol %) was dissolved in a solution of potassium hydroxide (5.61 mg, 0.1 mmol) and isopropanol (5 mL) in a two-necked flask. The solution was heated at 80°C for 30 min under reflux conditions. Subsequently, acetophenone (0.12 mL, 1.0 mmol) was added. After the desired reaction time, an aliquot of the reaction mixture was quenched with 1M HCl and extracted with diethyl ether. The organic phase was separated and collected. The reaction progress was monitored by ¹H NMR spectroscopy and the results for each system are the average of three separate runs.

X-ray crystallography

Crystallography data for complexes **15**, **16**, **17**, **19** and **20** were collected with an Agilent SuperNova diffractometer using Mo K α radiation (λ = 0.71073 Å). All the raw data frames were reduced and corrections were applied for Lorentz, polarisation and absorption using the multi-scan methods with CrysAlisPro.³³ The X-ray structural data were solved by direct methods, with full-matrix least-squares refinement of F² using: Olex2,³⁴ Shelx³⁵ and Shelxtl³⁶ programs. Mercury³⁷ and Pluton³⁸ were used to investigate and report the structures. All non-H atoms were modelled with anisotropic displacement parameters, H-atoms were placed in idealised positions and refined with isotropic thermal parameters. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 1902665-1902668. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or email: deposit@ccdc.cam.ac.uk)

Conflicts of interest

There are no conflicts to declare.

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¹³C and ⁷⁷Se NMR parameters for fluorinated NHC ligand precursors provide simple measures of the catalytic transfer-hydrogenation reactivity of the corresponding [Rh(cod)Cl(NHC)] complexes.