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N-Heterocyclic Carbenes

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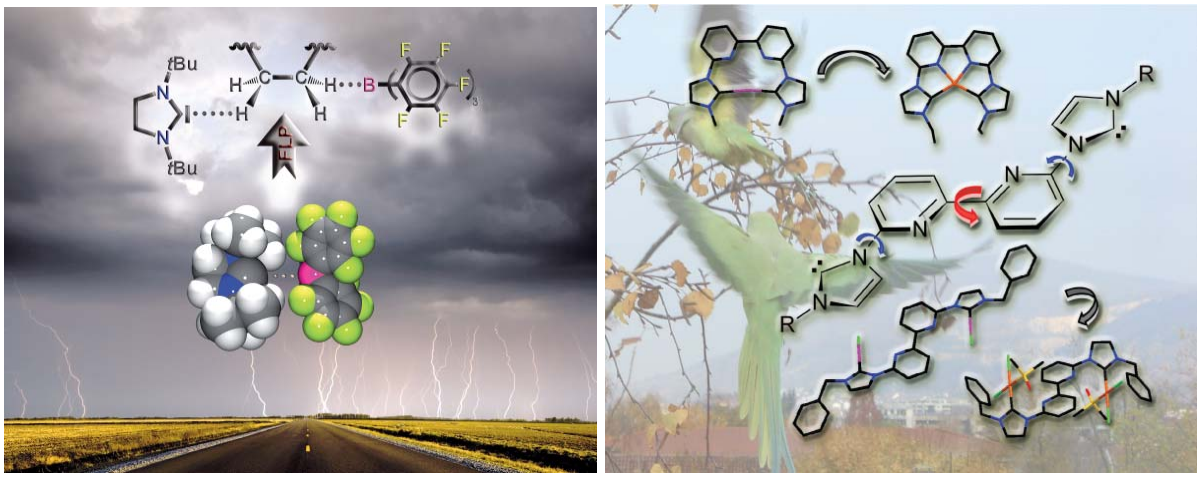

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Pyrazolyl-*N*-heterocyclic carbene complexes of rhodium as hydrogenation catalysts: The influence of ligand steric bulk on catalyst activity†

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A series of bidentate 1-(1-pyrazolylmethyl)-substituted NHC ligands (**13a–c**, **14a–c** and **15a–c**) were synthesised with substituents of varying steric bulk incorporated adjacent to the donor atoms. These ligands were coordinated to rhodium(I) to give a series of complexes of the general formula [Rh(L)(COD)]BPh_4 (where L = a mixed-donor pyrazolyl-NHC ligand and COD = 1,5-cyclooctadiene). The solid state structures of [Rh(**13b**)(COD)]BPh_4 (**16b**), [Rh(**13c**)(COD)]BPh_4 (**16c**), [Rh(**14a**)(COD)]BPh_4 (**17a**), [Rh(**14b**)(COD)]BPh_4 (**17b**), [Rh(**15a**)$_2$(COD)]BPh_4 (**18a**), and [Rh(**15b**)(COD)]BPh_4 (**18b**) were determined by single crystal X-ray diffraction. The complex [Rh(**15a**)$_2$(COD)]BPh_4 (**18a**) is unusual in that two of the pyrazolyl-NHC ligands (**15a**) are coordinated to the metal through the NHC donor instead of one ligand forming the expected chelate. These complexes (with the exception of **18a**) were found to be effective catalysts for the hydrogenation of styrene. The catalytic activity was correlated with complex structure, and it was found that the greater the steric bulk of the metal bound ligand, the slower the rate of the hydrogenation.

Introduction

N-heterocyclic carbenes (NHCs) are now recognised as effective and versatile donors in homogeneous transition metal catalysis.[1–4] In terms of their coordination chemistry they are frequently compared to electron rich phosphine ligands, yet they are generally stronger σ-donors and form complexes of higher thermal and hydrolytic stability.[1] In a desire to exploit these properties, NHCs were initially applied as phosphine substitutes in homogeneous catalysts of proven efficiency. This strategy was most successful in Pd(0) Heck reaction catalysts[5,6] and Ru(II) Grubbs metathesis catalysts,[7] where the use of NHC donors resulted in a vast improvement to catalytic activity and catalyst stability.

In an attempt to extend this success to catalytic Rh(I) and Ir(I) hydrogenation systems a number of NHC analogues of Wilkinsons ($Rh(PPh_3)_3Cl$, **1**)[8] and Crabtrees ([Ir(PCy_3)(py)(COD)]PF_6, **2**, COD = 1,5-cyclooctadiene, py = pyridine)[9] hydrogenation catalysts have since been reported.[10] In early work, Nolan *et al.* reported that the NHC complexes Rh(IMes)(PPh_3)$_2$Cl (**3**, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and [Ir(SIMes)(py)(COD)]PF_6 (**4**, SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) were much less active than the original phosphine systems **1** and **2**, respectively.[11,12] However, Crudden *et al.* found that in the presence of a phosphine scavenger such as CuCl the hydrogenation activity of **3** was significantly enhanced and TOFs (turnover frequencies) exceeding those of **1** could be obtained.[13,14] The *mono* and *bis* NHC Rh complexes Rh(ICy)(COD)Cl (**5**, ICy = 1,3-dicyclohexylimidazol-2-ylidene) and [Rh(IMe)$_2$(COD)]Cl (**6**, IMe = 1,3-dimethylimidazol-2-ylidene) were also shown to be moderately active catalysts for the reduction of simple alkenes.[15] The stability and activity of these complexes was, however, strongly dependent on the *addition* of phosphine ligands to the system, which suggested that the active catalyst was in fact a Rh-NHC-phosphine species similar to **3**. Extensive hydrogenation studies by Buriak *et al.* on NHC analogues of Crabtree's catalyst proved more successful.[16,17] Substitution of the pyridine ligand in **2** with an NHC was observed to yield catalysts of comparable hydrogenation activity. Optimisation of this catalyst motif by incorporating an alternative phosphine ligand and less coordinating counter-anion led to the development of the highly active catalyst system [Ir(IMe)(P^nBu_3)(COD)]BARF (**7**, BARF = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate). Importantly, this complex proved to be stable indefinitely under the catalytic conditions. This represented a significant advantage over Crabtree's catalyst which forms an inactive hydride-bridged trimer species after 1 h under hydrogenation conditions.[9]

Surprisingly the investigation of hydrogenation catalysts containing a more complicated ligand motif has received little attention. The use of a chelating ligand motif, in particular, where the NHC donor is tethered to a separate donor group, has the potential to moderate the lability of each donor group and influence the stability and reactivity of the complex.[18] Very recently, outstanding results were achieved by Burgess and coworkers with the Ir(I) hydrogenation catalysts **8**, which contain a chiral NHC-oxazolyl chelate.[19] These complexes were found to exhibit excellent activity and enantioselectivity (>98% ee) for the reduction of highly substituted prochiral alkenes. However, the hydrogenation activity of these species was highly dependent on the steric properties of the NHC-oxazole ligand. A much enhanced stability of these complexes was observed compared to the related phosphine-oxazole systems.[20] Only two other hydrogenation catalysts (**9**[21] and **10**[22]) have been reported with such mixed donor NHC ligands,

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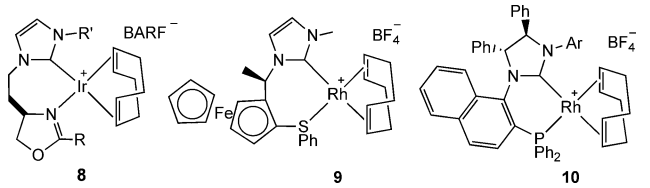
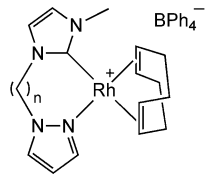
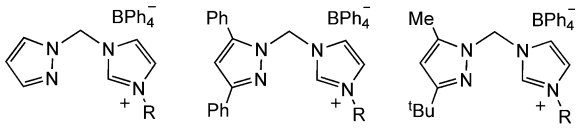
and both were found to be effective for the reduction of α-amido alkenes. The NHC-phosphanyl complex **10**, in particular, was found to afford high conversions and excellent enantioselectivities (up to 98% ee) under relatively mild reaction conditions.



We have previously reported the activity of the Rh(I) mixed donor NHC-pyrazolyl chelate complexes **11** and **12** as hydrogenation catalysts.[23] Both complexes showed good activity for the hydrogenation of styrene under relatively mild reaction conditions, and in an effort to further develop the chemistry of **11**, a series of mixed-donor imidazolium-pyrazolyl ligand precursors of varying steric bulk (**13–15**) and their corresponding NHC complexes with rhodium have been prepared.





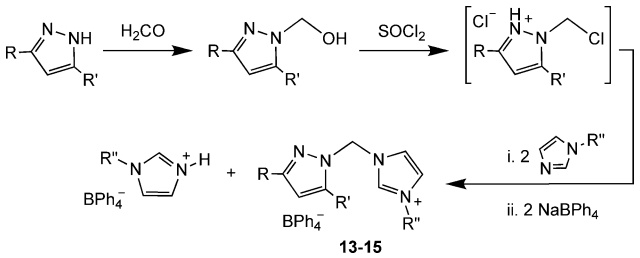
R= Me (**13a**)
R= Mesityl (**13b**)
R= ^{t}Bu (**13c**)

R= Me (**14a**)
R= Mesityl (**14b**)
R= ^{t}Bu (**14c**)

R= Me (**15a**)
R= Mesityl (**15b**)
R= ^{t}Bu (**15c**)

Results and discussion

The imidazolium-pyrazolyl ligand precursors (**13–15**) were synthesized according to Scheme 1.[23] The pyrazole moiety was reacted with formaldehyde under basic conditions to generate a hydroxymethylpyrazole species which upon reaction with thionyl chloride afforded a chloromethylpyrazole intermediate that was isolated as the hydrochloride salt. The high susceptibility of the chloro group to hydrolysis prevented isolation of the free base which was therefore used without further purification. Reaction of two equivalents of the *N*-substituted imidazole was required to yield the desired imidazolium-pyrazolyl products (**13–15**) and



Scheme 1

eliminate a corresponding equivalent of the imidazolium HCl salt. Anion metathesis with $NaBPh_4$ and recrystallization of the mixture afforded the products as white crystalline powders. In this context the solid state structure of one of these compounds (**13c**) was determined crystallographically (for details see Experimental section).

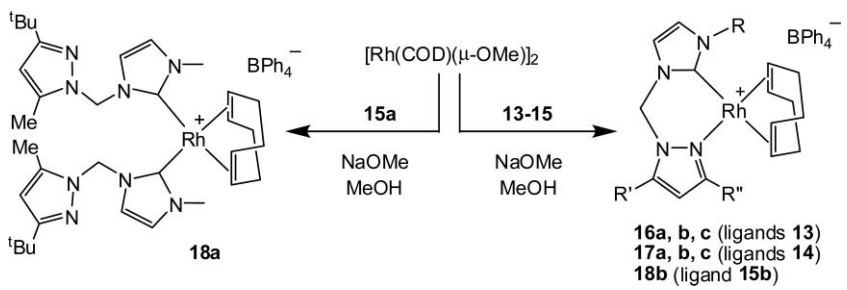
The rhodium *N*-heterocyclic carbene complexes **16–18** were synthesized according to Scheme 2. The complex $[Rh(COD)(\mu\text{-}OMe)]_2$ and the desired pyrazolyl-imidazolium salt (**13–15**) were added to a solution of sodium methoxide in methanol and the mixture refluxed for several hours. A bright yellow powder of the complex precipitated upon concentration of the solution *in vacuo*, which was collected and recrystallized from dichloromethane and hexane.

An anomalous result was observed for the ligand precursor **15a** which contains a bulky *tert*-butyl substituent on the pyrazolyl donor and a methyl substituent on the NHC. The reaction of only one equivalent of the ligand precursor per rhodium centre led to the isolation of the unusual biscarbene adduct **18a**, which has two NHC ligands coordinated to the rhodium centre with the pendant pyrazolyl donors remaining uncoordinated.

Several attempts were made to coordinate the bulky ligand precursor **15c**, which has *tert*-butyl substituents on both the pyrazole and NHC donor, to rhodium with no success. Despite refluxing a methanol solution of **15c** and $[Rh(COD)(\mu\text{-}OMe)]_2$ in the presence of excess sodium methoxide for 48 h, only unreacted ligand was recovered.

X-Ray crystal structure analysis

The solid state structures of **16b** and **c** (Fig. 1), **17a** and **b** (Fig. 2), and **18a** and **b** (Fig. 3) were determined by single crystal X-ray diffraction. Crystals suitable for analysis were obtained *via* slow diffusion of hexane into CH_2Cl_2 solutions of the complexes. Complexes **16b** and **16c** crystallized as pairs of crystallographically inequivalent formula moieties (**16b** and **16b***, **16c** and **16c***). Fig. 1



Scheme 2

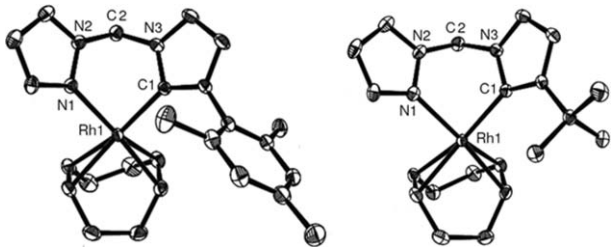


Fig. 1 ORTEP diagrams with 50% ellipsoids and partial crystal structure numbering scheme of the cationic fragments of complexes **16b** and **16c**.

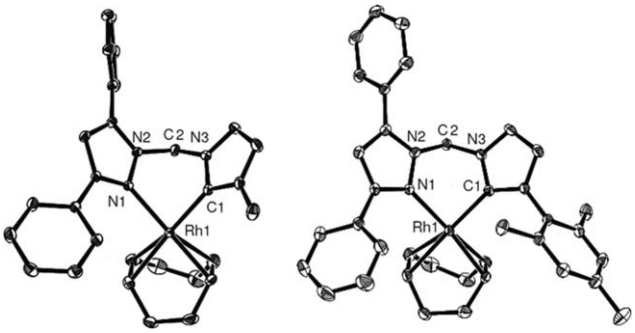


Fig. 2 ORTEP diagrams with 50% ellipsoids and partial crystal structure numbering scheme of the cationic fragments of complexes **17b** and **17c**.

depicts only one of the conformationally very similar cations for each structure.

In all of the crystal structures a square planar geometry around the metal centre is observed, with the metallocycle formed by the NHC-pyrazolyl chelate adopting a pseudo-boat conformation. A list of relevant bond lengths and angles is shown in Table 1. The metrics of complex **16a**, with the methyl substituted NHC and unsubstituted pyrazolyl donor, which was reported previously[23] are also included for comparison. An interesting trend is observed on comparing the rhodium–carbene Rh1–C1 bond lengths in the structures **16a** (2.053(2) Å), **16b** (2.0363(14) Å), **16b*** (2.0224(13) Å), **16c** (2.0829(13) Å), and **16c*** (2.0746(13) Å). These complexes vary only in relation to the size of the substituent on the NHC donor, and the Rh1–C1 bond lengths increase according to the nature of the NHC donor substituent in the order mesityl < methyl < *tert*-butyl. This order suggests that the steric influence of the methyl substituent is greater than that exerted by the mesityl substituent. The lesser apparent steric impact of the mesityl substituted ligand may in part be due to an interaction of the COD olefinic hydrogens with the aromatic π-system of the mesityl ring (**16b**: $CH_{COD}\cdots$mesityl ring centroid = 3.103 Å, **16b***: $CH_{COD}\cdots$mesityl ring centroid = 2.947 Å). A similar interaction was also observed in the crystal structures of **17b** ($CH_{COD}\cdots$mesityl ring centroid = 2.697 Å) and **18b** ($CH_{COD}\cdots$mesityl ring centroid = 2.728 Å). However, the rhodium–carbene Rh1–C1 bond length for complexes **17a** (2.0196(11) Å) and **17b** (2.0487(16) Å) (Fig. 2) follow the reverse order with the bond lengths for the substituents methyl < mesityl. This result suggests that factors other than the steric bulk of the NHC substituent, such as ring strain within the ligand metallocycle and the size of the pyrazolyl substituent, also influence the length of the rhodium–carbene bond.

When comparing the rhodium–pyrazolyl Rh1–N1 bond lengths in the structures **16b** (2.1152(12) Å), **16b*** (2.1243(13) Å), **17b** (2.1433(14) Å), and **18b** (2.2091(9) Å), which have identical NHC donor groups and vary only with respect to the substituents on the pyrazolyl donor, a clearer trend is observed. In this case, as expected, the Rh1–N1 bond lengths vary in proportion to the size of the pyrazolyl substituent in the order hydrogen < phenyl < *tert*-butyl. When comparing the bite angle (C1–Rh1–N1) formed by the ligand, no clear trend is observed in relation to the steric bulk of the substituents.

The tertiary-butyl pyrazolyl substituent in combination with the carbene methyl substituent of ligand **15a** leads to a different coordination, with a bis-monodentate arrangement of the ligand in complex **18a**. The crystal structure of **18a** shows the two NHC rings oriented perpendicular to the plane of the complex (Fig. 3). The Rh1–C1 and Rh1–C2 bond distances are 2.047(2) and 2.045(2) Å, respectively, and the C1–Rh1–C2 bite angle of 89.51(9)° approaches the ideal angle of 90° for a square planar geometry about the metal centre.

The preference of **18a** to coordinate two NHC ligands instead of coordinating a single chelating ligand can be attributed to two factors. Firstly, by adopting an orthogonal orientation of the NHC ring relative to the square plane of the metal complex, any steric

Table 1 Relevant bond lengths (Å) and angles (°) for Rh NHC complexes

Complex	Rh1–C1	Rh1–N1	C1–Rh1–N1
16a[23]	2.053(2)	2.0962(19)	85.14(7)
16b	2.0363(14)	2.1152(12)	85.02(5)
16b*	2.0224(13)	2.1243(13)	84.25(5)
16c	2.0829(13)	2.1075(11)	84.03(5)
16c*	2.0746(13)	2.1132(11)	84.30(5)
17a	2.0196(11)	2.1209(9)	82.09(4)
17b	2.0487(16)	2.1433(14)	85.43(6)
18a	2.047(2)	2.045(2) (Rh1–C2)	89.51(9) (C1–Rh1–C2)
18b	2.0351(11)	2.2091(9)	83.88(4)

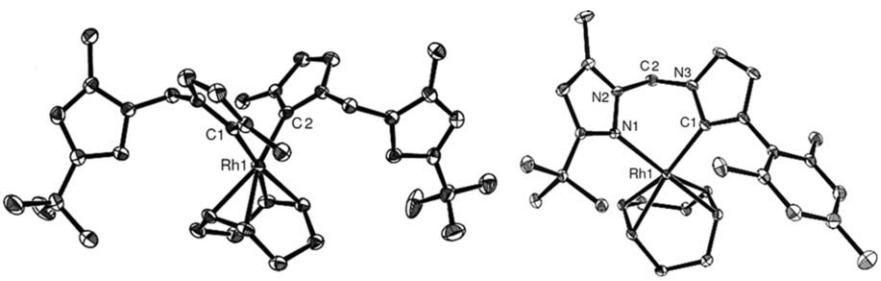


Fig. 3 ORTEP diagrams with 50% ellipsoids and partial crystal structure numbering scheme of the cationic fragments of complexes **18a** and **18b**.

interactions within the complex are minimized. It is interesting to note that the analogous mesityl substituted NHC ligand in **18b** forms the desired chelate. This suggests that the methyl substituent on the NHC ring of **18a** has a slightly greater steric interaction with the Rh(COD) fragment than the planar mesityl substituent in **18b**. This is consistent with the observation that the Rh1–C1 bond length increases in the order mesityl < methyl < *tert*-butyl for complexes **16a–c**.

The strength of the N-donor also contributes to the formation or otherwise of the N–C chelate. In the case of complexes **16a** and **17a**, which have a hydrogen and phenyl substitutent adjacent to the pyrazolyl N-donor atom, respectively, the Rh–N bond is strong enough to form the chelate. However, for **18a**, which has a very bulky *tert*-butyl group next to the N-donor atom, the Rh–N bond is much weaker and the preference to form the chelate in **18a** is reduced. This unusual type of bis-NHC bonding was previously reported by this group during the synthesis of the analogous iridium complex of ligand **13a**.[23]

Structural analysis of the Rh complexes using NMR spectroscopy

All complexes were fully characterised by ^{1}H and ^{13}C NMR spectroscopy. In the ^{1}H NMR spectra of complexes **16a**[23] and **16b**, the resonance due to the COD protons and the protons on the methylene bridge of the NHC-pyrazolyl chelate were significantly broadened due to fluxionality of the complex. The remaining complexes, **16c**, **17a–c**, and **18b**, however, which contain ligands of greater steric bulk, did not show an averaging of the diastereotopic proton resonances in their ^{1}H NMR spectra at 298 K. This is most likely because conformational exchange within each of these complexes is inhibited by steric interactions between the bulky NHC-pyrazolyl ligands and the Rh(COD) fragment.

The mesityl rings of complexes **17b** and **18b** undergo restricted rotation about the N–C bond as evidenced by the presence of two distinct resonances in the ^{1}H NMR spectrum for each of the *ortho*-methyl groups and each of the *meta*-protons on the mesityl ring. The observation of exchange peaks between each pair of resonances in the 2D NOESY spectra indicated that slow rotation of the mesityl ring about the N–C bond was occurring on the NMR time scale.

In solution, the *bis*-NHC complex **18a** exists in two isomeric forms in a ratio of *ca.* 1:0.9, as was determined by the ^{1}H NMR spectrum of the complex at 298 K. In the solid state structure of **18a**, described above, the two NHC ligands bind with the plane of the NHC ring oriented perpendicular to the square plane of the metal complex. The two isomers observed in solution most probably arise from a *syn* or *anti* orientation of these two NHC ligands, with a *syn* orientation indicating the methyl NHC substituents are on the same face of the metal complex and an *anti* orientation indicating that they are on opposite faces. In the 2D NOESY spectrum of **18a** (Fig. 4), exchange peaks between resonances of the two isomers indicate that the isomers are exchanging over the time frame of the NMR experiment. NMR spectroscopic investigations of similar Rh complexes showing hindered rotation of the NHC have previously been reported.[24]

A strong coupling was observed between the NHC C2 carbon and the spin half ^{103}Rh nucleus in the ^{13}C NMR spectra of each of the complexes **16a** (50.0 Hz), **16b** (51.5 Hz), **17a** (61.6 Hz), **17b** (52.5 Hz), **17c** (49.3 Hz), and **18a** (58.1 Hz). This coupling was not determined for complexes **16c** and **18b** due to insufficient resolution of the C2 carbon resonance from the baseline of the spectrum. When correlated with the crystal structure of the complexes it is apparent that the size of the coupling constant is inversely proportional to the length of the Rh–C bond.

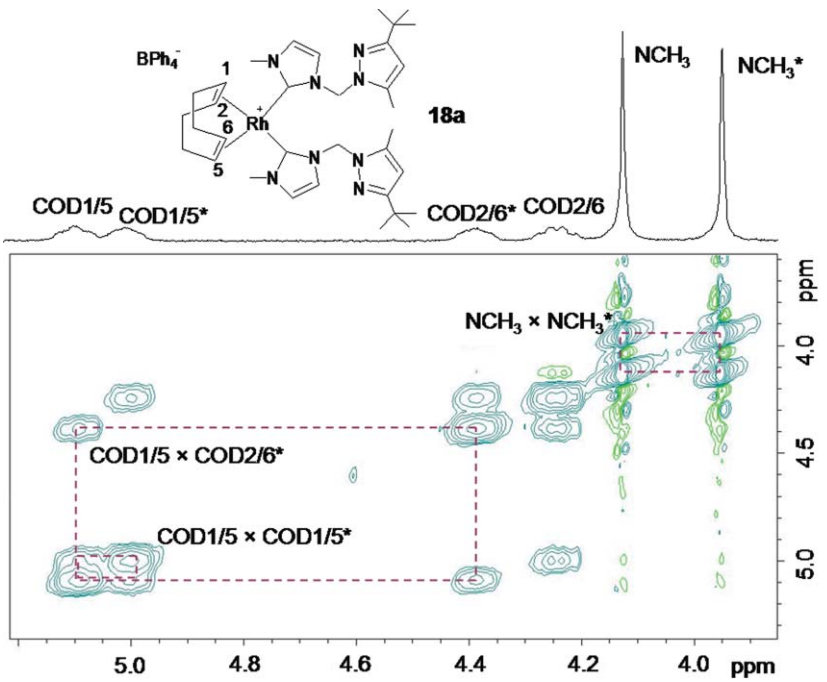


Fig. 4 NOESY spectrum of **18a** showing the COD ethenyl, and *N*-methyl protons of the two isomers, with the resonances due to the minor isomer labelled (*). A selection of the exchange peaks between the resonances of the two isomers is highlighted.

Table 2 TOFs for the Rh NHC catalyzed hydrogenation of styrene at 50 psi H_2 pressure, 300 K, and 0.5 mol% catalyst loading for each of the catalysts **16a–c**, **17a–c** and **18b**[a]

Catalyst	**16a**	**16b**	**16c**	**17a**	**17b**	**17c**	**18b**
TOF/h^{-1}	484	476	161	328	142	243	187

[a] TOF = mol product/mol catalyst/time at 50% conversion

Hydrogenation studies

The efficiency of complexes **16–18** as catalysts for the hydrogenation of styrene to ethylbenzene was investigated. The reactions were performed with a catalyst loading of 0.5 mol% under 50 psi of H_2 gas at 300 K. A plot of the substrate conversion (%) *versus* time (min) is shown in Fig. 5, and the corresponding TOFs are set out in Table 2.

It can be seen from Fig. 5 that the complexes **16a**, **16b**, and **17a**, which contain the smallest degree of steric bulk on the NHC-pyrazolyl ligand, were the fastest catalysts of the series. The complexes **16a**, **16b**, and **17a** all had a very similar catalytic activity, with >98% conversion achieved within approximately 50 min of reaction. However, the initial rate of reaction for complexes **16a** and **16b** was faster than the initial rate of reaction for **17a**. This difference is reflected in the TOFs of 484, 476, and 328 h^{-1} for the catalysts **16a**, **16b**, and **17a**, respectively. It is possible that the slower initial reaction rate of **17a** is due to the large phenyl substituents on the pyrazolyl donor inhibiting the initial hydrogenation of the COD coligand.

In comparison, the complexes **16c** and **17c**, which contain a *tert*-butyl group on the NHC donor, had much slower reaction rates. This was particularly the case for **16c** which required approximately 115 min to achieve complete conversion of the substrate, whereas **17c** achieved complete reduction of styrene within 73 min of reaction. A similar catalytic activity was obtained with complex **18b**, which contains a *tert*-butyl substituent on the pyrazolyl donor. This catalyst required approximately 84 min to achieve complete reduction of styrene. These results indicate that the bulky *tert*-butyl substituents in the complexes **16c**, **17c**, and **18b** severely limit the activity of the catalysts. This effect is most probably due to the inhibition of substrate coordination due to steric interaction with the bulky *tert*-butyl substituent. Interestingly, an unusually low catalytic activity was also observed for complex **17b**. In the solid state structure of **17b** (Fig. 2), the two planar phenyl and mesityl substituents can be seen to shield one face of the complex. While these substituents may not be bulky enough to inhibit coordination of the styrene substrate to the metal centre, they may obstruct the initial approach of the substrate to the complex and thereby inhibit the reaction rate of the catalyst.

The bis-NHC complex **18a** was shown to be entirely inactive under the chosen reaction conditions and no conversion of the substrate was observed even after several hours of reaction. This observation is consistent with studies on analogous bis-NHC systems reported in the literature.[21,23]

Conclusions

A series of new NHC-pyrazolyl ligands of varying steric bulk and their RhCOD complexes were synthesized. The structure of the complexes was investigated in solution using NMR spectroscopy, and in the solid state using X-ray crystallography, with the solid state structures of **16b–c**, **17a–b**, and **18a–b** obtained. It was observed that the steric bulk of the ligands had a pronounced effect on the structure of the complexes. The size of the ligand substituents was observed to strongly influence the length of the

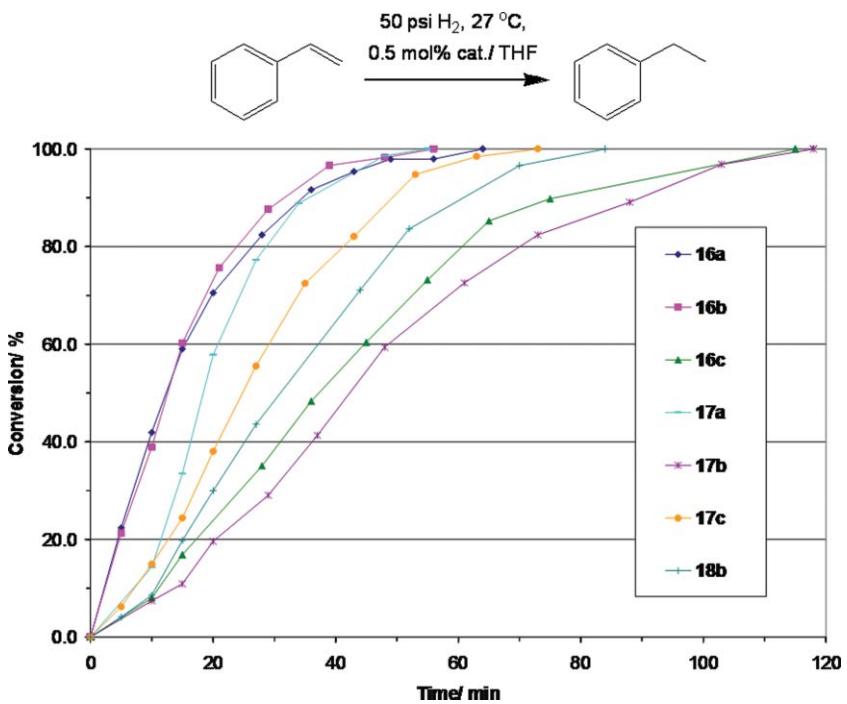


Fig. 5 Time courses for the catalysed hydrogenation of styrene to ethylbenzene at 50 psi H_2 pressure, 300 K, and 0.5 mol% catalyst loading for each of the catalysts **16a–c**, **17a–c** and **18b**.

Rh–C(NHC) and Rh–N bonds. Surprisingly, for complexes **16a–c** the rhodium–carbene bond lengths increased according to the nature of the NHC donor substituent in the order mesityl < methyl < *tert*-butyl, which suggested a lesser steric interaction between the planar mesityl ring and the Rh(COD) fragment compared to the smaller methyl substituent. Evidence for a positive interaction between the COD olefinic hydrogen atoms and the aromatic π-system of the mesityl ring was observed in the crystal structures of **16b**, **17b** and **18b**. The small difference in steric impact of the two substituents (methyl and mesityl) was observed to have a pronounced effect on the complex structure for ligands **15a** and **15b**. Where coordination of the methyl substituted NHC ligand **15a** to rhodium gave the unusual bis-NHC complex **18a**, the mesityl substituted NHC ligand **15b** preferred to form the more sterically demanding chelate complex **18b**. The size of the ligand substituents also had a pronounced affect on the solution behaviour of the complexes, with the complexes of lesser steric bulk (**16a**, **b**) displaying fluxionality on the NMR time scale.

The steric bulk of the ligands had a significant effect on the hydrogenation activity of the complexes. It was observed that an increased steric shielding of the metal centre resulted in a greatly reduced activity of the catalyst. The highest reaction rates were obtained with complexes **16a**, **b** and **17a**, which contain a very small degree of steric shielding about the metal centre. However, for complexes **16c**, **17c** and **18b**, which contain a bulky *tert*-butyl substituent on one of the donor groups, a much slower reaction rate was observed. This effect was most probably due to the increased bulk of the ligand inhibiting the coordination of the alkene substrate.

Experimental

All manipulations or metal complexes and air sensitive reagents were carried out using standard Schlenk techniques[25] or in a nitrogen filled glove box. For the purpose of air sensitive manipulations and in the preparation of metal complexes, solvents were dried and distilled under an atmosphere of argon using standard procedures.[26] The ligand **13a**,[23] the rhodium complex **16a**,[23] and all pyrazole,[27] hydroxymethylpyrazole,[28,29] and imidazole[30–32] compounds were synthesized according to published procedures.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 spectrometer. The spectra were recorded at 298 K unless otherwise specified. Chemical shifts (δ) are quoted in ppm. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts were referenced internally to residual solvent resonances. Coupling constants (J) are given in Hz. In assigning the NMR spectra the superscripts *im* and *pz* are used to denote resonances from imidazolyl and pyrazolyl rings, respectively with positions on the ring are denoted in the standard way (1-5). The superscripts *o* (ortho), *m* (meta), and *p* (para) are used to denote positions on phenyl moieties and the superscrits *a* and *b* used to distinguish between diastereotopic proton environments. Elemental analyses were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. X-ray diffraction data were collected in phi and omega scans on a Nonius KappaCCD diffractometer using Mo-K_α radiation. The structures were solved with direct methods (SHELXS97) and refined by full-matrix least-squares refinement of F^2 using SHELXL97.[33–35] (For details see Table 3.) Crystals of **13c**, **16b**, (**16c**)$_2$·CH_2Cl_2, **17a**, **17b**, **18a** and **18b**·CH_2Cl_2 suitable for X-ray crystallography were grown from layering hexane over a

Table 3 Summary of crystallographic data for **13c**, **16b**, (**16c**)$_2$·CH_2Cl_2, **17a**, **17b**, **18a** and **18b**·CH_2Cl_2

	13c	**16b**	(**16c**)$_2$·CH_2Cl_2	**17a**	**17b**	**18a**	**18b**·CH_2Cl_2
Empirical formula	$C_{35}H_{37}BN_4$	$C_{48}H_{50}BN_4Rh$	$C_{87}H_{98}B_2Cl_2N_8Rh_2$	$C_{52}H_{50}BN_4Rh$	$C_{60}H_{58}BN_4Rh$	$C_{58}H_{72}BN_8Rh$	$C_{54}H_{62}BCl_2N_4Rh$
M (g mol^{-1})	524.50	796.64	1554.07	844.68	948.82	994.96	951.70
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Triclinic
Space group	*P*-1	$P2_1$	*P*-1	*P*-1	$P2_1/n$	*Pbca*	*P*-1
a (Å)	9.6457(3)	16.1877(2)	12.3719(2)	10.4027(2)	12.9939(3)	25.2736(4)	13.4959(2)
b (Å)	11.0776(6)	9.2908(1)	14.3921(2)	12.9461(2)	18.8994(3)	12.7805(2)	13.5060(2)
c (Å)	14.2768(8)	26.4808(3)	21.9391(3)	16.4453(2)	20.5054(4)	31.9609(6)	14.0357(2)
α (°)	75.011(2)	90	97.527(1)	70.599(1)	90	90	82.846(1)
β (°)	84.346(3)	93.842(1)	98.504(1)	80.016(1)	108.262(1)	90	70.731(1)
γ (°)	80.266(3)	90	96.085(1)	84.831(1)	90	90	86.942(1)
V (Å^3)	1449.97(12)	3973.67(8)	3798.74(10)	2056.11(6)	4782.02(16)	10323.7(3)	2396.04(6)
D_c (g cm^{-3})	1.201	1.332	1.359	1.364	1.318	1.280	1.319
Z	2	4	2	2	4	8	2
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal size (mm)	0.21 × 0.16 × 0.15	0.55 × 0.33 × 0.20	0.53 × 0.21 × 0.19	0.54 × 0.18 × 0.12	0.57 × 0.28 × 0.07	0.23 × 0.19 × 0.07	0.56 × 0.54 × 0.22
θ range (°)	2.66–25.00	2.59–35.00	2.55–33.00	2.55–35.00	2.71–29.00	2.60–26.00	2.56–35.00
Completeness (%)	99.8	99.2	99.8	98.9	99.9	99.9	99.8
Index ranges	$-11 \geq h \geq 11$	$-25 \geq h \geq 26$	$-18 \geq h \geq 18$	$-16 \geq h \geq 16$	$-17 \geq h \geq 17$	$-31 \geq h \geq 29$	$-21 \geq h \geq 21$
	$-13 \geq k \geq 13$	$-14 \geq k \geq 14$	$-22 \geq k \geq 21$	$-20 \geq k \geq 20$	$-25 \geq k \geq 25$	$-15 \geq k \geq 14$	$-21 \geq k \geq 21$
	$-16 \geq l \geq 16$	$-42 \geq l \geq 40$	$-33 \geq l \geq 33$	$-26 \geq l \geq 26$	$-27 \geq l \geq 27$	$-39 \geq l \geq 39$	$-22 \geq l \geq 22$
Reflns measured	18020	98011	106162	64528	65743	74638	79673
Unique reflns	5095	34298	28579	17905	12682	10136	21076
R_{int}	0.0653	0.0437	0.0442	0.0581	0.0634	0.0696	0.0637
GoF (all)	1.008	1.020	1.056	1.055	1.057	1.034	1.041
Flack parameter	—	–0.017(7)	—	—	—	—	—
R_1 ($I > 2\sigma(I)$)	0.0463	0.0301	0.0312	0.0333	0.0340	0.0388	0.0354
wR_2 ($I > 2\sigma(I)$)	0.1025	0.0665	0.0698	0.0810	0.0819	0.0807	0.0760
R_1 (all data)	0.0807	0.0360	0.0480	0.0413	0.0494	0.0700	0.0490
wR_2 (all data)	0.1135	0.0685	0.0740	0.0838	0.0868	0.0892	0.0799

concentrated CH_2Cl_2 solution of the respective compound. Mass spectra were acquired at the Bioanalytical Mass Spectroscopy Facility (BMSF), University of New South Wales, on a Finnigan Micromass QToF spectrometer.

Synthesis of pyrazolyl-imidazolium ligand precursors

General procedure. To a solution of the desired 1-hydroxymethylpyrazole (3.0 mmol) in chloroform (20 mL) was added thionyl chloride (1 mL, *ca.* 14 mmol) and the solution was stirred at room temperature for several hours. A small amount of white solid precipitated from solution which was reduced to dryness under vacuum without filtering to give a beige residue of the corresponding 1-chloromethylpyrazole hydrochloride salt. The product was suspended in toluene (40 mL), the desired imidazole (6.0 mmol) was added, and the mixture was refluxed for 2 h to form a brown to yellow oily suspension of the pyrazolyl-imidazolium chloride salt and the imidazolium hydrochloride side product. $NaBPh_4$ (6.0 mmol) was added to the suspension and the reaction mixture was refluxed for 5 min, and then stirred at room temperature for 1 h resulting in the formation of a beige residue. The residue was filtered and recrystallized from either acetone, or ethyl acetate, and diethyl ether to yield the pyrazolyl-imidazolium salt.

13b (65%): Anal. found: C, 81.72; H, 6.76; N, 9.70. $C_{40}H_{39}BN_4$ requires: C, 81.90; H, 6.70; N, 9.55. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.17 (t, 1H, ^4J(H2^{im}–H4/5^{im}) = 1.5 Hz, *H*2^{im}), 8.01 (d, 1H, ^3J(H5^{pz}–H4^{pz}) = 2.3 Hz, *H*5^{pz}), 7.94 (apparent t, 1H, $^{3/4}$J(H5^{im}–H4/2^{im}) = 1.6 Hz, *H*5^{im}), 7.67 (d, 1H, ^3J(H3^{pz}–H4^{pz}) = 1.8 Hz, *H*3^{pz}), 7.65 (apparent t, 1H, $^{3/4}J$(H4^{im}–H5/2^{im}) = 1.6 Hz, *H*4^{im}), 7.35 (m, 8H, o-BPh$_4$), 7.13 (2, 2H, *H*^{m}), 6.92 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.77 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.63 (s, 2H, C*H*$_2$), 6.41 (t, 1H, ^3J(H4^{pz}–H3/5^{pz}) = 1.8 Hz, *H*4^{pz}), 2.36 (s, 3H, p-C*H*$_3$), 2.00 (s, 6H, o-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 165.2 (q, ^1J(C–B) = 49.4 Hz, B–*C*), 143.1 (*C*3^{pz}), 142.1 (*C*^{p}), 138.3 (*C*2^{im}), 137.0 (q, ^2J(C–B) = 1.4 Hz, o-BPh$_4$), 135.4 (N–*C*), 132.1 (*C*5^{pz}), 131.9 (*C*^{o}), 130.4 (*C*^{m}), 126.1 (q, ^3J(C–B) = 2.8 Hz, m-BPh$_4$), 125.6 (*C*4^{im}), 123.6 (*C*5^{im}), 122.3 (p-BPh$_4$), 108.3 (*C*4^{pz}), 63.4 (*C*H$_2$), 21.0 (p-*C*H$_3$), 17.3 (o-*C*H$_3$) ppm. MS (ESI+) *m*/*z* (%): 267.1 [M]$^+$ (100).

13c (62%): Anal. found: C, 80.08; H, 7.14; N, 10.73. $C_{35}H_{37}BN_4$ requires: C, 80.15; H, 7.11; N, 10.68. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.52 (t, 1H ^4J(H2^{im}–H4/5^{im}) = 1.6 Hz, *H*2^{im}), 8.02 (d, 1H, ^3J(H5^{pz}–H4^{pz}) = 2.3 Hz, *H*5^{pz}), 7.92 (apparent t, 1H $^{3/4}J$(H4^{im}–H2/5^{im}) = 1.9 Hz, *H*4^{im}), 7.81 (apparent t, 1H $^{3/4}$J(H5^{im}–H2/4^{im}) = 1.9 Hz, *H*5^{im}), 7.62 (d, 1H, ^3J(H3^{pz}–H4^{pz}) = 1.6 Hz, *H*3^{pz}), 7.35 (m, 8H, o-BPh$_4$), 6.92 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.78 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.59 (s, 2H, C*H*$_2$), 6.37 (t, 1H, ^3J(H4^{pz}–H3/5^{pz}) = 2.1 Hz, *H*4^{pz}), 1.73 (s, 9H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 165.0 (q, ^1J(C–B) = 49.4 Hz, B-*C*), 142.8 (*C*3^{pz}), 137.1 (q, ^2J(C–B) = 1.4 Hz, o-BPh$_4$), 132.0 (*C*5^{pz}), 126.0 (q, ^3J(C–B) = 2.8 Hz, m-BPh$_4$), 123.4 (*C*5^{im}), 122.3 (p-BPh$_4$), 121.8 (*C*4^{im}), 108.2 (*C*4^{pz}), 63.1 (*C*H$_2$), 61.7 (*C*(CH$_3$)$_3$), 29.5 (C(*C*H$_3$)$_3$) ppm. MS (ESI+) *m*/*z* (%): 205.1 [M]$^+$ (100).

14a (69%): Anal. found: C, 79.92; H, 6.54; N, 7.99. $C_{44}H_{39}BN_4$·EtOAc requires: C, 79.88; H, 6.70; N, 7.60. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.75 (brs, 1H, *H*2^{im}), 7.93 (m, 2H, Ph*H*), 7.66–7.29 (m, 10H, Ph*H*, *H*4^{im} and *H*5^{im}), 7.35 (m, 8H, o-BPh$_4$), 6.96 (s, 1H, *H*4^{pz}), 6.92 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.77 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.56 (s, 2H, C*H*$_2$), 3.87 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 165.0 (q, ^1J(C–B) = 49.4 Hz, B-*C*), 154.0 (*C*3^{pz}), 147.5 (*C*5^{pz}), 137.4 (*C*2^{im}), 137.0 (brq, ^2J(C–B) = 1.5 Hz, o-BPh$_4$), 133.4 (Ph*C*), 130.6 (Ph*C*), 130.3 (Ph*C*), 129.9 (Ph*C*), 129.8 (Ph*C*), 129.6 (Ph*C*), 129.4 (Ph*C*), 126.6 (Ph*C*), 126.1 (q, ^3J(C–B) = 2.7 Hz, m-BPh$_4$), 125.2 (*C*4^{im}), 122.8 (*C*5^{im}), 122.3 (p-BPh$_4$), 106.2 (*C*4^{pz}), 61.6 (*C*H$_2$), 36.9 (*C*H$_3$) ppm. MS (ESI+) *m*/*z* (%): 315.2 [M]$^+$ (100).

14b (66%): ^{1}H NMR (300 MHz, acetone-d_6): δ 9.30 (t, 1H, ^4J(H2^{im}–H4/5^{im}) = 1.6 Hz, *H*2^{im}), 7.97 (m, 2H, Ph*H*), 7.91 (brd, ^3J(H5^{im}–H4^{im}) = 1.9 Hz, *H*5^{im}), 7.78 (brd, ^3J(H4^{im}-H5^{im}) = 1.9 Hz, *H*4^{im}), 7.60 (m, 5H, Ph*H*), 7.40 (m, 3H, Ph*H*), 7.34 (m, 8H, o-BPh$_4$), 7.12 (s, 2H, *H*^{m}), 7.02 (s, 1H, *H*4^{pz}), 6.91 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.83 (s, 2H, C*H*$_2$), 6.76 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 2.34 (s, 3H, p-C*H*$_3$), 1.99 (s, 6H, o-C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 165.0 (q, ^1J(C–B) = 49.4 Hz, B-*C*), 154.2 (*C*3^{pz}), 147.6 (*C*5^{pz}), 142.1 (*C*^{p}), 138.3 (*C*2^{im}), 137.0 (brq, ^2J(C–B) = 1.4 Hz, o-BPh$_4$), 135.4 (*C*^{o}), 133.4 (Ph*C*), 131.9 (N-*C*), 130.6 (Ph*C*), 130.4 (*C*^{m}), 130.3 (Ph*C*), 129.8 (Ph*C*), 129.7 (Ph*C*), 129.6 (Ph*C*), 129.5 (Ph*C*), 126.6 (Ph*C*), 126.0 (q, ^3J(C–B) = 2.7 Hz, m-BPh$_4$), 125.7 (*C*4^{im}), 123.6 (*C*5^{im}), 122.3 (p-BPh$_4$), 106.4 (*C*4^{pz}), 62.4 (*C*H$_2$), 21.0 (p-*C*H$_3$), 17.3 (o-*C*H$_3$) ppm. MS (ESI+) *m*/*z* (%): 419.2 [M]$^+$ (100).

14c (61%): Anal. found: C, 83.38; H, 6.78; N, 8.42. $C_{47}H_{45}BN_4$ requires: C, 83.42; H, 6.70; N, 8.28. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.00 (t, 1H, ^4J(H2^{im}–H4/5^{im}) = 1.6 Hz, *H*2^{im}), 7.93 (m, 2H, Ph*H*), 7.76 (brd, ^3J(H4^{im}–H5^{im}) = 1.9 Hz, *H*4^{im}), 7.63–7.31 (m, 9H, Ph*H* and *H*5^{im}), 7.36 (m, 8H, o-BPh$_4$), 6.94 (s, 1H, *H*4^{pz}), 6.93 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.78 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.51 (s, 2H, C*H*$_2$), 1.63 (s, 9H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 164.9 (q, ^1J(C–B) = 49.6 Hz, B-*C*), 153.7 (*C*3^{pz}), 147.3 (*C*5^{pz}), 137.0 (brq, ^2J(C–B) = 1.4 Hz, o-BPh$_4$), 135.0 (*C*2^{im}), 133.4 (Ph*C*), 130.6 (Ph*C*), 130.2 (Ph*C*), 129.9 (Ph*C*), 129.8 (Ph*C*), 129.6 (Ph*C*), 129.4 (Ph*C*), 126.6 (Ph*C*), 126.0 (q, ^3J(C–B) = 2.8 Hz, m-BPh$_4$), 123.0 (*C*5^{im}), 122.3 (p-BPh$_4$), 121.7 (*C*4^{im}), 106.3 (*C*4^{pz}), 61.8 (*C*H$_2$), 61.6 (*C*(CH$_3$)$_3$), 29.5 (C(*C*H$_3$)$_3$) ppm. MS (ESI+) *m*/*z* (%): 357.2 [M]$^+$ (100).

15a (61%): Anal. found: C, 80.38; H, 7.73; N, 10.26. $C_{37}H_{41}BN_4$ requires: C, 80.43; H, 7.48; N, 10.14. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.02 (brs, 1H, *H*2^{im}), 7.69 (apparent t, 1H $^{3/4}J$(H5^{im}–H2/4^{im}) = 1.7 Hz, *H*5^{im}), 7.58 (apparent t, 1H $^{3/4}J$(H4^{im}–H2/5^{im}) = 1.7 Hz, *H*4^{im}), 7.35 (m, 8H, o-BPh$_4$), 6.92 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.77 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.45 (s, 2H, C*H*$_2$), 6.06 (s, 1H, *H*4^{pz}), 3.93 (s, 3H, NC*H*$_3$), 2.38 (s, 3H, CC*H*$_3$), 1.24 (s, 9H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, acetone-d_6): δ 165.1 (q, ^1J(C–B) = 49.3 Hz, B–*C*), 164.2 (*C*3^{pz}), 141.4 (*C*5^{pz}), 137.3 (*Cy*]2^{im}), 137.1 (brs, o-BPh$_4$), 126.1 (q, ^3J(C–B) = 2.9 Hz, m-BPh$_4$), 125.3 (*C*4^{im}), 122.7 (*C*5^{im}), 122.4 (p-BPh$_4$), 104.9 (*C*4^{pz}), 60.8 (*C*H$_2$), 37.0 (N*C*H$_3$), 32.8 (*C*(CH$_3$)$_3$), 30.6 (C(*C*H$_3$)$_3$), 10.9 (C*C*H$_3$) ppm. MS (ESI+) *m*/*z* (%): 233.2 [M]$^+$ (100).

15b (69%): Anal. found: C, 82.29; H, 7.73; N, 8.62. $C_{45}H_{49}BN_4$ requires: C, 82.30; H, 7.52; N, 8.53. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.41 (t, 1H ^4J(H2^{im}–H4/5^{im}) = 1.6 Hz, *H*2^{im}), 8.05 (apparent t, 1H $^{3/4}J$(H5^{im}–H2/4^{im}) = 1.8 Hz, *H*5^{im}), 7.83 (apparent t, 1H $^{3/4}J$(H4^{im}–H2/5^{im}) = 1.9 Hz, *H*4^{im}), 7.34 (m, 8H, o-BPh$_4$), 7.14 (s, 2H, *H*^{m}), 6.92 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.77 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.65 (s, 2H, C*H*$_2$), 6.11

(s, 1H, $H4^{pz}$), 2.47 (s, 3H, CCH_3), 2.36 (s, 3H, p-CH_3), 2.04 (s, 6H, o-CH_3), 1.24 (s, 9H, C(CH_3)$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 165.0 (q, ^1J(C–B) = 49.3 Hz, B-*C*), 164.5 (*C*3^{pz}), 142.1 (*C*^{p}), 141.4 (*C*5^{pz}), 138.2 (*C*2^{im}), 137.0 (q, ^2J(C–B) = 1.4 Hz, o-BPh$_4$), 135.4 (*C*^{o}), 132.0 (N–*C*), 130.4 (*C*^{m}), 126.0 (q, ^3J(C–B) = 2.9 Hz, m-BPh$_4$), 125.6 (*C*4^{im}), 123.5 (*C*5^{im}), 122.3 (p-BPh$_4$), 104.8 (*C*4^{pz}), 61.3 (*C*H$_2$), 32.8 (*C*(CH$_3$)$_3$), 30.6 (C(*C*H$_3$)$_3$), 21.0 (p-*C*H$_3$), 17.3 (o-*C*H$_3$), 10.8 (C*C*H$_3$) ppm. MS (ESI+) *m*/*z* (%): 337.2 [M]$^+$ (100).

15c (66%): Anal. found: C, 80.71; H, 8.14; N, 9.51. $C_{40}H_{47}BN_4$ requires: C, 80.79; H, 7.97; N, 9.42. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.36 (t, 1H ^4J(H2^{im}–H4/5^{im}) = 1.6 Hz, *H*2^{im}), 7.90 (apparent t, 1H $^{3/4}J$(H4^{im}–H2/5^{im}) = 1.8 Hz, *H*4^{im}), 7.72 (apparent t, 1H $^{3/4}J$(H5^{im}–H2/4^{im}) = 1.8 Hz, *H*5^{im}), 7.34 (m, 8H, o-BPh$_4$), 6.92 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.77 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.41 (s, 2H, CH_2), 6.06 (s, 1H, *H*4^{pz}), 2.37 (s, 3H, CCH_3), 1.72 (s, 9H, NC(CH_3)$_3$), 1.25 (s, 9H, CC(CH_3)$_3$) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, acetone-d_6): δ 165.5 (q, ^1J(C–B) = 49.3 Hz, B–*C*), 164.7 (*C*3^{pz}), 141.9 (*C*5^{pz}), 137.6 (brs, o-BPh$_4$), 135.5 (*C*2^{im}), 126.6 (q, ^3J(C–B) = 2.9 Hz, m-BPh$_4$), 123.6 (*C*5^{im}), 122.8 (p-BPh$_4$), 122.3 (*C*4^{im}), 105.2 (*C*4^{pz}), 62.1 (N*C*(CH$_3$)$_3$), 61.3 (*C*H$_2$), 33.3 (C*C*(CH$_3$)$_3$), 31.1 (CC(*C*H$_3$)$_3$), 30.1 (NC(*C*H$_3$)$_3$), 11.4 (C*C*H$_3$) ppm. MS (ESI+) *m*/*z* (%): 275.2 [M]$^+$ (100).

Synthesis of rhodium complexes

General procedure. A freshly prepared solution of NaOMe (35 mg, 1.5 mmol, of Na in 20 mL of methanol) was filtered into a methanol (10 mL) solution of the metal precursor [Rh(COD)(μ-OMe)]$_2$ (73 mg, 0.15 mmol) and the desired pyrazolyl-imidazolium ligand precursor (0.30 mmol). The solution was refluxed for several hours to form a yellow solution that was cooled to room temperature and the volume reduced under vacuum until a bright yellow precipitate formed. The precipitate was filtered, washed with diethyl ether, and dried *in vacuo* to yield the rhodium NHC complex which was further purified *via* recrystallization from DCM and hexane. The products were observed to decompose in solutions of chloroform upon prolonged standing, therefore all spectra were acquired in DCM-d_2.

16b (89%): Anal. found: C, 68.56; H, 6.17; N, 6.70. $C_{48}H_{50}BN_4Rh{\cdot}0.66CH_2Cl_2$ requires: C, 68.54; H, 6.07; N, 6.57. ^{1}H NMR (300 MHz, DCM-d_2): δ 7.44 (m, 8H, o-BPh$_4$), 7.35 (d, 1H, ^3J(H3^{pz}–H4^{pz}) = 2.3 Hz, *H*3^{pz}), 7.27 (d, 1H, ^3J(H5^{pz}–H4^{pz}) = 2.3 Hz, *H*5^{pz}), 7.06 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.2 Hz, m-BPh$_4$), 7.03 (s, 2H, *H*^{m}), 6.92 (t, 4H, ^3J(p-m-BPh$_4$) = 7.2 Hz, p-BPh$_4$), 6.71 (d, 1H, ^3J(H5^{im}-H4^{im}) = 1.8 Hz, *H*5^{im}), 6.64 (d, 1H, ^3J(H4^{im}–H5^{im}) = 1.8 Hz, *H*4^{im}), 6.28 (t, 1H, ^3J(H4^{pz}–H3/5^{pz}) = 2.4 Hz, *H*4^{pz}), 5.28 (brs, 2H, CH_2), 4.65 (brs, 2H, COD1/2), 3.68 (brs, 2H, COD5/6), 2.50–1.70 (brm, 8H, COD3/4/7/8), 2.37 (s, 3H, p-CH_3), 1.99 (s, 6H, o-CH_3) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DCM-d_2): δ 177.0 (d, ^1J(C–Rh) = 51.5 Hz, *C*2^{im}), 164.6 (q, ^1J(C–B) = 49.0 Hz, B-*C*), 142.4 (*C*3^{pz}), 140.6 (*C*^{p}), 136.6 (brs, o-BPh$_4$), 135.5 (*C*^{o}), 133.6 (*C*5^{pz}), 129.8 (*C*m), 126.5 (q, ^3J(C–B) = 2.8 Hz, m-BPh$_4$), 123.7 (*C*4^{im}), 122.6 (p-BPh$_4$), 121.9 (*C*5^{im}), 108.2 (*C*4^{pz}), 97.4 (brs, COD1/2), 63.6 (*C*H$_2$), 32.7 (brs, COD4/7), 29.4 (brs, COD3/8), 21.4 (p-*C*H$_3$), 18.5 (o-*C*H$_3$) ppm (COD5/6 and N-C undefined). MS (ESI+) *m*/*z* (%): 477.6 [M]$^+$ (100), 1273.4 [2M + BPh$_4$]$^+$ (26).

16c (71%): Anal. found: C, 67.59; H, 6.56; N, 7.19. $C_{43}H_{48}BN_4Rh{\cdot}0.5CH_2Cl_2$ requires: C, 67.24; H, 6.36; N, 7.21. ^{1}H NMR (300 MHz, DCM-d_2): δ 7.40 (m, 8H, o-BPh$_4$), 7.29 (d, 1H, ^3J(H3^{pz}–H4^{pz}) = 1.9 Hz, *H*3^{pz}), 7.22 (d, 1H, ^3J(H5^{pz}–H4^{pz}) = 2.4 Hz, *H*5^{pz}), 7.05 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.4 Hz, m-BPh$_4$), 6.91 (t, 4H, ^3J(p-m-BPh$_4$) = 7.4 Hz, p-BPh$_4$), 6.90 (d, 1H, ^3J(H5^{im}–H4^{im}) = 1.9 Hz, *H*5^{im}), 6.66 (d, 1H, ^3J(H4^{im}-H5^{im}) = 1.9 Hz, *H*4^{im}), 6.48 (d, 1H, ^2J(H^a-H^b) = 13.8 Hz, NC*H*^{a}H^b), 6.24 (t, 1H, ^3J(H4^{pz}-H3/5^{pz}) = 2.4 Hz, *H*4^{pz}), 5.11 (d, 1H, ^2J(H^b-H^a) = 13.8 Hz, NCH^a*H*^{b}), 4.88 (t, 1H, *J* = 7.3 Hz, COD1), 4.64 (t, 1H, *J* = 6.4 Hz, COD5), 4.20 (q, 1H, *J* = 7.6 Hz, COD2), 4.10 (q, 1H, *J* = 7.6 Hz, COD6), 2.92–1.62 (m, 8H, COD3/4/7/8), 1.74 (s, 9H, C(CH_3)$_3$) ppm (C2^{im} undefined). $^{13}C\{^1H\}$ NMR (75 MHz, DCM-d_2): δ 165.5 (q, ^1J(C–B) = 49.5 Hz, B-*C*), 142.2 (*C*3^{pz}), 136.6 (brs, o-BPh$_4$), 133.2 (*C*5^{pz}), 126.4 (q, ^3J(C–B) = 2.9 Hz, m-BPh$_4$), 122.6 (p-BPh$_4$), 121.5 (*C*4^{im}), 120.2 (*C*5^{im}), 108.3 (*C*4^{pz}), 97.2 (d, ^1J(C–Rh) = 8.8 Hz, COD2), 94.7 (d, ^1J(C–Rh) = 7.6 Hz, COD1), 81.9 (d, ^1J(C–Rh) = 13.9 Hz, COD5), 73.0 (d, ^1J(C–Rh) = 12.7 Hz, COD6), 64.9 (*C*H$_2$), 59.1 (*C*(CH$_3$)$_3$), 36.1 (COD), 32.6 (C(*C*H$_3$)$_3$), 32.5 (COD), 29.1 (COD), 27.1 (COD) ppm (C2^{im} undefined). MS (ESI+) *m*/*z* (%): 415.9 [M]$^+$ (100), 1149.3 [2M + BPh$_4$]$^+$ (48).

17a (74%): Anal. found: C, 73.50; H, 5.98; N, 7.26. $C_{52}H_{50}BN_4Rh$ requires: C, 73.94; H, 5.97; N, 6.63. ^{1}H NMR (300 MHz, DCM-d_2): δ 7.96 (m, 2H, Ph*H*), 7.63 (m, 6H, Ph*H*), 7.38 (m, 2H, Ph*H*), 7.31 (m, 8H, o-BPh$_4$), 6.99 (t, 8H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$), 6.90 (d, 1H, ^2J(H^a–H^b) = 13.4 Hz, NC*H*^{a}H^b), 6.86 (t, 4H, ^3J(p-m-BPh$_4$) = 7.3 Hz, p-BPh$_4$), 6.60 (s, 1H, *H*4^{pz}), 6.58 (d, 1H, ^3J(H4^{im}–H5^{im}) = 1.9 Hz, *H*4^{im}), 6.52 (d, 1H, ^3J(H5^{im}–H4^{im}) = 1.9 Hz, *H*5^{im}), 5.93 (d, 1H, ^2J(H^b-H^a) = 13.4 Hz, NCH^a*H*^{b}), 4.73 (brq, 1H, J= 6.3 Hz, COD1), 4.60 (brt, 1H, J= 6.3 Hz, COD5), 4.30 (brt, 1H, J= 6.3 Hz, COD6), 3.72 (brq, 1H, J= 6.3 Hz, COD2), 3.70 (s, 3H, CH_3), 2.62–1.78 (m, 8H, COD3/4/7/8) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DCM-d_2): δ 177.4 (d, ^1J(C-Rh) = 61.5 Hz, *C*2^{im}), 164.6 (q, ^1J(C–B) = 49.5 Hz, B–*C*), 156.1 (*C*3^{pz}), 148.6 (*C*5^{pz}), 136.5 (brs, o-BPh$_4$), 131.3 (Ph*C*), 131.2 (Ph*C*), 131.0 (Ph*C*), 130.3 (Ph*C*), 129.5 (Ph*C*), 129.4 (Ph*C*), 129.3 (Ph*C*), 127.9 (Ph*C*), 126.2 (q, ^3J(C–B) = 2.9 Hz, m-BPh$_4$), 123.9 (*C*4^{im}), 122.3 (p-BPh$_4$), 121.2 (*C*5^{im}), 108.0 (*C*4^{pz}), 101.7 (d, ^1J(C–Rh) = 8.6 Hz, COD1), 95.8 (d, ^1J(C–Rh) = 6.7 Hz, COD2), 78.9 (d, ^1J(C–Rh) = 11.9 Hz, COD6), 74.8 (d, ^1J(C–Rh) = 12.6 Hz, COD5), 62.4 (*C*H$_2$), 38.2 (*C*H$_3$), 33.2 (COD), 32.3 (COD), 29.2 (COD), 28.8 (COD) ppm. MS (ESI+) *m*/*z* (%): 526.0 [M]$^+$ (100).

17b (71%): Anal. found: C, 76.08; H, 6.21; N, 6.07. $C_{60}H_{58}BN_4Rh$ requires: C, 75.95; H, 6.16; N, 5.90. ^{1}H NMR (300 MHz, DCM-d_2): δ 8.02 (m, 2H, Ph*H*), 7.62 (m, 6H, Ph*H*), 7.42 (m, 2H, Ph*H*), 7.30 (m, 8H, o-BPh$_4$), 7.16 (s, 1H, *H*^{m}), 6.98 (t, 9H, ^3J(m-o/p-BPh$_4$) = 7.3 Hz, m-BPh$_4$ and *H*$^{m\prime}$), 6.85 (m, 5H, p-BPh$_4$ and NC*H*^{a}H^b), 6.66 (brs, 2H, *H*4^{im} and *H*5^{im}), 6.63 (s, 1H, *H*4^{pz}), 6.01 (d, 1H, ^2J(H^b–H^a) = 13.7 Hz, NCH^a*H*^{b}), 4.80 (brt, 1H, J= 7.2 Hz, COD1), 4.07 (brq, 1H, J= 6.1 Hz, COD5), 3.50 (m, 2H, COD2 and COD6), 2.52–1.42 (m, 8H, COD3/4/7/8), 2.41 (s, 3H, p-CH_3), 2.10 (s, 3H, o-CH_3), 1.99 (s, 3H, o-CH_3′) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, DCM-d_2): δ 177.7 (d, ^1J(C-Rh) = 52.5 Hz, *C*2^{im}), 164.6 (q, ^1J(C–B) = 49.6 Hz, B-*C*), 156.3 (*C*3^{pz}), 148.4 (*C*5^{pz}), 140.8 (*C*^{p}), 136.6 (brs, o-BPh$_4$), 135.3 (*C*^{o}), 135.2 (*C*^{o}), 131.4 (Ph*C*), 131.0 (Ph*C*), 130.9 (Ph*C*), 130.4 (Ph*C*), 130.0 (*C*^{m}), 129.6 (Ph*C*), 129.6 (Ph*C*), 129.1 (Ph*C*), 127.8 (Ph*C*), 126.2 (q, ^3J(C–B) = 2.9 Hz, m-BPh$_4$), 124.4 (*C*4^{im}), 122.3 (p-BPh$_4$), 121.4 (*C*5^{im}), 108.5 (*C*4^{pz}), 101.9 (d, ^1J(C–Rh) = 7.3 Hz, COD1), 94.0

(d, ^1J(C–Rh) = 7.3 Hz, COD2), 78.2 (d, ^1J(C–Rh) = 12.9 Hz, COD6), 77.7 (d, ^1J(C–Rh) = 12.9 Hz, COD5), 62.4 (CH_2), 34.2 (COD), 31.2 (COD), 31.0 (COD), 27.2 (COD), 21.5 (p-CH_3), 18.8 (o-CH_3), 18.0 (o-CH_3') ppm. MS (ESI+) m/z (%): 630.1 $[M]^+$ (100).

17c (91%): Anal. found: C, 74.44; H, 6.44; N, 6.45. $C_{55}H_{56}BN_4Rh$ requires: C, 74.49; H, 6.37; N, 6.32. ^{1}H NMR (300 MHz, DCM-d_2): δ 7.84 (m, 2H, PhH), 7.61 (m, 6H, PhH), 7.38 (m, 2H, PhH), 7.31 (m, 9H, o-BPh_4 and NCH^aH^b), 6.99 (t, 8H, ^3J(m-o/p-BPh_4) = 7.3 Hz, m-BPh_4), 6.91 (d, 1H, ^3J(H4^{im}–H5^{im}) = 2.1 Hz, $H4^{im}$), 6.85 (t, 4H, ^3J(p-m-BPh_4) = 7.3 Hz, p-BPh_4), 6.60 (d, 1H, ^3J(H5^{im}–H4^{im}) = 2.1 Hz, $H5^{im}$), 6.59 (s, 1H, $H4^{pz}$), 6.03 (d, 1H, ^2J(H^b-H^a) = 13.7 Hz, NCH$^aH^b$), 4.53 (brt, 1H, J = 7.0 Hz, COD5), 4.37 (brq, 1H, J= 7.6 Hz, COD1), 4.24 (brq, 1H, J = 7.0 Hz, COD6), 3.86 (brt, 1H, J = 7.6 Hz, COD2), 2.67–1.58 (m, 8H, COD3/4/7/8), 1.82 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, DCM-d_2): δ 176.8 (d, ^1J(C–Rh) = 49.3 Hz, $C2^{im}$), 164.6 (q, ^1J(C–B) = 49.6 Hz, B–C), 155.5 ($C3^{pz}$), 148.6 ($C5^{pz}$), 136.5 (brs, o-BPh_4), 131.3 (PhC), 130.9 (PhC), 130.3 (PhC), 129.5 (PhC), 129.4 (PhC), 129.4 (PhC), 129.0 (PhC), 127.9 (PhC), 126.2 (q, ^3J(C–B) = 2.9 Hz, m-BPh_4), 122.3 (p-BPh_4), 121.2 ($C5^{im}$), 120.5 ($C4^{im}$), 107.7 ($C4^{pz}$), 98.8 (d, ^1J(C–Rh) = 8.9 Hz, COD1), 93.9 (d, ^1J(C-Rh) = 7.3 Hz, COD2), 80.6 (d, ^1J(C–Rh) = 13.8 Hz, COD5), 74.0 (d, ^1J(C–Rh) = 13.01 Hz, COD6), 63.4 (CH_2), 59.3 (C(CH$_3$)$_3$), 35.2 (COD), 32.5 (C(CH$_3$)$_3$), 30.9 (COD), 29.7 (COD), 27.5 (COD) ppm. MS (ESI+) m/z (%): 568.1 $[M]^+$ (100).

18a (26%): Anal. found: C, 69.50; H, 7.33; N, 11.26. $C_{58}H_{72}BN_8Rh$ requires: C, 70.01; H, 7.29; N, 11.26. (**18aa**) ^{1}H NMR (300 MHz, DCM-d_2): δ 7.31 (m, 8H, o-BPh_4), 7.00 (t, 8H, ^3J(m-o/p-BPh_4) = 7.3 Hz, m-BPh_4), 6.85 (t, 5H, ^3J(p-m-BPh_4) = 7.3 Hz, p-BPh_4 and $C4^{im}$), 6.65 (d, 1H, ^2J(H^a–H^b) = 13.3 Hz, NCH^aH^b), 6.57 (d, 1H, ^3J(H5^{im}–H4^{im}) = 1.9 Hz, $H5^{im}$), 6.37 (d, 1H, ^2J(H^b–H^a) = 13.3 Hz, NCH$^aH^b$), 6.01 (s, 1H, $H4^{pz}$), 5.01 (brs, 2H, COD1/5), 4.39 (brs, 2H, COD2/6), 3.96 (s, 3H, NCH_3), 2.71–2.11 (m, 8H, COD3/4/7/8), 2.34 (s, 3H, CCH_3), 1.19 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, DCM-d_2): δ 181.7 (d, ^1J(C–Rh) = 58.1 Hz, $C2^{im}$), 164.6 (q, ^1J(C–B) = 49.3 Hz, B-C), 164.3 ($C3^{pz}$), 140.4 ($C5^{pz}$), 136.5 (brs, o-BPh_4), 126.2 (q, ^3J(C–B) = 2.7 Hz, m-BPh_4), 124.7 ($C4^{im}$), 122.3 (p-BPh_4), 120.0 ($C5^{im}$), 104.5 ($C4^{pz}$), 92.1 (d, ^1J(C–Rh) = 8.4 Hz, COD1/5), 91.5 (d, ^1J(C-Rh) = 8.4 Hz, COD2/6), 62.3 (CH_2), 39.4 (NCH_3), 32.4 (COD), 31.4 (COD), 30.6 (C(CH_3)$_3$), 30.4 (C(CH$_3$)$_3$), 11.6 (CCH_3) ppm. (**18ab**) ^{1}H NMR (300 MHz, DCM-d_2): δ 7.31 (m, 8H, o-BPh_4), 7.00 (t, 8H, ^3J(m-o/p-BPh_4) = 7.3 Hz, m-BPh_4), 6.85 (t, 5H, ^3J(p-m-BPh_4) = 7.3 Hz, p-BPh_4 and $C4^{im}$), 6.59 (d, 1H, ^2J(H^a–H^b) = 13.3 Hz, NCH^aH^b), 6.52 (d, 1H, ^3J(H5^{im}–H4^{im}) = 1.9 Hz, $H5^{im}$), 6.07 (d, 1H, ^2J(H^b–H^a) = 13.3 Hz, NCH$^aH^b$), 6.02 (s, 1H, $H4^{pz}$), 5.09 (brt, 2H, J = 6.8 Hz, COD1/5), 4.25 (brq, 2H, J = 6.2 Hz, COD2/6), 4.13 (s, 3H, NCH_3), 2.71–2.11 (m, 8H, COD3/4/7/8), 2.28 (s, 3H, CCH_3), 1.21 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, DCM-d_2): δ 181.7 (d, ^1J(C-Rh) = 58.1 Hz, $C2^{im}$), 164.6 (q, ^1J(C–B) = 49.3 Hz, B–C), 164.2 ($C3^{pz}$), 140.3 ($C5^{pz}$), 136.5 (brs, o-BPh_4), 126.2 (q, ^3J(C–B) = 2.7 Hz, m-BPh_4), 124.5 ($C4^{im}$), 122.3 (p-BPh_4), 120.2 ($C5^{im}$), 104.4 ($C4^{pz}$), 93.1 (d, ^1J(C-Rh) = 8.4 Hz, COD1/5), 90.6 (d, ^1J(C–Rh) = 8.4 Hz, COD2/6), 62.2 (CH_2), 39.6 (NCH_3), 32.7 (COD), 31.4 (COD), 30.6 (C(CH_3)$_3$), 30.4 (C(CH$_3$)$_3$), 11.4 (CCH_3) ppm. MS (ESI+) m/z (%): 676.2 $[M]^+$ (100).

18b (87%): Anal. found: C, 70.51; H, 6.99; N, 5.97. $C_{53}H_{60}BN_4Rh{\cdot}0.5CH_2Cl_2$ requires: C, 70.67; H, 6.76; N, 6.16. ^{1}H NMR (300 MHz, DCM-d_2): δ 7.37 (m, 8H, o-BPh_4), 7.04 (m, 10H, m-BPh_4, NCH^aH^b, and H^m), 6.98 (brs, 1H, $H^{m'}$), 6.88 (t, 4H, ^3J(p-m-BPh_4) = 7.4 Hz, p-BPh_4), 6.78 (d, 1H, ^3J(H5^{im}–H4^{im}) = 1.9 Hz, $H5^{im}$), 6.58 (d, 1H, ^3J(H4^{im}-H5^{im}) = 1.9 Hz, $H4^{im}$), 6.03 (s, 1H, $H4^{pz}$), 5.65 (d, 1H, ^2J(H^b–H^a) = 14.1 Hz, NCH$^aH^b$), 5.11 (t, 1H, J = 7.3 Hz, COD1), 4.75 (q, 1H, J = 7.6 Hz, COD2), 3.88 (brq, 1H, J = 6.8 Hz, COD5), 3.46 (brt, 1H, J = 6.8 Hz, COD6), 2.72–1.30 (m, 8H, COD3/4/7/8), 2.37 (s, 3H, p-CH_3), 2.28 (s, 3H, CCH_3), 1.93 (s, 3H, o-CH_3), 1.82 (s, 3H, o-CH_3'), 1.42 (s, 9H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (75 MHz, DCM-d_2): δ 166.6 ($C3^{pz}$), 164.6 (q, ^1J(C–B) = 49.4 Hz, B–C), 143.6 ($C5^{pz}$), 140.6 (C^p), 136.6 (brs, o-BPh_4), 135.4 (C^o), 135.1 (N–C), 134.8 ($C^{o'}$), 129.8 (C^m), 129.7 ($C^{m'}$), 126.3 (q, ^3J(C–B) = 2.9 Hz, m-BPh_4), 124.4 ($C4^{im}$), 122.5 (p-BPh_4), 121.2 ($C5^{im}$), 106.9 ($C4^{pz}$), 101.0 (d, ^1J(C–Rh) = 7.3 Hz, COD1), 94.2 (d, ^1J(C-Rh) = 7.0 Hz, COD2), 75.7 (d, ^1J(C–Rh) = 14.5 Hz, COD5), 74.2 (d, ^1J(C–Rh) = 12.4 Hz, COD6), 61.8 (CH_2), 35.8 (COD), 32.7 (COD), 32.2 (C(CH_3)$_3$), 32.1 (C(CH$_3$)$_3$), 29.7 (COD), 26.3 (COD), 21.4 (p-CH_3), 18.7 (o-CH_3), 18.0 (o-CH_3'), 12.1 (CCH_3) ppm (C2^{im} undefined). MS (ESI+) m/z (%): 548.1 $[M]^+$ (100), 1413.6 $[2M + BPh_4]^+$ (**18**).

General procedure for catalytic hydrogenations

The hydrogenation reactions were carried out in a 40 mL steel bomb reactor (Parr Instrument Co. USA) equipped with a stainless steel cannular dip tube. The temperature of the bomb was maintained by positioning the bomb on a magnetic stirrer hotplate, which also facilitated mixing of the solution through a magnetic stirrer bar placed inside the bomb. A THF (20 mL) solution of styrene (54.4 mM), and an internal standard toluene (71.4 mM) was added to the catalyst (0.5 mol%), the bomb was sealed and purged with H_2 gas for 30 s and then pressurized under 50 psi of H_2 gas at 27 °C. Aliquots (0.2 mL) of the reaction solution were taken at regular intervals through the stainless steel dip tube, which was purged with solution (1.0 mL) prior to collecting the aliquot.

The aliquots were analyzed using capillary electrophoresis using the micellar electrokinetic capillary chromatography (MECC) technique. Prior to analysis, 15 μL of the aliquot was diluted with methanol (235 μL), SDS, (500 mM, 100 μL), and water (650 μL). Separation of the analytes, styrene, ethylbenzene, and toluene was achieved using an aqueous buffer solution of sodium borate (50 mmol, pH = 8.5), SDS (50 mM), and MeOH (5% v/v). The samples were run through an 8.5 cm capillary, at a 15 kV separation voltage, and 5 s injection time, with elution of the analytes complete within 10 min of injection. A UV detector was used to detect the aromatic analyte species with peak integrals being measured at 195 nm.

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