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PAPER

Investigation of ligand steric effects on a highly *cis*-selective Rh(I) cyclopropanation catalyst†‡

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Four new Rh(I) complexes bearing chelating imine-functionalized *N*-heterocyclic carbene ligands have been synthesized and characterized. The catalytic activity of these new Rh(I) complexes has been tested in the cyclopropanation reaction between ethyl diazoacetate and styrene. One of the new complexes, having ethyl groups on the ligand *N*-aryl ring, exhibited a reactivity and a *cis*-diastereoselectivity that were comparable to our previously reported Rh(I) cyclopropanation catalyst of this type, and a higher yield and *cis*-diastereoselectivity were obtained at lower catalyst loadings and higher temperatures. The other new Rh(I) complexes were found to be inferior to the previously reported Rh(I) cyclopropanation catalyst. The catalytic study gave important information about the effect that changing the steric requirements of the substituents at the ligand system has on the efficiency and *cis*-diastereoselectivity of the complexes as cyclopropanation catalysts.

Introduction

N-Heterocyclic carbenes (NHC's) have since Arduengo's report on a stable NHC in 1991[1,2] been extensively used as ligands for transition metal complexes.[3–7] The NHC metal complexes are excellent catalysts for a wide range of chemical transformations,[3,8,9] for example, for olefin metathesis[10] and C–C cross-coupling reactions,[11,12] where the use of NHC ligands has allowed for major improvements. Chelating NHC ligands have also attracted considerable attention, and metal catalysts bearing these ligands have successfully been used in a range of different reactions.[13–15] So far, the NHC ligands have not yet been greatly utilized in the much studied carbenoid cyclopropanation and insertion reactions. Perez and co-workers[16,17] have reported the use of some NHC Ag, Au, and Cu complexes in these reactions, showing promising results. A Rh(I) complex with a NHC ligand has also previously been tested in cyclopropanation reactions, giving high yields but low diastereoselectivity.[18]

We have recently reported the synthesis of a novel Rh(I) complex **1** (Fig. 1) bearing a chelating imine-functionalized NHC ligand, and the use of this complex in cyclopropanation reactions.[19]

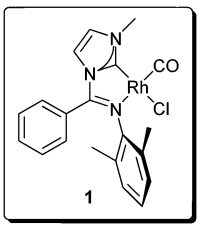
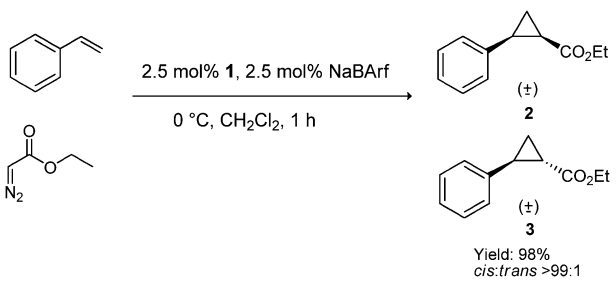


Fig. 1 Rh(I) complex **1**, bearing a chelating *N*-heterocyclic imino-carbene ligand.

This Rh(I) complex, after activation with AgOTf[19] or, even better with NaBArf,[20] displays a remarkably high reactivity and *cis*-diastereoselectivity in the cyclopropanation reaction between ethyl diazoacetate (EDA) and styrene (Scheme 1). Excellent results are also obtained with a range of substituted



Scheme 1 Highly *cis*-selective cyclopropanation reaction between EDA and styrene catalyzed by Rh(I) complex **1**.

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† Dedicated to Prof. Didier Astruc on the occasion of his 65th birthday.

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alkenes.[19,20] It can be a challenge in intermolecular cyclopropanation reactions to achieve good diastereoselectivity, especially with simple α-diazoacetates like EDA.[21]

There are numerous reports on highly efficient and selective catalysts for the formation of the thermodynamically favored *trans* isomer.[21–23] On the other hand, efficient and selective synthesis of the unfavored *cis* isomer remains more of a challenge. There are just a few reports on highly *cis*-selective catalysts.[21,24–37] The reported results using Rh(I) catalyst **1** are among the highest *cis*-selectivities reported in these reactions and, to the best of our knowledge, the highest *cis*-selectivities reported thus far using a Rh catalyst. This report was also the first on the use of a chelating imine-functionalized NHC ligand system in cyclopropanation reactions.

In this contribution, we present the synthesis of several new Rh(I) complexes that bear chelating imine-functionalized NHC ligands. These new Rh(I) complexes are analogues of complex **1** in which substituents at the ligand system have been varied. The catalytic activity of the new complexes has been tested in cyclopropanation reactions, giving useful information about the importance of certain substituents on the ligand system for obtaining high yields and *cis*-selectivities.

Results and discussion

Synthesis

Four new Rh(I) complexes have been synthesized (Fig. 2). In complexes **4**, **5**, and **6** the methyl groups at the *N*-aryl ring in **1** have been replaced with more sterically demanding ethyl (**4**) and *iso*-propyl groups (**5**) and less sterically demanding hydrogens (**6**). In complex **7**, the *N*-methyl group at the NHC in complex **1** has been replaced by a bulkier *tert*-butyl group. Complexes **4**, **5**, and **6** were synthesized in good yields by adaptation of the reported method for preparation of **1** (Scheme 2).[19,38,39]

Complex **7** was synthesized by the route shown in Scheme 3. 1-*tert*-Butyl imidazole is not commercially available and was prepared by the method of Gridnev and Mihaltseva.[40] In the synthesis of the imidazolium salt **13**, the procedure of Green and co-workers[41] was followed. The reaction mixture was heated at 60 °C for two hours instead of our commonly employed procedure of stirring the reaction mixture at ambient temperature (Scheme 2).[19,38,39] For the synthesis of imidazolium salt **13**, this procedure proved to be more efficient. Imidazolium salt **13** was reacted with Rh(acac)CO_2 and complex **7** was formed.

Characterization

As previously reported for complex **1**,[19] complexes **4**, **5** and **7** display characteristic doublets for the carbene carbon in the

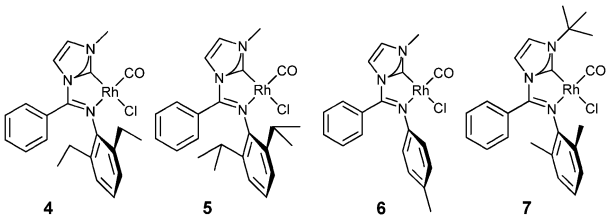
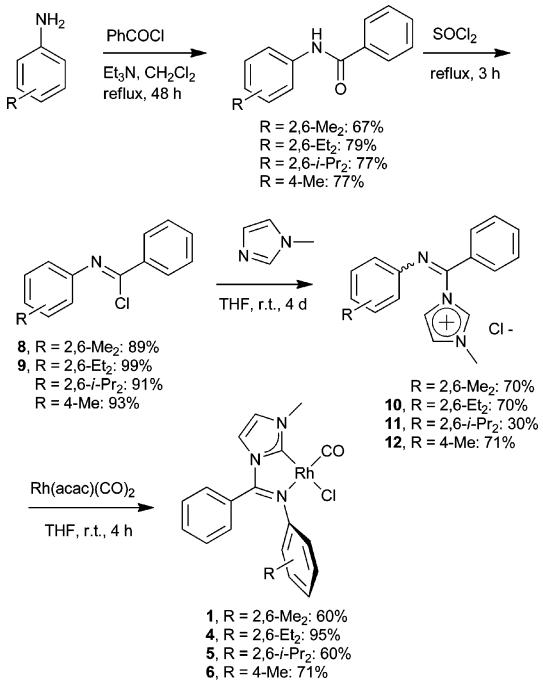
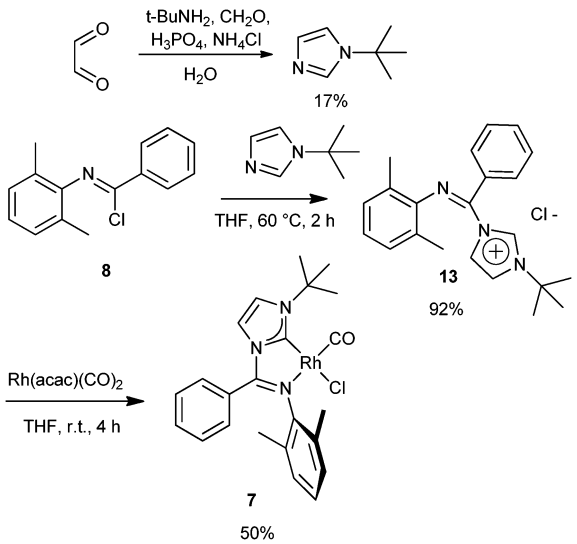


Fig. 2 The four new Rh(I) complexes.



Scheme 2 Synthesis of complexes **1**,[19] **4**, **5** and **6**.



Scheme 3 Synthesis of complex **7**.

^{13}C NMR spectra (δ 185.5–183.5) with coupling constants $J(^{103}Rh–^{13}C)$ = 58–62 Hz, confirming the bonding of the NHC ligand to Rh.[42] Because of the very low solubility of **6**, a ^{13}C NMR spectrum could not be obtained for this complex. The ^{1}H NMR spectrum of complex **4** exhibits two signals for the ethyl-CH_2 protons at the *N*-aryl ring. Two doublets of quartets at δ 2.74 and 2.32 were observed.

This indicates that rotation around the *N*(imine)-aryl bond is severely restricted, rendering the CH_2 hydrogens diastereotopic. A similar feature was also observed in the ^{1}H NMR spectra of complex **5**, where two doublets from the diastereotopic *i*-Pr–CH_3 groups were found at δ 1.28 and 0.90. This has also been reported for Pd and Pt complexes bearing the same

ligand system.[39] There is a rather large separation in chemical shifts between the two diastereotopic signals in complex **4** (0.42 ppm) and in **5** (0.38 ppm). This agrees with a previously reported trend, based on a large number of 5- and 6-membered chelate ring complexes, in that the separation between these signals is larger in κ^2(C,N) chelating iminocarbene structures (typically 0.3–0.6 ppm) than in non-chelating κ^1(C) iminocarbene complexes (<0.2 ppm).[39,43] The IR $\nu_{C=N}$ absorption of the imine was lowered by 48–69 cm^{-1} in the new Rh(I) complexes compared to that of the imidazolium salts. This indicates coordination of the imine nitrogen to the Rh center with resulting back-bonding into the C=N bond. The combined data strongly suggest that the iminocarbene ligands have formed a κ^2(C,N) chelate at Rh.

The results from single-crystal X-ray structure determinations of **5** and **7** are presented in Fig. 3 and 4, respectively. The X-ray structure analyses confirmed the expected monomeric structures with chelating NHC iminocarbene ligands and a *cis* relationship between the NHC and the CO ligands. The complexes assume a slight distortion from the square-planar geometry, as expected for unsymmetrically substituted four-coordinate d^8 species. Some selected bond lengths and angles for **5** and **7** are shown in Table 1. Bond lengths and angles for **1** from the previously reported X-ray structure[19] are included for comparison. As can be seen in Table 1, the carbene C1–Rh bond is shortest in complex **5** and longest in complex **7**. For all complexes **1**, **5**, and **7**, there are deviations from the ideal 90° L–Rh–L′ angles, ranging from 78–79° for the N1–Rh–C1 chelate bite angle to 97–102° for the C1–Rh–CO angle. These observations are consistent with the reported structures of Pd and Pt complexes bearing this type of ligand systems.[38,39] The C1–Rh–CO angle is greatest in complex **7**, presumably a result of the larger steric pressure from the adjacent *N*-*tert*-butyl group in **7** compared to the *N*-methyl group in **1**. This also results in smaller OC–Rh–Cl and Cl–Rh–N1 angles in **7** than in **1** and **5**. Significant ring strain in the chelate in complexes **1**, **5** and **7** is evident from the 27–34° difference between the N3–C1–Rh and N2–C1–Rh angles.

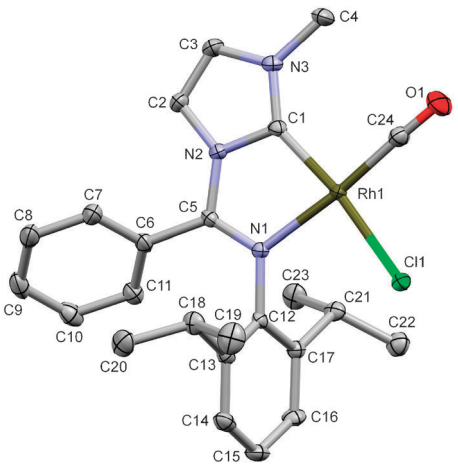


Fig. 3 ORTEP drawing of complex **5** at 105 K (H atoms and CH_2Cl_2 omitted for clarity, ellipsoids at 50% probability).

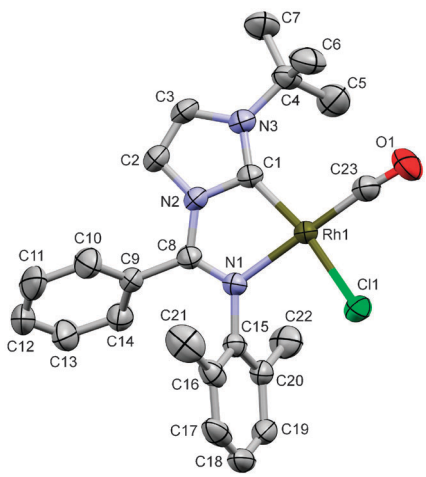


Fig. 4 ORTEP drawing of complex **7** at 293 K (H atoms omitted for clarity, ellipsoids at 50% probability).

Table 1 Selected bond lengths (Å) and angles (°) from the X-ray structures of complexes **1**, **5**, and **7**

Bond lengths and angles	**1**[19]	**5**	**7**
Rh–C1	1.953(2)	1.937(2)	1.979(3)
Rh–CO	1.813(3)	1.819(2)	1.808(2)
Rh–N1	2.131(2)	2.130(2)	2.117(2)
Rh–Cl	2.367(6)	2.366(5)	2.351(1)
C1–Rh–CO	97.39(1)	96.73(9)	101.6(1)
OC–Rh–Cl	90.38(8)	91.39(7)	87.64(2)
Cl–Rh–N	93.40(6)	93.66(5)	91.51(6)
N1–Rh–C1	78.53(9)	78.22(7)	79.14(1)
N2–C1–Rh	113.6(2)	114.9(1)	111.5(2)
N3–C1–Rh	142.4(2)	141.5(2)	145.0(2)

Catalysis

We have reported that in order for the cyclopropanation catalyst **1** to be active, it has to be activated prior to the reactions, presumably by generation of a vacant coordination site through removal of the chloride ligand. Both AgOTf[19] and NaBArf[20] have been found to be efficient activating agents. Some of the previously reported results are summarized in Table 2. As can be seen, excellent results were obtained with both activating agents in the cyclopropanation reaction of styrene with EDA when a catalyst loading of 5 mol% was used (Table 2, entries 1 and 5). However, NaBArf (which has a larger and more loosely coordinating anion than AgOTf[44,45]) proved to be superior at lower catalyst loadings (entries 2, 3, 6, and 7). The best conditions found so far for cyclopropanation with EDA catalyzed by **1** are in CH_2Cl_2 at 0 °C. Increasing the reaction temperature to ambient results in lower diastereoselectivity (entry 4). Formal carbene dimerization is a common side reaction in carbenoid reactions. In order to circumvent this problem, the diazo compound is often added very slowly to the reaction mixture, resulting in rather time consuming cyclopropanation procedures. Using catalyst **1**, EDA can be added in one portion without any sign of dimerization. However, when the catalyst loading is reduced to 1 mol%, the yield of the cyclopropanes and the diastereoselectivity are reduced (entries 3 and 7) and formal carbene dimerization is observed.

Table 2 Previously reported results from cyclopropanation reactions with EDA and styrene using **1** as catalyst and AgOTf or NaBArf as activating agent[a]

Entry	Mol% **1**	Equiv. styrene	Mol% activator	*T*/°C	Time/h	Yield %[f] (*cis* : *trans*)[g]
1[b]	5	5	5[d]	0	2	98 (>99 : 1)
2[b]	2.5	10	2.5[d]	0	3	89 (94 : 6)
3[b]	1	10	1[d]	0	48	50 (92 : 8)
4[b]	5	10	5[d]	20	3	96 (92 : 8)
5[c]	5	5	5[e]	0	1	98 (>99 : 1)
6[c]	2.5	5	2.5[e]	0	2	98 (>99 : 1)
7[c]	1	5	1[e]	0	24	49 (96 : 4)

[a] Reaction conditions: 1.00 mmol of EDA and given quantities of **1**, activating agent and styrene in 20 mL CH_2Cl_2. [b] From ref. 19. [c] From ref. 20. [d] AgOTf. [e] NaBArf. [f] Isolated yield based on EDA limiting reagent. [g] *cis* : *trans* ratio determined by ^{1}H NMR and GC.

Catalysts **4–7** were also tested in the cyclopropanation reaction between EDA and styrene, following the previously reported procedure. These results are presented in Table 3. With 2.5 mol% of catalyst **4** and NaBArf as the activating agent (entry 1) it was found that **4**, which is 2,6-diethyl substituted at the *N*-aryl ring, is as efficient and selective as catalyst **1** which is 2,6-dimethyl substituted at the *N*-aryl ring. Reducing the catalyst loading to 1 mol% of **4** at 0 °C (entry 2) led to lower yield and diastereoselectivity, as was also reported for **1**.[19,20] A notable difference between the two catalysts **1** and **4** was that the reaction was slower with catalyst **4** than with **1**, and after 24 hours there was still unreacted EDA left in the reaction mixture. The reaction temperature was raised to ambient in the hope that this would improve the yield and diastereoselectivity. Indeed, it turned out that by increasing the temperature, the yield increased to 99% and a quite satisfactory *cis* : *trans* selectivity of 98 : 2 was still obtained (entry 3). As mentioned earlier,[19,20] increasing the reaction temperature using catalyst **1** resulted in lower yield and diastereoselectivity.

For complex **5**, with the even bulkier *iso*-propyl groups at the 2,6-positions of the *N*-aryl ring, both yield and selectivity were considerably lower than for **1** when AgOTf was used as the activating agent (entry 4). An increase of the temperature (entry 5) did not have the same positive effect as for catalyst **4**; the yield was improved but, as observed for catalyst **1**, the selectivity was lowered. By changing the activating agent to NaBArf, both yield and selectivity were improved (entry 6), but the results were still significantly poorer than for **1** and **4**. Complete conversion of EDA was achieved in five hours using NaBArf as the activating agent, but formal carbene dimerization was observed. It appears that the *iso*-propyl groups impose too much of a steric hindrance, resulting in a slower and less diastereoselective cyclopropanation catalyst.

Interestingly, for catalyst **6**, with no *ortho* substituents at the *N*-aryl ring, the results were strikingly different from those observed for catalyst **1**. The cyclopropanes **2** and **3** were formed in only 29% yield using AgOTf as an activating agent and the *cis*-selectivity was completely lost, as a 50 : 50 mixture of the *cis* and *trans* isomers was obtained (entry 7). Changing the activating agent to NaBArf had little effect on the yield and selectivity (entry 8), but did result in a more reactive catalyst. With AgOTf there was still unreacted EDA left in the reaction mixture after 24 hours, while with NaBArf complete conversion of EDA was achieved within 1 hour. Products from formal carbene dimerization were observed as the only byproducts with both activating agents. There were no signs of homologated products.

Complex **7**, in which the *N*-methyl group at the NHC has been replaced with a bulkier *tert*-butyl group, also proved to be a less efficient and less diastereoselective cyclopropanation catalyst than catalyst **1** (entry 9). With a catalyst loading of 5 mol% of **7** and NaBArf as the activating agent, 74% of the cyclopropanes **2** and **3** were formed, and the diastereomeric ratio was 93 : 7 in favor of the *cis* isomer. Reducing the catalyst loading did not reduce the reactivity or selectivity (entry 10).

Rh(I) catalyst **1** is a highly efficient and *cis*-diastereoselective cyclopropanation catalyst in reactions between EDA and sterically unhindered, electron rich alkenes and cyclic alkenes.[19,20] On the other hand, with the acyclic aliphatic alkene 1-octene, the reactivity is good, but the *cis*-selectivity is only moderate (Table 4, entry 1).

Table 3 Catalytic testing of complexes **4–7** in the cyclopropanation reaction between EDA and styrene[a]

Entry	Cat.	Mol% cat.	Mol% activator	*T*/°C	Time/h	Yield %[d] (*cis* : *trans*)[e]
1	**4**	2.5	2.5[c]	0	2	98 (>99 : 1)
2	**4**	1	2.5[c]	0	24	55 (96 : 4)
3	**4**	1	1[c]	r.t.	2	99 (98 : 2)
4	**5**	5	5[b]	0	24	53 (92 : 8)
5	**5**	5	5[b]	r.t.	24	73 (89 : 11)
6	**5**	5	5[b]	0	5	65 (95 : 5)
7	**6**	5	5[b]	0	24	29 (50 : 50)
8	**6**	5	5[c]	0	1	30 (53 : 47)
9	**7**	5	5[c]	0	3	74 (93 : 7)
10	**7**	2.5	2.5[c]	0	5	71 (95 : 5)

[a] Reaction conditions: 1.00 mmol of EDA, 5 equiv. of styrene and given quantities of catalysts **4–7** and activating agent in 20 mL CH_2Cl_2. [b] AgOTf. [c] NaBArf. [d] Isolated yield based on EDA limiting reagent. [e] *cis* : *trans* ratio determined by ^{1}H NMR and GC.

Table 4 Catalytic testing of complexes **1**, **4** and **7** in the cyclopropanation reaction between EDA and 1-octene[a]

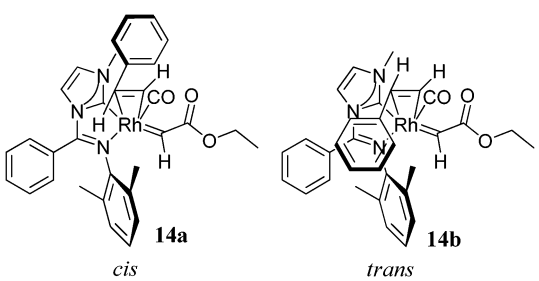
Entry	Cat.	Mol% cat.	Mol% NaBArf	T/°C	Time/h	Yield %[b] (*cis* : *trans*)[c]
1	**1**	2.5	2.5	0	5	95 (75 : 25)[20]
2	**4**	2.5	2.5	0	5	85 (77 : 23)
3	**7**	5	5	0	24	55 (68 : 32)

[a] Reaction conditions: 1.00 mmol of EDA, 5 equiv. of 1-octene and given quantities of catalysts **1**, **4**, and **7** and NaBArf in 20 mL CH_2Cl_2. [b] Isolated yield based on EDA limiting reagent. [c] *cis* : *trans* ratio determined by ^{1}H NMR and GC.

Complexes **4** and **7** were also tested as catalysts for the cyclopropanation reaction between EDA and 1-octene, to see whether larger substituents at the NHC nitrogen or at the *N*-aryl ring would have a positive effect on the diastereoselectivity. Catalyst **4** gave the same selectivity as obtained with catalyst **1** (entry 2), and with catalyst **7** both yield and diastereoselectivity were lower than for **1** (entry 3).

The above results show that the steric bulk of the substituents at the imine-functionalized NHC ligand plays a major role for both the efficiency and the diastereoselectivity of the Rh(I) catalyzed cyclopropanations. By exchanging the methyl groups at the *N*-aryl ring in catalyst **1** with ethyl groups (catalyst **4**), the high yields and diastereoselectivities observed with catalyst **1** were maintained. In addition, catalyst **4** is a more efficient and diastereoselective catalyst at lower catalyst loadings and higher temperatures. Increasing the steric bulk even further with *iso*-propyl groups at the *ortho*-positions (catalyst **5**), on the other hand, gives lower yields and selectivity. The catalytic results obtained with catalyst **6** further confirm the importance of the *ortho* substituents at the *N*-aryl ring. Removing the *ortho* substituents resulted in low yields of the cyclopropanes (**2** and **3**) and the *cis*-selectivity was lost completely. The catalytic results obtained using catalyst **7** show that increasing the steric bulk of the substituent at the NHC nitrogen has a detrimental effect on the reactivity and selectivity.

An ongoing computational mechanistic study indicates that the origin of the high *cis*-selectivities lies in an unfavorable steric interaction in the transition state between the alkene substituent and the *ortho* substituents of the *N*-aryl ring in the path leading to the *trans* isomer (Scheme 4). This explains why the *cis*-selectivity is affected by changing the steric bulk of the *ortho* substituents and why the *cis*-selectivity is lost when the *ortho* substituents are removed. Increasing the steric bulk of the NHC nitrogen as in catalyst **7** affects the transition state leading to the *cis* isomer and thereby lowers the *cis*-selectivity.



Scheme 4 Depiction of transition states leading to *cis* and *trans* products.

Conclusion

Four new Rh(I) complexes **4–7** which bear chelating imine-functionalized NHC ligands have been synthesized and characterized. The testing of these complexes in cyclopropanation reactions showed that the substituents at the *ortho* positions of the *N*-aryl ring are very important for achieving high *cis*-selectivity in these Rh(I) catalyzed cyclopropanations. The results also show that having sterically too demanding substituents at the *N*-aryl ring or at the NHC nitrogen has a detrimental effect on the efficiency and diastereoselectivity of the catalysts. Complex **4** with ethyl groups at the *ortho* positions on the *N*-aryl ring was shown to be an even more efficient and *cis*-selective cyclopropanation catalyst than the original catalyst **1** at lower catalyst loadings and higher temperatures. These interesting results broaden the scope, selectivity and efficiency of our recently discovered, highly *cis*-selective Rh(I) catalyzed cyclopropanation reactions.

Experimental

General procedures

All reactions involving organometallic compounds were carried out with the use of dry box and inert-atmosphere techniques unless otherwise noted. Solvents for reactions were dried according to standard procedures. THF, CH_2Cl_2, Et_2O, and CH_3CN were dried using a MB SPS-800 solvent purifying system from MBraun. NMR spectra were recorded on Bruker Avance DPX 200, DPX 300, and DRX 500 instruments. The NMR spectra were recorded at 25 °C. The assignment of ^{1}H and ^{13}C signals was aided by COSY 45, HMQC, NOESY, and HMBC spectroscopy. For brevity, the following abbreviations are used for the assignment: Ph = phenyl, Dmp = 2,6-dimethylphenyl, Dipp = 2,6-di-*iso*-propylphenyl, Dep = 2,6-diethylphenyl: $H_{o/m/p}$ and $C_{i/o/m/p}$ denote the *ipso*/*ortho*/*meta*/*para* atoms relative to the point of attachment to the imine nitrogen. The imidazolium salts **10–12** were synthesized according to previously reported procedures.[19,38] Mass spectra were obtained on a Micromass QTOF II spectrometer (ESI) and on a Fisons VG Prospec sector instrument at 70 eV (EI). Elemental analyses were performed by Mikro Kemi AB, Uppsala, Sweden, and Mikroanalytisches Laboratorium Kolbe, Germany. When appropriate, the presence of CH_2Cl_2 in the stated proportions was assumed on the basis of the fit with the analyses for C, H, and N and confirmed by ^{1}H NMR spectroscopy.

Imidazolium salt 10. 1-Methyl imidazole (0.32 mL, 4.05 mmol, 1.1 equiv.) was added dropwise to the iminochloride **9** (1.00 g, 3.68 mmol, 1.0 equiv.) in dry THF (19 mL). The reaction

mixture was stirred at ambient temperature for 4 days. The THF was removed under vacuum. The crude product was recrystallized from CH_2Cl_2/THF. This yielded **10** (0.911 g, 70%) as a yellow solid. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.63 (s, 1H, NC*H*N), 8.01–7.97 (m, 1H, NC*H*CHN), 7.88 (br s, 1H, NCHC*H*N), 7.55–7.30 (m, 5H, Ph–*H*), 7.01 (s, 3H, Dep-*H*), 4.30 (s, 3H, NCH_3), 2.50–2.38 (m, 2H, CH_2CH$_3$), 2.35–2.20 (m, 2H, CH_2CH$_3$), 1.09 (t, 6H, J = 7.5 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 147.8, 142.4, 138.9 (N*C*HN), 132.6, 132.1 (Ph-*C*H), 129.5 (Ph-*C*H), 129.2 (Ph-*C*H), 126.3 (Dep-*C*H), 125.3 (Dep-*C*H), 125.0 (N*C*HCHN), 119.6 (NCH*C*HN), 37.6 (N*C*H$_3$), 24.8 (*C*H$_2$CH$_3$), 13.6 (CH$_2$*C*H$_3$). One quaternary carbon was not observed. ESI-MS (CH_3CN): m/z 346 (M^+–Cl^-). IR (CH_2Cl_2): $\nu_{C=N}$ 1673 cm^{-1}.

Complex 4. The imidazolium salt **10** (0.200 g, 0.566 mmol, 1.0 equiv.) and Rh(acac)(CO)$_2$ (0.146 g, 0.566 mmol, 1.0 equiv.) were mixed in a round-bottom flask in the dry box. Dry degassed THF (30 mL) was added and the reaction mixture was stirred at ambient temperature under an argon atmosphere for 4 h. THF was removed under reduced pressure and the crude product was recrystallized from dry CH_2Cl_2/pentane. This yielded **4** (0.260 g, 97%) as a red/orange crystalline solid. ^{1}H NMR (CD_2Cl_2, 600 MHz): δ 7.47 (t, 1H, J = 7.6 Hz, Ph-H_p), 7.36 (t, 2H, J = 7.9 Hz, Ph-H_m), 7.23 (d, 2H, J = 7.6 Hz, Ph-H_o), 7.09 (t, 1H, J = 7.6 Hz, Dep-H_p), 6.99 (d, 2H, J = 7.6 Hz, Dep-H_m), 6.85 (d, 1H, J = 2.3 Hz, NC*H*CHNCH$_3$), 6.81 (d, 1H, J = 2.3 Hz, NCHC*H*NCH$_3$), 3.72 (s, 3H, NCH_3), 2.74 (dq, 2H, J = 15.0, 7.5 Hz, CH_2CH$_3$), 2.32 (dq, 2H, J = 15.0, 7.5 Hz, CH_2CH$_3$), 1.21 (t, 6H, J = 7.5 Hz, CH$_2$CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 151 MHz): δ 191.5 (d, ^1J(^{103}Rh–^{13}C) = 80 Hz, *C*O), 185.5 (d, ^1J(^{103}Rh–^{13}C) = 58 Hz, *C*(carbene)), 159.4, 140.4, 136.3, 131.8 (Ph-*C*H), 128.7 (Ph-*C*H), 128.1 (Ph-*C*H), 126.8, 126.4 (Dep-*C*H$_p$), 124.5 (Dep-*C*H$_m$), 123.5 (NCH*C*HNCH$_3$), 116.7 (N*C*HCHNCH$_3$), 38.6 (N*C*H$_3$), 24.5 (*C*H$_2$CH$_3$), 13.0 (CH$_2$*C*H$_3$). IR (CH_2Cl_2): $\nu_{C=N}$ 1612 cm^{-1}, $\nu_{C=O}$ 1986 cm^{-1}. ESI-MS (CH_3CN): m/z 489 (M^+–Cl + CH_3CN). Anal. calcd. for $C_{22}H_{23}N_3RhOCl$: C, 54.61; H, 4.79; N, 8.69%. Found: C, 54.26; H, 4.46; N, 8.69%.

Complex 5. The imidazolium salt **11** (0.100 g, 0.262 mmol, 1.0 equiv.) and Rh(acac)(CO)$_2$ (0.0676 g, 0.262 mmol, 1.0 equiv.) were mixed in a round-bottom flask in the dry box. Dry degassed THF (17 mL) was added and the reaction mixture was stirred at ambient temperature under an argon atmosphere for 4 h. THF was removed under reduced pressure and the crude product was recrystallized from dry CH_2Cl_2/pentane. This yielded **5** (0.0794 g, 60%) as a red crystalline solid. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.47 (t, 1H, J = 7.6 Hz, Ph-H_p), 7.36 (t, 2H, J = 7.9 Hz, Ph-H_m), 7.25 (d, 2H, J = 7.9 Hz, Ph-H_o), 7.16 (t, 1H, J = 7.7 Hz, Dipp-H_p), 7.01 (d, 2H, J = 7.7 Hz, Dipp-H_m), 6.94 (d, 1H, J = 2.3 Hz, NC*H*CHNCH$_3$), 6.85 (d, 1H, J = 2.3 Hz, NCHC*H*NCH$_3$), 3.73 (s, 3H, NCH_3), 2.99 (sept., 2H, J = 6.8 Hz, C*H*Me$_2$), 1.28 (d, 6H, J = 6.8 Hz, CH(CH_3)$_2$, 0.90 (d, 6H, J = 6.9 Hz, CH(CH_3)$_2$. ^{13}C{^{1}H} NMR (CD_2Cl_2, 135 MHz): δ 191.8 (d, ^1J(^{103}Rh–^{13}C) = 82 Hz, *C*O), 185.9 (d, ^1J(^{103}Rh–^{13}C) = 58 Hz, *C*(carbene)), 159.5 (*C*=N), 141.6 (Dipp-C_o), 139.1 (Dipp-C_i), 132.3 (Ph-*C*H), 129.5 (Ph-C_o), 129.1 (Ph-C_i), 127.4 (Ph-*C*H), 127.0 (Dipp-C_p), 123.9 (NCH*C*HCH$_3$), 123.5 (Dipp-C_m), 117.3 (N*C*HCHNCH$_3$), 39.0 (NCHCHN*C*H$_3$), 28.9 (*C*H(CH$_3$)$_2$), 24.7 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$). ESI-MS (CH_3CN): m/z 517 (M^+–Cl + CH_3CN). IR (CH_2Cl_2): $\nu_{C=N}$ 1602 cm^{-1}, $\nu_{C=O}$ 1978 cm^{-1}. Anal. calc. for $C_{24}H_{27}N_3RhOCl \times 1/7\ CH_2Cl_2$: C, 55.4; H, 5.32; N, 8.21%. Found: C, 55.5; H, 5.2; N, 8.1%.

Complex 6. The imidazolium salt **12** (0.100 g, 0.321 mmol, 1.0 equiv.) and Rh(acac)(CO)$_2$ (0.0828 g, 0.321 mmol, 1.0 equiv.) were mixed in a round-bottom flask in the dry box. Dry degassed THF (21 mL) was added and the reaction mixture was stirred at ambient temperature under an argon atmosphere for 4 h. THF was removed under reduced pressure and the crude product was recrystallized from dry CH_2Cl_2/pentane. This yielded **6** (0.101 g, 71%) as a green crystalline solid. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.50–7.34 (m, 3H), 7.30–7.24 (m, 2H), 7.01 (d, 2H, J = 8.5 Hz), 6.84–6.75 (m, 4H), 3.70 (s, 3H, NCH_3), 2.24 (s, 3H, tolyl-CH_3). Solubility problems precluded ^{13}C NMR and further assignments. ESI-MS (CH_3CN): m/z 447 (M^+–Cl + CH_3CN). IR (CH_2Cl_2): $\nu_{C=N}$ 1605 cm^{-1}, $\nu_{C=O}$ 1962 cm^{-1}. Anal. calcd. for $C_{19}H_{17}N_3RhOCl \times 1/7\ CH_2Cl_2$: C, 50.7; H, 3.8; N, 9.3%. Found: C, 51.0; H, 3.9; N, 9.1%.

Imidazolium salt 13. Iminochloride **8** (1.21 g, 4.97 mmol, 1.0 equiv.) in dry THF (25.4 mL) was added to 1-*tert*-butylimidazole (0.679 g, 5.47 mmol, 1.1 equiv.). The reaction mixture was heated at 60 °C for 2 h and then cooled to ambient temperature. The volatiles were removed under vacuum. It was then attempted to recrystallize the crude product from CH_2Cl_2/pentane, but without success. The solvents were removed and this yielded **13** as a light yellow foam (1.68 g, 92%) that was used without further purification. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.95 (s, 1H, NC*H*N), 7.53–7.22 (m, 5H, Ph-*H*), 7.22 (br s, 1H, NC*H*CHN), 7.09–7.00 (m, 3H, Dmp-*H*), 6.95–6.90 (m, 1H, NCHC*H*N), 2.21 (s, 6H, Dmp-CH_3), 1.60 (s, 9H, *t-Bu*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 166.2 (*C*=N), 136.5, 135.6, 134.6, 132.5 (N*C*HN), 131.5, 128.4, 128.2, 128.0, 127.0, 119.9 (N*C*HCHN), 119.1 (NCH*C*HN), 59.5 (*C*(CH$_3$)$_3$), 29.9 (C(*C*H$_3$)$_3$), 18.5 (Dmp-*C*H$_3$). ESI-MS (CH_3CN): m/z 208 (M^+–$C_7H_{12}N_2$). HR-MS: m/z 208.1120, calcd. for $C_{15}H_{14}N$ 208.1126 (−3.0 ppm). IR (CH_2Cl_2): $\nu_{C=N}$ 1673 cm^{-1}.

Complex 7. The imidazolium salt **13** (0.226 g, 0.615 mmol, 1.0 equiv.) and Rh(acac)(CO)$_2$ (0.159 g, 0.615 mmol, 1.0 equiv.) were mixed in a round-bottom flask in the dry box. Dry degassed THF (40 mL) was added and the reaction mixture was stirred at ambient temperature under an argon atmosphere for 4 h. The solvent was removed under reduced pressure and the crude product was recrystallized from dry CH_2Cl_2/pentane. This yielded **7** (0.152 g, 50%) as a red crystalline solid. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.24 (tt, 1H, J = 7.4, 1.6 Hz, Ph-H_p), 7.39 (tt, 2H, J = 7.4, 1.2 Hz, Ph-H_m), 7.26 (dt, 2H, J = 7.4, 1.6 Hz, Ph-H_o), 7.08 (d, 1H, J = 2.5 Hz, NCHC*H*N-*t*-Bu), 6.97–6.89 (m, 3H, Dmp-*H*), 6.78 (d, 1H, J = 2.5 Hz, NC*H*CHN-*t*-Bu), 2.20 (s, 6H, Dmp-CH_3), 1.89 (s, 9H, *t*-Bu). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75 MHz): δ 193.2

(d, $^1J(^{103}Rh\text{-}^{13}C)$ = 79 Hz, *C*═O), 183.5 (d, $^1J(^{103}Rh\text{-}^{13}C)$ = 62 Hz, *C*(carbene), 160.3 (*C*═N), 142.1, 132.1, 131.6, 129.0, 128.2, 127.6, 127.4, 126.3, 120.3 (NCH*C*HN-*t*-Bu), 116.4 (N*C*HCHN-*t*-Bu), 59.4 ($C(CH_3)_3$), 31.2 ($C(CH_3)_3$), 19.3 (Dmp-CH_3). ESI-MS (CH_3CN): *m*/*z* 503.2 (M^+-Cl + CH_3CN). HR-MS: *m*/*z* 503.1304, calcd. for $C_{25}H_{28}ON_4Rh$ 503.1318 (−2.8 ppm). IR (CH_2Cl_2): $\nu_{C=N}$ 1625 cm^{-1}, $\nu_{C=O}$ 1984 cm^{-1}. Anal. calcd. for $C_{23}H_{25}N_3RhOCl \times 0.35\ CH_2Cl_2$: C, 53.2; H, 4.8; N, 8.9%. Found: C, 53.0; H, 4.9; N, 8.4%.

General procedure for cyclopropanation reactions

The selected Rh(I) complex and the activating agent were stirred in dry CH_2Cl_2 (13.0 mL) at ambient temperature for 1 h under an argon atmosphere. The reaction mixture was cooled to 0 °C and the alkene was added. Then EDA (0.12 mL, 1.00 mmol, 1.0 equiv.) in dry CH_2Cl_2 (7.0 mL) was added in one portion. The reaction mixture was stirred at 0 °C. CH_2Cl_2 was removed *in vacuo* and the crude product was purified by flash chromatography on silica gel (ethyl acetate:hexane) to afford the cyclopropanes. The *cis* : *trans* ratio and characterization of the cyclopropanes were determined with GC analysis and ^1H NMR spectroscopy by comparison with literature data.

Ethyl *cis*-2-phenylcyclopropane-1-carboxylate (2)[46]

^1H NMR ($CDCl_3$, 300 MHz): δ 7.3 (m, 4H, Ph-*H*), 7.18 (m, 1H, Ph-*H*), 3.87 (q, 2H, *J* = 7.1 Hz, OCH_2CH_3), 2.67–2.52 (m, 1H, cyclopropane-*H*), 2.06 (ddd, 1H, *J* = 9.3, 7.9, 5.7 Hz, cyclopropane-*H*), 1.70 (ddd, 1H, *J* = 9.3, 7.4, 5.3 Hz, cyclopropane-*H*), 1.40–1.23 (m, 1H, cyclopropane-*H*), 0.95 (t, 3H, *J* = 7.1 Hz, OCH_2CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 170.8 (*C*O), 136.5 (Ph-*C*), 129.2 (Ph-*C*H), 127.7 (Ph-*C*H), 126.5 (Ph-*C*H), 60.0 (OCH_2CH_3), 25.3 (cyclopropane-*C*H), 21.7 (cyclopropane-*C*H), 13.9 (OCH_2CH_2), 11.0 (cyclopropanes-CH_2). EI-MS: *m*/*z* (%) 190 (M^+, 42), 162 (7), 145 (20), 117 (100), 91 (24).

X-Ray crystallography

Crystals of complexes **5** and **7** were grown from dichloromethane/pentane. The crystal of complex **5** was mounted on a glass fiber with perfluoropolyether, and the data were collected at 105 K. The crystal of complex **7** was mounted on thin glass fiber clamped on a brass pin and the data were collected at 293 K. Data for both complexes were collected on a Bruker D8 diffractometer with an Apex II detector and an Oxford Cryosystems Cryostream Plus device, using graphite-monochromated Mo Kα radiation. Data collection method: φ and ω-scans, range 0.5°. The data were integrated with SAINT[47] and semiempirical absorption correction was performed with SADABS.[48] The structure of complex **5** was solved with Sir92,[49] and refined on F with the program Crystals.[50] The structure of complex **7** was solved by direct methods with Sir92[49] and refined using full matrix least squares against $|F|^2$ with SHELXL as implemented in Farrugia's WinGX suite.[51] For both complexes the non-hydrogen atoms were refined with anisotropic thermal parameters; the H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–98, Å) and isotropic ADPs (U(H) in the range 1.2–1.5 × U_{equiv} of the adjacent atom), after which they were refined with riding constraints. Table 5 lists the experimental and crystallographic data. Crystallographic data for both complexes may be obtained as individual CIF files in the ESI.†

Table 5 Crystallographic data for complexes **5** and **7**

Compound	**5**	**7**
Formula	$C_{24}H_{27}ClN_3ORh\cdot CH_2Cl_2$	$C_{25}H_{25}ClN_3ORh$
Formula weight	596.79	497.82
Crystal system	Monoclinic	Orthorhombic
Colour	Red	Red
Space group	$P2_1/n$	$Fdd2$
a/Å	11.1361(8)	19.6410(7)
b/Å	14.0517(11)	47.2800(14)
c/Å	17.3518(13)	9.725(3)
α/°	90	90
β/°	100.9510(10)	90
γ/°	90	90
V/Å^3	2665.8(3)	9031(3)
Z	4	16
T/K	105	293
F(000)	1216	4064
Radiation	0.17073	0.71073
θ range/°	1.88–28.2	1.72–28.62
Reflections measured	23 563	19 450
Unique reflections	6344	5446
No. of data/restraint/param.	4788/0/298	5446/1/262
Goodness of fit, F	1.1229	1.025
R_1, wR_2 [$I > 3\sigma(I)$]	0.0255, 0.0262	0.0226, 0.0253
R_1, wR_2 (all data)	0.0359, 0.0374	0.0515, 0.0530
Large diff. peak/e Å^{-3}	−0.42 to 0.47	−0.198 to 0.290

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