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Hydrogen bonding ligand functionality and catalytic selectivity in homogeneous hydrosilylation of enones with rhodium complexes

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Abstract

Hydrogen bonding ligand functionality is introduced into the N-heterocyclic carbene (NHC) ligand of [Rh(cod)(NHC)(PPh_3)]OTf (cod = 1,5-cyclooctadiene) to look for molecular recognition effects on the selectivity of the reduction of PhCH=CHCOMe by Et_3SiH. Selectivity differences are indeed found between the control catalyst and those containing molecular recognition groups, particularly in the *E*:*Z* ratios of the silyl enol ether product.

Keywords: Hydrosilylation; Molecular recognition; Salt effect; Rhodium catalyst; Carbene

1. Introduction

Current homogeneous catalysts are usually designed with minimal reference to enzymes, yet the latter are accepted as having many superior qualities in terms of selectivity and rate [1–3]. While very useful for many specific transformations, enzymes are not major contributors to organic synthesis and industrial chemistry because they have limitations, for example, in terms of robustness, both thermally and to poisons, in ease of product isolation, in their requirements for expensive cofactors, which are sometimes even required in stoichiometric amounts because they enter into the reaction itself (e.g., NADH in certain reductions [1]). We are trying to combine molecular recognition [4] with homogeneous catalysis by building a variety of homogeneous catalysts that embody hydrogen bonding groups, as found in natural enzymes [1].

Efforts along this line have had limited success to date. Synthetic catalysts have been reported where a rigid pocket is provided, for example, by molecular imprinting [5], or via an organic receptor [6]. Organic recognition-based catalysts are also known [7], including one from our own group [7b]. The generally modest rate accelerations seen from these catalysts may indicate that the substrate or product may be bound too tightly to the catalyst for optimal reaction rate. On the simple Pauling model of catalytic action, this could result from the binding site providing too high a stabilization for the bound reagent or bound product states and not sufficient to the bound transition state. Catalytic antibodies provide an interesting approach but rates are still far from enzyme-like, partly for the same reason [8].

Recent advances in the study of enzymes have led to a more dynamic model of catalytic action with the recognition of the role of active site flexibility in promoting reaction. This new view has been supported by theoretical studies, site directed mutagenesis, structural studies, and NMR studies of the dynamics [9]. Recent studies in asymmetric organometallic catalysis suggest that introduction of a judicious degree of flexibility in the ligand system can give improved selectivity [10–15].

2. Catalyst design

Our design for the catalyst, shown as **1**, attempts to avoid the rigidity possibly associated with excessively tightly

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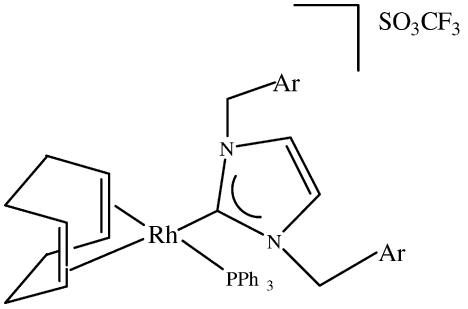


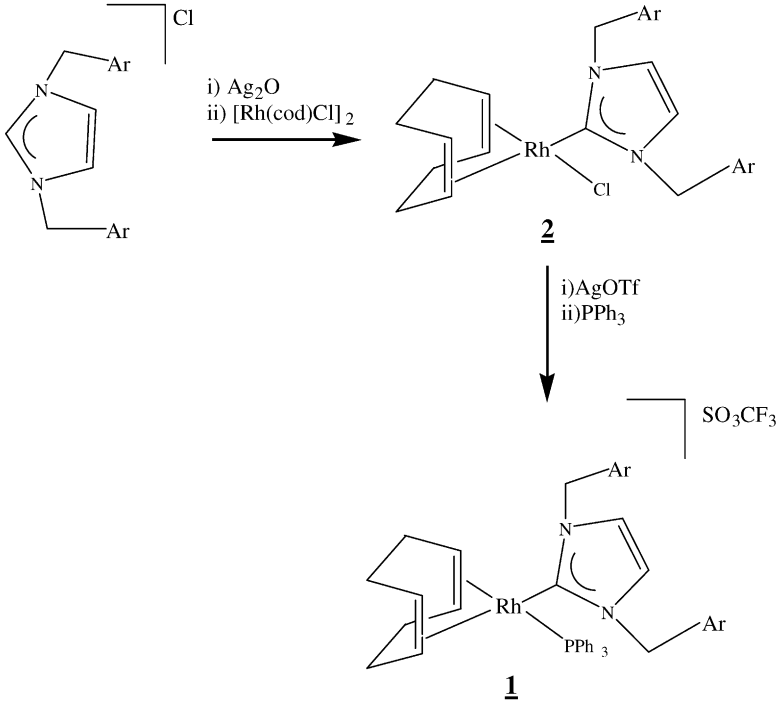
Fig. 1. Rhodium catalyst **1**, Ar = *m*-C_6H_4NHCO(*n*-Bu) (**1a**) and C_6H_5 (**1b**).

coupled catalytic and recognition groups by using a flexible linker between the two, in this case a $-CH_2-$ group. Another advantage of this arrangement is electronic isolation because the electronic effect of the ligand on the metal is expected to remain essentially invariant between the hydrogen bonding and non-hydrogen bonding control catalyst. The Ar group was either C_6H_5 (no H bonding) or *m*-C_6H_4NHCO(*n*-Bu) (H bonding). The position of the recognition group (amide) was expected to be important for the interaction with the substrate. Compounds containing the latter H bonding group are designated by a superscript HB, as in **1a**^{HB}. Clearly, any experimental search for selectivity differences has to involve a comparison, such as that between **1a**^{HB} and **1b** (Fig. 1), and any such comparison should preferably be uncontaminated by ligand electronic effects so as to identify the role of hydrogen bond.

The N-heterocyclic carbene [16] (NHC) ligand was chosen for this purpose because it promotes a variety of catalytic reactions and the wingtip groups at N1 and N3 are readily varied. In addition, the wingtip groups are not only mobile, giving the desired flexibility, but also can easily point in the direction of the metal so that they can in principle interact with the catalytic transition state(s) involved. Other classic catalytic ligands, such as PR_3, are harder to modify, have R groups that point away from the metal, and any hydrogen bond functionality is harder to isolate electronically from the ligand core making safe comparisons more difficult. The presence of one PPh_3 group on the metal along with the NHC group was expected to give better catalyst performance because the PPh_3 was expected to block the position *trans* to the NHC and encourage the catalytic chemistry to occur *cis* to the NHC where the hydrogen bonding groups could have their maximum effect. The weakly coordinating and weakly hydrogen bonding triflate anion was satisfactory for isolation of the complexes and to avoid the anion outcompeting the substrate for hydrogen bonding.

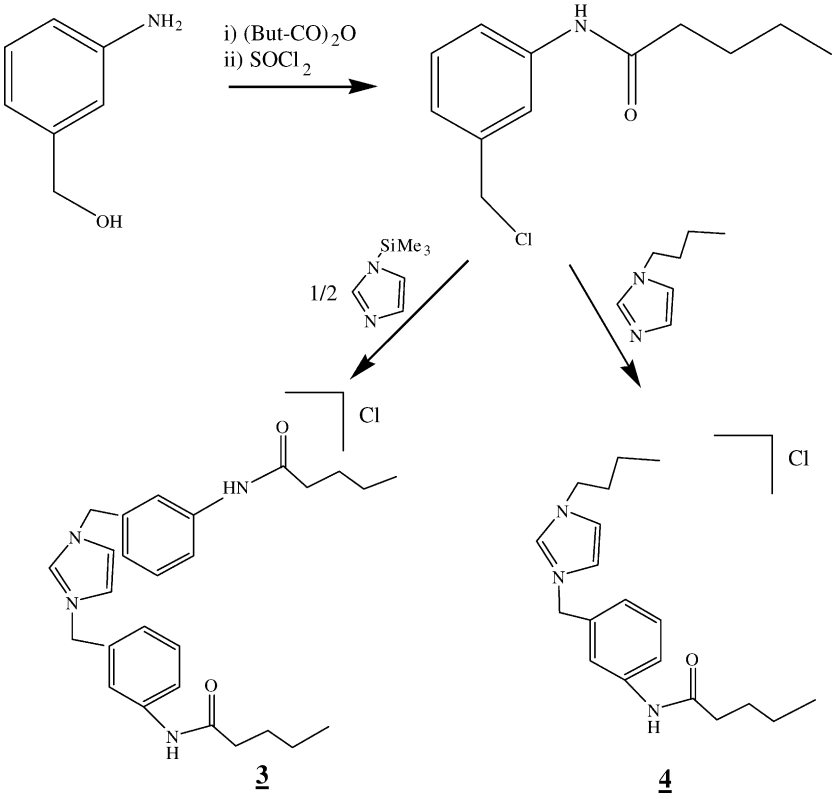
3. Results

The new complexes were made by the sequence of Scheme 1, using Ag_2O to form the silver carbene, then transmetallating to Rh(I), as already reported by our group [17]. After halide removal with silver triflate (silver



Ar =*m*-C_6H_4NHCO(n-Bu) (**1a**^{HB}); C_6H_5 (**1b**)

Scheme 1.

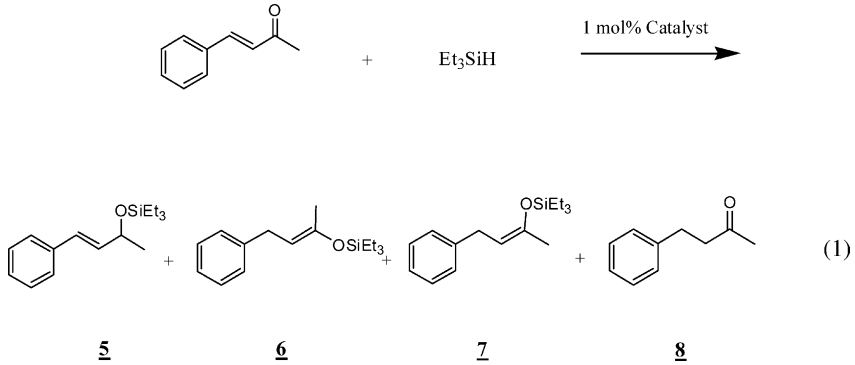


Scheme 2.

trifluoromethane sulfonate), triphenylphosphine is added. This mild route avoids the problems of unselective BuLi deprotonation that would occur if the usual route [16] via the free carbene had been chosen, the hydrogen bonding amide group being readily deprotonated by BuLi. The complexes were identified from their NMR spectra by comparison with closely related derivatives reported [25a] previously.

The ligand with Ar (C_6H_5) wingtips was made as previously reported [18]. The ligand with hydrogen bonding wingtips was made following Scheme 2.

Catalytic studies were carried out on Et_3SiH hydrosilylation of PhCH=CHCOMe (Eq. (1)) in refluxing dried THF and followed by NMR spectroscopy and by comparison with authentic products. PhCH=CHCOMe hydrosilylation was chosen because it is an unselective reaction where the effect of catalyst HB groups could best be tested: it has a hydrogen bonding acceptor function (C=O) and having two functional groups, can exhibit several types of selectivity changes. A variety of products in principle possible, for example, reduction of C=C versus C=O or of both groups; *E* versus *Z* isomers are also possible in many cases.



(1)

5 **6** **7** **8**

The hydrogenation product $PhCH_2CH_2COMe$ was also formed in some of these experiments along with the expected hydrosilylation products. This H_2 could arise from silane dehydromerization or silane hydrolysis pathways which would give coproducts R_3SiSiR_3 or $R_3SiOSiR_3$, respectively, depending on which path is followed. The O atom in the latter would have to come from the water present so we looked to see if the catalytic results were affected by using specially dried materials, but even with dried solvents the reduction

Table 1
Salt effects in the hydrosilylation of PhCH=CHCOMe by Et_3SiH

Catalyst	$NaBF_4$ (mmol)	Ratio of products (%)			
		5	**6**	**7**	**8**
1b	0	29.6	25.9	22.2	22.2
1a^{HB}	0	33.3	26.7	26.7	13.3
1b	0.01	35.0 ± 4[a]	28.0 ± 4[a]	26.6 ± 3[a]	10.5 ± 6[a]
1a^{HB}	0.01	14.9 ± 8[a]	61.1 ± 12[a]	12.5 ± 6[a]	11.6 ± 2[a]

Catalyst: $[Rh(cod)(NHC)(PPh_3)]SO_3CF_3$, 0.01 mmol, substrate: 1.00 mmol, solvent: 5 ml of THF, time: 20 min.
[a] Standard deviation.

still occurs. To better test which pathway was involved in our case we looked for the presence of R_3SiSiR_3 or $R_3SiOSiR_3$ and found that $R_3SiOSiR_3$ was indeed formed in amounts sufficient to account for the hydrogenation. Compounds **1** and **2** are clearly excellent silane hydrolysis catalysts but we have not developed this aspect in the present paper. Similar complexes have proved to be catalysts for the related alcoholysis reaction in the past [19]. In these cases the mechanism was found to be nucleophilic attack by the alcohol on an (η^2-R_3Si–H)M intermediate, so a similar path may occur here, but we defer discussion to a future study.

Comparison of **1a**^{HB} and **1b** as catalyst shows only small selectivity changes (Table 1). However, the addition of a catalytic amount of sodium tetrafluoroborate enhances these changes, largely for **1a**^{HB} (Table 1) presumably by a salt effect. Experiments with different salts show that $NaBF_4$ causes the largest changes. The concentration of the salt does not play an important role, which may mean that the salt helps remove water that might otherwise interfere with hydrogen bonding. The differences seen are real: standard deviations were determined for the last two entries of Table 1.

In order to understand better this behavior, several control experiments were carried out.

First of all, we wanted to check, if the BF_4 counterion by itself can give us selectivity changes. We carried out the catalysis with tetrafluoroborate as catalyst counterion instead of trifluoromethanesulfonate. Indeed, the ratio of the product **6** from 1,4 addition is enhanced and the selectivity is further improved by the addition of sodium tetrafluoroborate (Table 2).

The hydrogen bonding group must necessarily be attached to the catalyst in order to obtain selectivity. We looked at the catalyst without any hydrogen bonding donor wingtip (**1b**)

Table 2
Hydrosilylation of PhCH=CHCOMe by Et_3SiH catalyzed by **1**

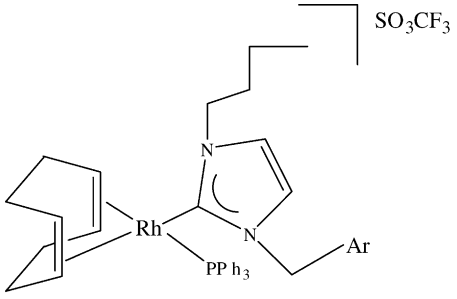
R	Time (min)	Ratio of products (%)			
		5	**6**	**7**	**8**
CH_2Ar	460	34.7	25.7	29.8	9.9
CH_2Ar^{HB}	460	27.6	40.6	18.0	13.8
CH_2Ar^{HB} + salt	65	15.5	61.9	14.4	8.3

Catalyst: 0.01 mmol, substrates: 1 mmol, salt: 0.01 mmol $NaBF_4$, solvent: 5 ml THF.

Table 3
Effect of addition of wingtip mimic in the hydrosilylation of PhCH=CHCOMe by Et_3SiH catalyzed by **1b** in the presence of *n* mmoles of PhCONH(*n*-Bu) (**4**)

n (mmol)	Time (h)	Ratio of products (%)			
		5	**6**	**7**	**8**
1	No reaction	–	–	–	–
0.01	22	37.2	27.9	30.2	4.7

Catalyst: 0.01 mmol, substrates: 1 mmol, solvent: 5 ml THF.



9

Fig. 2. Catalyst **9**.

to which was added the hydrogen donor ligand mimic (**4**) PhCONH(*n*-Bu) in 1:1 mole ratio but this gave no special selectivity effects (Table 3).

The hydrogen bonding effect is independent of the number of X–H groups [24]. The catalyst with the hydrogen bonding group present in only one arm **9** (Fig. 2) gave essentially the same results (Table 4). The one armed catalyst is more readily available so this gives a practical advantage. It also suggests that only one NHCO group is involved in giving the selectivity.

The N–H group of the wingtip is essential because when it was replaced by oxygen (**10**) or by an NMe (**11**) group no selectivity was observed (Table 5).

The *meta* orientation is also essential because neither the *ortho* (**12**) nor the *para* (**13**) position gave selectivity enhancement of product **6** (Table 6). Both cases showed a small enhancement of allylic ether.

Other electronic and geometric modifications of the amide group were also carried out. Giving more flexibility to the wingtip as in compound **14** (Fig. 3), gave no special selec-

Table 4
One versus two HB wingtips in the hydrosilylation of PhCH=CHCOMe with Et_3SiH with $NaBF_4$ added

Catalyst	Ratio of products (%)			
	5	**6**	**7**	**8**
1a^{HB}	14.9	61.1	12.5	11.6
9	14.3	61.9	13.3	10.5

Catalyst **9** with only one Ar = *m*-C_6H_5NHCO(*n*-Bu) wingtip group: 0.01 mmol, substrates: 1 mmol, $NaBF_4$: 0.01 mmol, solvent: 5 ml THF, time: 20 min.

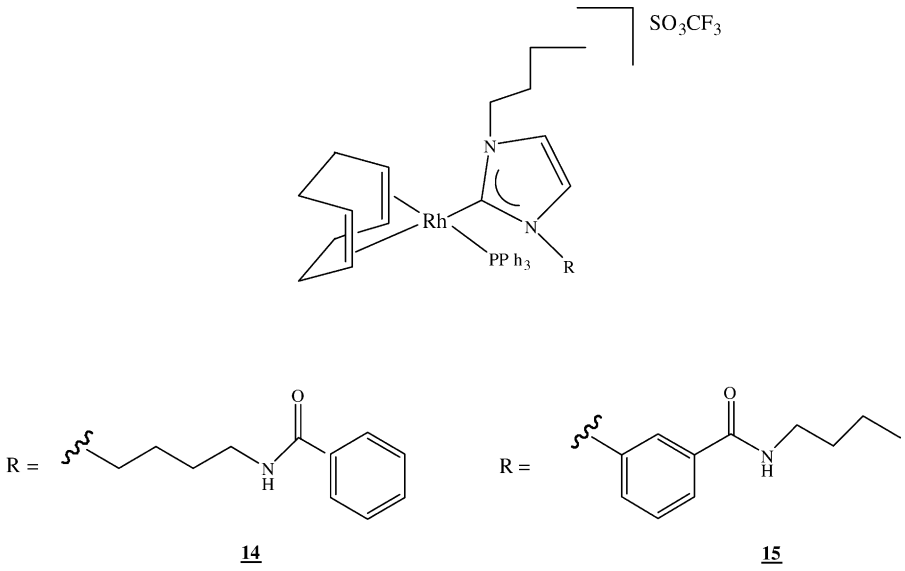


Fig. 3. Catalysts **14** and **15**.

tivity enhancements for **6** (Table 7), even when salt is added. As in Table 6, some enhancement of **5** was seen.

Changing the amide for stronger hydrogen bonding donor sulfonamide (**16**) in the wingtips of the catalyst gave salt dependent selectivity changes but none as great in magnitude as we saw for the amide case (Table 8). Since the sulfonamide has greater acid character than the amide [7b], we tried to improve the selectivity with this wingtip, by using a stronger hydrogen bond acceptor salt such as F^-, but without result. The proportion of the product coming from 1,2 addition is reduced. Another way to change the donor properties of the N–H group is by the interchange of NH and CO to give wingtip **15** (Fig. 3). This experiment gave us much enhanced selectivity (Table 9). This catalyst was the most selective of the entire series.

Table 5
Effect of peptide mutation in the hydrosilylation of PhCH=CHCOMe by Et_3SiH and $NaBF_4$ added

Ar	Ratio of products (%)			
	5	**6**	**7**	**8**
m-C_6H_5OCO(*n*-Bu)	32.7	22.9	21.6	22.9
m-$C_6H_5NCH_3$(*n*-Bu)	38.3	23.4	28.7	9.57

Catalyst **9**: 0.01 mmol, substrates: 1 mmol, $NaBF_4$: 0.01 mmol, solvent: 5 ml THF, time: 20 min.

Table 6
Effect of the HB wingtip orientation in the hydrosilylation of PhCH=CHCOMe by Et_3SiH with $NaBF_4$ added

Position	Ratio of products (%)			
	5	**6**	**7**	**8**
Ortho	39.4	23.6	25.2	11.8
Para	39.0	27.4	27.4	6.32
Meta	14.3	61.9	13.3	10.5

Catalyst **9** with Ar = C_6H_5NHCO(*n*-Bu): 0.01 mmol, substrates: 1 mmol, $NaBF_4$: 0.01 mmol, solvent: 5 ml THF, time: 20 min.

Table 7
Effect of longer linker in the hydrosilylation of PhCH=CHCOMe by Et_3SiH with *n* mmoles of $NaBF_4$ added

n	Ratio of products (%)			
	5	**6**	**7**	**8**
0.01	41	27	24	7
0.0	34	20	22	23

Catalyst **9** with 15 as hydrogen bonding wingtip: 0.01 mmol, substrates: 1 mmol, solvent: 5 ml THF. Time: 20 min.

Table 8
Effect of sulfonamide wingtip in the hydrosilylation of PhCH=CHCOMe with Et_3SiH

Salt	Time	Ratio of products (%)			
		5	**6**	**7**	**8**
$NaBF_4$	20 min	37.8	22.2	22.2	17.8
$NaSO_3CF_3$	20 min	32.9	19.7	26.3	21.1
$LiSO_3CF_3$	80 min	25.8	7.9	12.4	53.9
LiF	80 min	18.9	14.1	23.5	11.7
Bu_4NF	20 min	37.5	25.5	21.5	15.5
Bu_4NBr[a]	38 h	13.3	15.9	12.3	6.3

Catalyst **9** (Ar = *m*-$C_6H_5NHSO_2$(*n*-Bu)): 0.01 mmol, substrates: 1 mmol, salt: 0.01 mmol, solvent: 5 ml THF.

[a] There is also 26.1% of unreacted α,β-ketone.

Table 9
Effect of inversion of the peptide bond in the hydrosilylation (Eq. (1) + n$NaBF_4$)

n	Ratio of products (%)			
	5	**6**	**7**	**8**
0.01	0	74	19	7
0.00	24	28	17	8

Catalyst **9** with *m*-C_6H_5CONH(*n*-Bu) as wingtip: 0.01 mmol, substrates: 1 mmol, solvent: 5 ml THF. Time: 20 min.

Table 10
Effect of different salts on hydrosilylation (Eq. (1)) with catalyst **1a**

Salt	Time	Ratio of products (%)			
		5	**6**	**7**	**8**
$LiBF_4$	135 min	33.0	31.4	15.0	14.1
$NaBF_4$	20 min	12.3	72.5	12.3	2.9
$NaBPh_4$	80 min	12.2	70.7	7.8	7.3
$RbBPh_4$	90 min	22.3	55.3	14.9	7.5
$LiSO_3CF_3$	100 min	36.8	32.4	20.6	10.3
$NaSO_3CF_3$	100 min	39.3	32.8	18.0	9.8
$MgSO_4$	165 min[1]	24.3	19.3	16.3	9.63
CaH_2	100 min[2]	28.0	20.6	17.8	13.1
Molecular sieves	60 min[3]	14.5	16.5	9.1	3.68

Catalyst **1a**^{HB}: 0.01 mmol, substrates: 1 mmol, salt: 0.01 mmol, solvent: 5 ml THF. For **1**, **2**, **3** there is 15.2, 10.3, 28.3 of unreacted α,β-ketone respectively.

Table 10 shows the effect of different salts on the selectivity. Large non-coordinating anions such as BF_4^- and BPh_4^- are best for enhancing the selectivity for 1,4 addition. In aprotic solvents, such as THF, the ionic dissociation constant increases with the size of the cation [20], so lithium salts are not very well dissociated, possibly explaining why lithium salts do not give enhanced selectivity (Tables 10 and 11).

If a more coordinating anion and therefore also a better hydrogen bond acceptor such as $SO_3CF_3^-$ or F^- is used, the proportion of the products becomes almost equal (Tables 10 and 11). The selectivity is improved somewhat when we increased the basic character of the salt, for example, going from NaF to Bu_4NF. Since the ratios depend on both cation and anion, we can assume that the entire salt is playing a role in the selectivity not just the cation or the anion.

Since the salts that give us selectivity can also act as desiccants, we used known desiccants in heterogeneous phase to see if simple removal of water gives enhanced selectivity. The results show that this is not the case, however, and selectivity with these dessicants is not as good as with $NaBF_4$ (Table 10) but reaction is also much slower in these cases and unreacted enone is also seen in the products.

Table 11
Effect of different salts on hydrosilylation (Eq. (1)) with catalyst **9**

Salt	Time	Ratio of products (%)			
		5	**6**	**7**	**8**
$NaBF_4$	20 min	5.4	77.0	6.8	10.8
Bu_4NBF_4	20 min	13.0	67.0	14.0	6.0
$NaBPh_4$	10 min	12.4	65.4	13.6	8.6
$KBPh_4$	100 min	17.7	55.1	16.3	11.0
$RbBPh_4$	40 min	13.8	63.8	12.8	8.8
$LiSO_3CF_3$	40 min	36.1	25.9	22.2	15.7
$NaSO_3CF_3$	80 min	22.5	27.9	23.4	26.1
LiF	1 h 40 min	28.6	30.2	22.2	19.1
NaF	60 min	31.3	25.3	22.9	20.5
Bu_4NF	2 h	25.7	45.8	20.8	7.6
Bu_4NBr	38.5 h[a]	14.2	17.9	13.9	4.2

Catalyst **9** (Ar = *m*-C_6H_5NHCO(*n*-Bu)): 0.01 mmol, substrates: 1 mmol, salt: 0.01 mmol, solvent: 5 ml THF.

[a] There is also 24.9% of unreacted α,β-ketone.

Table 12
Hydrosilylation of PhCH=CHCOMe by Et_3SiH with addition of *n* mmoles of $NaBF_4$

n	Ratio of products (%)			
	5	**6**	**7**	**8**
0.01	4.7	78.7	9.48	7.11
0.005	5.6	75.9	7.8	10.6
0.003	4.4	78.8	7.9	7.9

Catalyst **9** (Ar = *m*-C_6H_5NHCO(*n*-Bu)): 0.01 mmol, substrates: 1 mmol, solvent: 5 ml dried THF, time: 20 min.

Table 13
Hydrosilylation of PhCH=CHCOMe by Et_3SiH with addition of *n* mmoles of water with constant $NaBF_4$ (0.1 mmol)

n	Ratio of products (%)			
	5	**6**	**7**	**8**
0.02	9.4	75.7	7.3	7.5
0.1	24.6	49.9	13.7	11.9
1	24.1	41.2	15.4	19.3
2	25.5	29.1	15.0	23.6

Catalyst **1a**^{HB}: 0.01 mmol, substrates: 1 mmol, solvent: 5 ml of dried THF, $NaBF_4$: 0.1 mmol.

However, since it is known that there is always residual water in THF, and that this is not easy to remove, we decreased the concentration of $NaBF_4$ versus concentration of catalyst as another control experiment (Table 12). When the concentration of $NaBF_4$ is less than the concentration of catalyst, the selectivity is still enhanced, with similar results as when we have equal concentrations. This may indicate that the salt simply hydrates trace water more effectively than does the catalyst peptide group; the salt presumably associates with multiple water molecules per ion pair, accounting for the salt effect at lower ratios than 1:1. The fact that we do not detect any interaction between the peptide and the salt either by IR spectroscopy or electrospray MS tends to confirm this picture.

The addition of water to the system caused loss of selectivity when the concentration of water is greater than the concentration of $NaBF_4$, as shown in Table 13.

3.1. Discussion

These results suggest that hydrogen bonding wingtip group can play a role in determining the selectivity of the catalytic reaction.

It may be useful to consider this interaction in other catalytic reactions such as asymmetric catalysis, where small energy effects are involved in discriminating between two pathways.

4. Conclusions

We have shown that hydrogen bonding wingtip groups can be successfully introduced into metal carbene catalyst by a

mild transmetallation procedure. On their own, these groups do not lead to any useful improvement in the selectivity of the probe reaction. Addition of salts, that may tie up trace water, particularly $NaBF_4$, causes one of the four reaction products to be formed selectively. We propose that the transition state involves hydrogen bonding between the substrate and the catalyst. Control reactions show that the NH group of the hydrogen bonding wingtip group is required for selectivity.

5. Experimental

5.1. General methods

$[Rh(cod)Cl]_2$ [21], the substituted imidazolium salts [22], and their silver substituted derivatives [17] were synthesized as previously described. All synthesis were performed using reagent grade solvents, which were used as received. Isolated yields are given for all products. NMR spectra were recorded on 400 or 500 MHz Bruker spectrometers at 300 K (^{1}H NMR) and 100 or 125 MHz (^{13}C NMR), respectively, and referenced to $SiMe_4$ (δ in ppm, J in Hz). NMR spectra were obtained at room temperature unless otherwise noted. Infrared spectra were recorded on a Midac FT-IR spectrometer, using NaCl plates. Elemental analyses were performed by Atlantic Microlab, Inc.

5.2. [{1,3-Bis-(arylmethyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}chloro rhodium (I)] (**2a** and **2b**)

The metallation procedure used was that described previously [17], itself a modification of the procedure of Wang and Lin [23], $[Rh(diene)Cl]_2$ (0.420 mmol) and the appropriate [imidazolin-2-ylidine]silver dichloroargentate (0.840 mmol) were combined in CH_2Cl_2 (20 mL). The mixture was stirred at room temperature for 1 h, and filtered through Celite. The solution was carefully concentrated in vacuo at room temperature. The yellow powder so obtained was washed with pentane (3× 5 mL) and dried in vacuo. The data for the new compounds follows:

5.2.1. Compound **2a**^{HB}

Yield: 0.5117 g (87.00%). ^{1}H NMR (CD_2Cl_2, 298 K): 7.66 (pd, 2H, C–*H*, aromatic benzyl); 7.62 (s, 2H, N–*H*); 7.57 (s, 1H, C–*H*, aromatic benzyl); 7.32 (t, 2H, C–*H*, aromatic benzyl); 7.15 (pd, 1H, C–*H*, aromatic benzyl, J = 7.20); 6.75 (s, 2H, backbone imidazolin); 5.99 (d, 2H, CH_2, benzyl, J = 15.20); 5.55 (d, 2H, CH_2, benzyl, J = 14.80); 4.97 (s-broad, 2H, C–*H*, cod); 3.33 (s-broad, 2H, C–*H*, cod); 2.32 (pt, 4H, CH_2, *n*-butylamide); 2.32 (pt, 4H, CH_2, cod); 1.89 (m, 4H, CH_2, cod); 1.65 (m, 4H, CH_2, *n*-butylamide); 1.37 (m, 4H, CH_2, *n*-butylamide); 0.92 (t, 6H, CH_3, *n*-butylamide, J = 7.20). ^{13}C NMR (CD_2Cl_2, 298 K): 172.24 (*C*O); 139.84, 138.34, 130.02, 124.13, 119.99, 119.91 (aromatic benzyl); 121.99 (*C*–H, backbone imidazolin); 99.45 (*C*–H, cod, $J_{Rh–C}$ = 10.94); 69.44 (*C*–H, cod, $J_{Rh–C}$ = 14.34); 45.62 (*C*H_2, benzyl); 33.63, 29.53 (*C*H_2, cod); 38.17, 28.40, 23.16 (*C*H_2, amide); 14.37 (*C*H_3, amide). Anal. Calcd. for $C_{35}H_{46}O_2N_4ClRh$ (MW = 693.11): C, 60.65; H, 6.69; N, 8.08. Found: C, 60.59; H, 6.78; N, 8.01.

5.2.2. Compound **2b**

Yield: 0.4027 g (83.26%). ^{1}H NMR (CD_2Cl_2, 298K): 7.40 (m, 10H, C–*H*, aromatic); 6.72 (s, 2H, C–*H*, backbone imidazolin); 6.00 (d, 2H, CH_2, benzyl, J = 14.80 Hz); 5.65 (d, 2H, CH_2, benzyl, J = 14.80 Hz); 4.99 (broad, 2H, C–*H*, cod); 3.33 (s, broad, 2H, C–*H*, cod); 2.34 (m, 4H, CH_2 cod); 1.91 (m, 4H, CH_2, cod). ^{13}C NMR (CD_2Cl_2): 184.56 (d, N*C*N, $J_{Rh–C}$ = 51.69); 121.69 (*C*–H, backbone imidazolin); 137.60, 129.37, 129.00, 128.81 (aromatic benzyl); 99.34 (d, *C*–H, cod, $J_{Rh–C}$ = 6.79); 69.18 (d, *C*–H, cod, $J_{Rh–C}$ = 14.46); 55.26 (*C*H_2, benzyl); 33.61, 29.56 (*C*H_2, cod). Anal. Calcd. for $C_{25}H_{28}N_2ClRh$ (MW = 494.87): C, 60.68; H, 5.70; N, 5.66. Found: C, 59.05; H, 5.64; N, 5.35.

5.3. [{1,3-Bis-(arylmethyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium(I)] trifluoromethanesulfonate (**1a** and **1b**)

Complexes **2a** and **b** were treated with PPh_3 (0.5 mmol) and sodium trifluoromethanesulfonate (0.5 mmol) in acetone (20 mL) for 1 h to give a solution that was filtered, and hexanes added to precipitate the complex. Recrystallization from CH_2Cl_2/hexanes gave analytically pure material.

5.3.1. Compound **1a**^{HB}

Yield: 0.2957 g (54.95%). ^{1}H NMR (CD_2Cl_2, 298 K): 8.59 (s, 2H, N–*H*), 7.91 (pd, 2H, C–*H*, aromatic benzyl); 7.53, 7.45, 7.35 (m, 15H, C–*H*, aromatic phosphine); 7.30 (pd, 2H, C–*H*, aromatic benzyl); 7.26 (s, 2H, C–*H*, aromatic benzyl); 6.8 (s, 2H, C–*H*, backbone imidazolin); 6.74 (pd, 2H, C–*H*, aromatic benzyl); 5.82 (d, 2H, CH_2, benzyl, J = 14.80); 4.85 (broad, 2H, C–*H*, cod); 4.36 (d, 2H, CH_2, benzyl, J = 15.20); 2.35 (pt, 4H, CH_2, *n*-butyl); 2.35 (pt, 4H, CH_2, cod); 2.17 (m, 4H, CH_2, cod); 1.63 (m, 4H, CH_2, *n*-butyl); 1.36 (m, 4H, CH_2, *n*-butyl); 0.913 (t, 6H, CH_3, *n*-butyl, J = 7.20). ^{13}C NMR (CD_2Cl_2): 179.24 (dd, N*C*N, $J_{Rh–C}$ = 50.24, $J_{C–P}$ = 14.15); 173.25 (*C*O); 141.12, 136.22, 130.16, 123.99, 120.40, 118.65 (aromatic benzyl); 134.38 (d, aromatic phosphine, $J_{P–C}$ = 11.70); 129.78 (d, aromatic phosphine, $J_{P–C}$ = 9.56); 131.80, 131.75 (aromatic phosphine); 122.69 (*C*–H, backbone imidazolin); 98.95 (d, *C*–H, cod); 95.20 (d, *C*–H, cod); 31.18, 30.79 (*C*H_2, cod); 55.14 (*C*H_2, benzyl); 37.69, 28.43, 23.08 (*C*H_2, *n*-butyl); 14.39 (*C*H_3, *n*-butyl). ^{19}F NMR (CD_2Cl_2): −79.13 (s, C*F*$_3$). ^{31}P NMR: 27.08 (d, $J_{Rh–P}$ = 155.81). Anal. Calcd. for $C_{54}H_{61}O_5N_4F_3PSRh$ (MW = 1069.12): C, 60.67; H, 5.75; N, 5.24. Found: C, 60.47; H, 6.00; N, 5.34.

5.3.2. Compound **1b**

Yield: 0.3870 g (85.00%). ^{1}H NMR (CD_2Cl_2, 298 K): 7.53 (pt, 2H, C–*H*, aromatic benzyl); 6.98 (m, 3H,

C–*H*, aromatic benzyl); 7.45, 7.38 (m, 15H, C–*H*, aromatic phosphine); 6.73 (s, 2H, C–*H*, backbone imidazolin); 5.67 (d, 2H, CH_2, benzyl, J = 14.80 Hz); 4.80 (s-broad, 2H, C–*H*, cod); 4.30 (s-broad, 2H, C–*H*, cod); 2.39 (m, 4H, CH_2, cod); 2.26 (m, 4H, CH_2, cod). ^{13}C NMR (CD_2Cl_2, 298 K): 179.16 (dd, N*C*N, $J_{Rh–C}$ = 50.24, $J_{C–P}$ = 14.43); 134.79, 129.70, 129.23, 128.17 (aromatic benzyl); 134.01 (d, aromatic phosphine, $J_{P–C}$ = 11.32); 131.56, 131.40 (aromatic phosphine); 129.53 (d, aromatic phosphine, $J_{P–C}$ = 9.68); 97.59, 97.57, 95.37 (*C*–H, cod); 123.13 (*C*–H, backbone imidazolin); 55.07 (*C*H_2, benzyl); 30.89, 30.51 (CH_2, cod). ^{19}F NMR (CD_2Cl_2, 298 K): −79.92 (s). ^{31}P NMR (CD_2Cl_2, 298 K): 26.80 (d, $J_{Rh–P}$ = 157.49). Anal. Calcd. for $C_{44}H_{44}O_3N_2F_3PSRh$ (MW = 871.79): C, 60.69; H, 4.98; N, 3.22. Found: C, 60.12; H, 4.97; N, 3.19.

5.4. 3-Butylamide benzyl alcohol

3-Amino benzyl alcohol (20 mmol) and valeric anhydride (20 mmol) were stirred in ethyl acetate (25 mL) for 5 h. After the evaporation of the solvent in vacuo, the desired compound was obtained. Recrystallization from acetone–hexanes gave white crystals.

Yield: 1.4533 (59.00%). ^{1}H NMR (acetone-d_6, 298 K): 9.08 (s, 1H, N–*H*); 7.65 (s, 1H, C–*H*, aromatic); 7.56 (pd, 1H, C–*H*, aromatic); 7.22 (pt, 1H, C–*H*, aromatic); 7.02 (pd, 1H, C–*H*, aromatic); 4.59 (d, 2H, CH_2, benzyl, J = 6.00); 4.24 (*t*, 1H, J = 5.60, OH); 2.35 (pt, 2H, CH_2, *n*-butyl); 1.65 (m, 2H, CH_2, *n*-butyl); 1.37 (m, 2H, CH_2, *n*-butyl); 0.91 (t, 3H, CH_3, *n*-butyl). ^{13}C NMR (acetone-d_6): 172.38 (*C*O); 144.45, 140.85, 129.63, 122.49, 118.88, 118.58 (aromatic); 64.99 (*C*H_2, benzyl); 37.88, 28.83, 23.41 (*C*H_2, *n*-butyl); 14.53 (*C*H_3, *n*-butyl). Anal. Calcd. for $C_{12}H_{17}O_2N$ (MW = 207.275): C, 69.54; H, 8.27; N, 6.76. Found: C, 69.52; H, 8.30; N, 6.76.

5.5. 3-Butylamide benzyl chloride

3-Butylamide benzyl alcohol (10 mmol) and thionyl chloride (11.4 mmol) were stirred in benzene (50 mL) at 40 °C for 2 h. The solvent was evaporated in vacuo, an oil was gotten and washed with hexanes (5× 10 ml). White crystals were gotten.

Yield: 1.6315 g (78.71%). ^{1}H NMR (acetone-d_6, 298 K): 7.81 (s, 1H, C–*H*, aromatic); 7.60 (d, 1H, C–*H*, aromatic); 7.28 (t, 1H, C–*H*, aromatic); 7.11 (d, 1H, C–*H*, aromatic); 4.67 (s, 2H, CH_2, benzyl); 2.36 (t, 2H, CH_2, *n*-butyl); 1.65 (m, 2H, CH_2, *n*-butyl); 1.37 (m, 2H, CH_2, *n*-butyl); 0.92 (t, 3H, CH_3, *n*-butyl). ^{13}C NMR (acetone-d_6, 298 K): 172.42 (*C*O); 141.18, 139.76, 130.21, 124.52, 120.51, 120.14 (aromatic); 47.32 (*C*H_2, benzyl); 37.80, 28.73, 23.40 (*C*H_2, *n*-butyl); 14.51 (*C*H_3, *n*-butyl). Anal. Calcd. for $C_{12}H_{16}ONCl$ (MW = 225.717): C, 63.86; H, 7.15; N, 6.21. Found: C, 64.12; H, 7.11; N, 6.23.

5.6. 1,3-Bis-(3-butylamidebenzyl)-imidazolium chloride (*3*)

The synthesis was done as reported method [21].

Yield: 0.3913 g (40%). ^{1}H NMR (acetone-d_6): 11.00 (s, 1H, N–*H*); 9.60 (s, 1H, C–*H*, backbone imidazolium); 8.19 (pd, 2H, C–*H*, aromatic); 7.76 (m, 1H, C–*H*, aromatic); 7.71 (pd, C–*H*, backbone imidazolium); 7.24 (pt, C–*H*, aromatic); 7.09 (pd, C–*H*, aromatic); 5.57 (s, CH_2, benzyl); 2.50 (t, CH_2, *n*-butyl); 1.63 (m, CH_2, *n*-butyl); 1.36 (m, CH_2, *n*-butyl); 0.91 (t, CH_3, *n*-butyl). ^{13}C NMR (acetone-d_6): 173.10 (*C*O); 142.66, 138.18, 130.31, 123.48, 120.73, 119.39 (aromatic benzyl); 135.69, 124.47 (*C*–H, imidazolium); 54.04 (*C*H_2, benzyl); 37.72, 28.98, 23.47 (*C*H_2, *n*-butyl); 14.65 (*C*H_3, *n*-butyl). Anal. Calcd. for $C_{27}H_{35}O_2N_4Cl$ (MW = 483.055): C, 67.13; H, 7.30; N, 11.60. Found: C, 64.65; H, 7.38; N, 11.03.

5.7. 1-Butyl-3-(3-butylamidebenzyl)-imidazolium chloride (*4*)

N-butyl imidazole (2 mmol) and 3-(butylamide)benzyl chloride (2 mmol) were made to react in toluene under reflux overnight. The compound was recrystallized from methanol–diethyl ether.

Yield: 0.7751 g (71.43%). ^{1}H NMR ($CDCl_3$): 9.94 (s, 1H, N–*H*); 9.69 (s, 1H, C–*H*, imidazolium); 7.50 (pd, 2H, C–*H*, aromatic); 7.18 (pd, 2H, C–*H*, backbone imidazolium); 6.79 (pt, 1H, C–*H*, aromatic); 6.72 (pd, 1H, C–*H*, aromatic); 5.03 (s, 2H, CH_2, benzyl); 3.87 (t, 2H, CH_2, *n*-butyl); 2.09 (t, 2H, CH_2, *n*-butylamide); 1.48 (m, 2H, CH_2, *n*-butylamide); 1.25 (m, 2H, CH_2, *n*-butylamide); 0.55 (t, 3H, CH_3, *n*-butylamide); 0.5 (t, 3H, CH_3, *n*-butyl). ^{13}C NMR ($CDCl_3$): 173.23 (*C*O); 140.28, 136.33, 129.59, 123.31, 120.76, 119.99 (aromatic benzyl); 133.70 (*C*–H, imidazolium); 122.59, 122.38 (*C*–H, backbone imidazolium); 53.39 (*C*H_2, benzyl); 49.68, 32.39, 19.36 (*C*H_2, *n*-butylimidazolium); 36.91, 27.78, 22.42 (*C*H_2, *n*-butylamide); 13.90 (*C*H_3, *n*-butylamide); 13.42 (*C*H_3, *n*-butylimidazolium). Anal. Calcd. for $C_{19}H_{28}ON_3Cl{\cdot}H_2O$ (MW = 367.918): C, 62.03; H, 8.22; N, 11.42. Found: C, 60.05; H, 7.90; N, 10.94.

5.8. {*1-Butyl-3-(3-butylamidebenzyl)-imidazolin-2-ylidine*}{*1,5-cyclooctadiene*}*chloro rhodium (I)*

Yield: 0.17 g (53.03%). ^{1}H NMR ($CDCl_3$): 7.84 (pd, 1H, C–*H*, aromatic); 7.56 (s, 1H, N–*H*); 7.51 (s, 1H, C–*H*, aromatic); 7.32 (pt, 1H, C–*H*, aromatic); 7.51 (pd, 1H, C–*H*, aromatic); 6.84 (d, 1H, C–*H*, backbone imidazolin); 6.69 (d, 1H, C–*H*, backbone imidazolin); 6.15 (d, 1H, J = 14.40, CH_2 benzyl); 5.29 (d, 1H, J = 16.01, CH_2 benzyl); 5.04 (m, 2H, C–*H*, cod); 3.34 (m, 2H, C–*H*, cod); 2.37 (m, 6H, CH_2, cod + *n*-butylimidazolin); 1.96 (m, 6H, CH_2, cod + *n*-butylamide); 1.7 (m, 2H, CH_2, *n*-butylimidazolin); 1.52 (m, 2H, CH_2, *n*-butylamide); 1.39 (m, 2H, CH_2, *n*-butylamide); 1.27 (m, 2H, CH_2, *n*-butylimidazolin); 1.07 (t, 3H, CH_3, *n*-butylimidazolin); 0.94 (t, 3H, CH_3, *n*-butylamide). ^{13}C

NMR ($CDCl_3$): 182.05 (d, N*C*N, $J_{Rh–C}$ = 51.50); 171.75 (*C*O); 138.93, 137.12, 129.36, 123.53, 120.74, 120.55 (aromatic); 119.57, 119.54 (*C*–H, backbone imidazolin); 98.62 (d, *C*–H, cod, $J_{Rh–C}$ = 6.84); 68.39 (d, *C*–H, cod, $J_{Rh–C}$ = 14.48); 68.15 (*C*–H, cod, $J_{Rh–C}$ = 14.48); 54.34 (*C*H_2, benzyl); 50.70, 28.87, 22.40 (*C*H_2, *n*-butylimidazolin); 37.52, 27.62, 20.19 (*C*H_2, *n*-butylamide); 32.97, 31.62 (*C*H_2, cod); 13.86 (*C*H_3, *n*-butylamide); 13.90 (*C*H_3, *n*-butylimidazolin). Anal. Calcd. for $C_{27}H_{39}ON_3ClRh$ (MW = 559.98): C, 57.91; H, 7.02; N, 7.50. Found: C, 57.92; H, 7.14; N, 7.29.

*5.9. [{1-Butyl-3-(3-butylamidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate (**9**).*

Yield: 0.048 g (57.49%). ^{1}H NMR ($CDCl_3$): 9.27 (s, 1H, N–*H*); 8.04 (d, 1H, C–*H*, aromatic); 7.50 (s, 1H, C–*H*, aromatic); 7.50, 7.42, 7.28 (m, 15H, C–*H*, aromatic phosphine); 6.99 (s, 1H, C–*H*, backbone imidazolin); 6.91 (s, 1H, C–*H*, backbone imidazolin); 6.50 (d, 1H, C–*H*, aromatic); 5.60 (d, 1H, C*H*$_2$, benzyl, *J* = 15.60); 4.87 (broad, 1H, C–*H*, cod); 4.64 (broad, 1H, C–*H*, cod); 4.27 (d, 1H, C*H*$_2$, benzyl, *J* = 15.20); 4.22 (broad, 2H, C–*H*, cod); 2.46 (m, 2H, C*H*$_2$, *n*-butylimidazolin); 2.30 (broad, 4H, C*H*$_2$, cod); 1.68 (m, 4H, C*H*$_2$, *n*-butylimidazolin and amide); 1.38 (broad, 4H, C*H*$_2$, *n*-butylimidazolin and amide); 0.91 (pt, 6H, C*H*$_2$, *n*-butyl imidazolin and amide). ^{13}C NMR (CD_2Cl_2): 177.81 (dd, N*C*N, $J_{Rh–C}$ = 49.80, $J_{P–C}$ = 14.59); 173.19 (*C*O); 141.00, 136.08, 130.11, 124.05, 123.01, 122.37 (aromatic benzyl); 134.32 (d, *C*–H, aromatic phosphine, $J_{P–C}$ = 11.44); 131.71, 131.72 (*C*–H, aromatic phosphine); 129.74 (d, *C*–H, aromatic phosphine, $J_{P–C}$ = 9.93); 120.30, 119.60 (*C*–H, backbone imidazolin); 98.50, 97.54 (t, *C*H, cod); 95.95 (d, *C*H, cod, $J_{Rh–C}$ = 7.12); 94.35 (d, *C*H, cod, $J_{Rh–C}$ = 7.09); 55.09 (*C*F_3); 54.50 (CH_2 benzyl); 31.43, 31.12, 30.91, 30.81 (*C*H_2, cod); 51.67, 32.53, 23.09 (*C*H_2, butyl imidazolin); 37.71, 28.42, 21.02 (*C*H_2, butyl amide); 14.39 (*C*H_3, butyl imidazolin); 14.21 (CH_3, butyl amide). ^{19}F NMR ($CDCl_3$): −78.58 (s, C*F*$_3$). ^{31}P NMR ($CDCl_3$): 27.21 ($J_{Rh–P}$ = 153.37). Anal. Calcd. for $C_{46}H_{54}O_4N_3SF_3PRh$ (MW = 935.86): C, 59.04; H, 5.82; N, 4.49. Found: C, 58.88; H, 6.03; N, 4.21.

5.10. 3-Butylester benzyl chloride

^{1}H NMR ($CDCl_3$): 7.24, 7.12, 7.02, 6.94 (m, 4H, C–*H*, aromatic); 4.45 (s, 2H, C*H*$_2$, benzyl); 2.45 (t, 2H, C*H*$_2$, butyl); 1.63 (m, 2H, C*H*$_2$, butyl); 1.34 (m, 2H, C*H*$_2$, butyl); 0.86 (t, 3H, C*H*$_3$ butyl). ^{13}C NMR ($CDCl_3$): 172.55 (*C*O, carbonyl); 151.31, 139.37, 130.08, 126.18, 122.71, 122.03 (aromatics); 45.91 (*C*H_2, benzyl); 34.49, 27.37, 22.65 (*C*H_2, butyl); 14.14 (*C*H_2 butyl). Anal. Calcd. for $C_{12}H_{16}O_3$ (MW = 208.26): C, 69.21; H, 7.74. Found: C, 64.33; H, 6.80.

5.11. 1-Butyl-3-(3-butylesterbenzyl)-imidazolium chloride

Yield: 0.3 g (96.74%). ^{1}H NMR (CD_2Cl_2): 10.27 (s, 1H, C–*H*, imidazolium); 7.60 (s, 1H, C–*H*, aromatic); 7.52 (s, 1H, C–*H*, backbone imidazolium); 7.40 (pd, 1H, C–*H*, aromatic); 7.28 (pt, 1H, C–*H*, aromatic); 7.24 (s, 1H, C–*H*, backbone imidazolium); 6.97 (pd, 1H, C–*H*, aromatic); 5.59 (2H, C*H*$_2$, benzyl); 4.17 (pt, 2H, C*H*$_2$, *N*-butylimidazolium); 2.47 (pt, 2H, C*H*$_2$, *n*-butylester); 1.73 (m, 2H, C*H*$_2$, *N*-butylimidazolium); 1.61 (m, 2H, C*H*$_2$, *n*-butylester); 1.33 (m, 2H, C*H*$_2$, *n*-butylester); 1.20 (m, 2H, C*H*$_2$, *N*-butylimidazolium); 0.87 (t, 3H, C*H*$_3$, *N*-butylimidazolium); 0.81 (t, 3H, C*H*$_3$, *n*-butylester). ^{13}C NMR (CD_2Cl_2): 172.87 (*C*O); 136.00 (*C*–H, imidazolium); 152.12, 138.97, 131.09, 127.03, 123.44, 122.99 (aromatic); 122.59, 122.39 (*C*–H, backbone imidazolium); 53.28 (*C*H_2, benzyl), 50.68, 32.71, 22.97 (*C*H_2, *n*-butylimidazolium); 34.69, 27.61, 20.25 (*C*H_2, *n*-butylester); 14.25 (*C*H_3, *n*-butylimidazolium); 13.96 (*C*H_3, *n*-butylester). Anal. Calcd. for $C_{29}H_{27}O_2N_2Cl$ (MW = 350.88): C, 65.05; H, 7.76; N, 7.98. Found: C, 63.44; H, 7.90; N, 7.94.

5.12. {1-Butyl-3-(3-butylesterbenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene} chloro rhodium (I)

Yield: 0.33 g (71.06%). ^{1}H NMR (CD_2Cl_2): 7.36, 7.28, 7.14, 7.05 (m, 4H, C–*H*, aromatic); 6.91 (d, 1H, C–*H*, backbone imidazolin); 6.74 (d, 1H, C–*H*, backbone imidazolin); 5.97 (d, 1H, C*H*$_2$ (benzyl), *J* = 15.21); 5.61 (d, 1H, C*H*$_2$ (benzyl), *J* = 14.80); 4.95 (broad, 2H, C–*H*, cod); 3.44 (q, 2H, C*H*$_2$, *n*-butylimidazolin); 3.30 (m, 2H, C–*H*, cod); 2.55 (t, 2H, C*H*$_2$, *n*-butylamide); 2.36 (m, 4H, C*H*$_2$, cod); 1.93 (m, 6H, C*H*$_2$, cod + *n*-butyl imidazolin); 1.71 (m, 2H, C*H*$_2$, *n*-butylamide); 1.50 (m, 2H, C*H*$_2$, *n*-butylamide); 1.44 (m, 2H, C*H*$_2$, *n*-butylimidazole); 1.056 (t, 3H, C*H*$_2$, *n*-butylimidazole); 0.967 (t, 3H, C*H*$_2$, *n*-butylamide). ^{13}C NMR (CD_2Cl_2): 183.72 (N*C*N, $J_{Rh–C}$ = 51.31); 172.88 (*C*O); 151.99, 139.43, 130.47, 126.48, 122.26, 122.15 (aromatic); 121.70, 121.22 (*C*–H, backbone imidazolin); 69.21 (*C*–H, cod, $J_{Rh–C}$ = 14.4); 68.60 (*C*–H, cod, $J_{Rh–C}$ = 14.10); 51.36 (*C*H_2, benzyl); 34.75, 29.47, 23.00 (*C*H_2, butylimidazolin); 33.73, 33.57 (*C*H_2, cod); 29.74, 27.71, 20.89 (*C*H_2, *n*-butylester); 14.44 (*C*H_3, *n*-butylimidazolin); 14.32 (*C*H_3, *n*-butylester). Anal. Calcd. for $C_{27}H_{38}O_2N_2ClRh$ (MW = 560.968): C, 57.81; H, 6.83; N, 4.99. Found: C, 56.83; H, 6.70; N, 4.95.

*5.13. [{1-Butyl-3-(3-butylesterbenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate **(10)***

Yield: 0.4 g (79.94%). ^{1}H NMR (CD_2Cl_2): 7.51, 7.42, 7.28 (m, 15H, C–*H*, aromatic phosphine); 7.37, 7.07, 6.81, 6.71 (m, 4H, C–*H*, aromatic benzyl); 7.00 (d, 1H, C–*H*, backbone imidazolin); 6.76 (d, 1H, C–*H*, backbone imida-

zolin); 5.60 (d, 1H, CH_2 (benzyl), J = 14.80); 4.50 (d, 1H, CH_2 (benzyl), J = 15.21); 4.83, 4.69 (2H, C–*H*, cod); 4.27 (broad, 2H, C–*H*, cod); 2.55 (t, 2H, CH_2, *n*-butylimidazolin); 2.46, 2.36, 2.24 (m, 8H, CH_2, cod); 1.70 (m, 2H, CH_2, *n*-butylester); 1.60 (m, 2H, CH_2, *n*-butylimidazolin); 1.40 (m, 2H, CH_2, *n*-butylester); 1.35 (m, 2H, CH_2, *n*-butylester); 1.30 (m, 2H, CH_2, *n*-butylimidazolin); 0.96 (t, 3H, CH_3, *n*-butylimidazolin); 0.93 (t, 3H, CH_3, *n*-butylester). ^{13}C NMR (CD_2Cl_2): 172.83 (carbonyl); 152.23, 136.80, 131.10, 125.64, 123.55, 122.89 (aromatic benzyl); 134.30 (d, aromatic phosphine, $J_{P–C}$ = 11.44 Hz); 131.89, 135.53 (aromatic phosphine); 129.83 (d, aromatic phosphine, $J_{P–C}$ = 9.81 Hz), 122.70, 122.02 (*C*–H, backbone imidazolin); 97.74 (t, *C*–H, cod); 97.66 (t, *C*–H, cod); 96.09 (d, *C*–H, cod, $J_{Rh–C}$ = 7.32); 94.99 (d, *C*–H, cod, $J_{Rh–C}$ = 6.95); 51.79 (*C*H_2, benzyl); 34.70, 27.63, 21.01 (*C*H_2, butylester); 32.59, 22.98, 15.88 (*C*H_2, butyl imidazolin); 14.28 (*C*H_3, butylester); 14.24 (*C*H_3, butylimidazolin). ^{19}F NMR (CD_2Cl_2): −79.39 (CF_3). ^{31}P NMR (CD_2Cl_2): 26.90 ($J_{Rh–C}$ = 155.05). Anal. Calcd. for $C_{46}H_{35}O_5N_2F_3PSRh$ (MW = 936.84): C, 58.98; H, 5.70; N, 2.99. Found: C, 58.03; H, 5.63; N, 3.02.

5.14. 4-Butylamide benzyl alcohol

Yield: 2.52 g (75%). ^{1}H NMR (acetone-d_6): 9.08 (s, 1H, N–*H*); 7.61 (d, 2H, C–*H*, aromatic); 7.26 (d, 2H, C–*H*, aromatic); 4.55 (s, 2H, CH_2, benzyl); 2.34 (t, 2H, CH_2, butyl); 1.64 (m, 2H, CH_2, butyl); 1.37 (m, 2H, CH_2, butyl); 0.91 (t, 3H, CH_3, butyl). ^{13}C NMR (acetone-d_6): 172.22 (*C*O); 139.69, 138.48, 128.27, 120.12 (aromatic); 64.74 (*C*H_2, benzyl); 37.81, 28.81, 23.42 (*C*H_2, butyl); 14.53 (*C*H_3, butyl). Anal. Calcd. for $C_{12}H_{17}O_2N$ (MW = 207.275): C, 69.54; H, 8.27; N, 6.76. Found: C, 69.50; H, 8.35; N, 6.76.

5.15. 4-Butylamide benzyl chloride

Yield: 2.5345 g (75.3%). ^{1}H NMR (acetone-d_6): 9.21 (s, 1H, N–*H*); 7.67 (pd, 2H, C–*H*, aromatic); 7.36 (pd, 2H, C–*H*, aromatic); 4.67 (s, 2H, CH_2, benzyl); 2.36 (t, 2H, CH_2, butyl); 1.65 (m, 2H, CH_2, butyl); 1.37 (m, 2H, CH_2, butyl); 0.91 (t, 3H, CH_3, butyl). ^{13}C NMR (acetone-d_6): 172.51 (*C*O); 141.07, 133.77, 130.59, 120.32 (aromatic); 47.23 (*C*H_2, benzyl); 37.85, 28.74, 23.40 (*C*H_2, butyl); 14.53 (*C*H_3, butyl). Anal. Calcd. for $C_{12}H_{16}ONCl$ (MW = 225.717): C, 63.86; H, 7.15; N, 6.21. Found: C, 63.89; H, 7.12; N, 6.15.

5.16. 1-Butyl-3-(4-butylamidebenzyl)-imidazolium chloride

Yield: 1.06 g (94.45%). ^{1}H NMR (DMSO-d_6): 10.26 (s, 1H, N–*H*); 9.42 (s, 1H, C–*H*, imidazolium); 7.86 (m, 2H, C–*H*, backbone imidazolium); 7.71 (d, 2H, C–*H*, aromatic); 7.40 (d, 2H, C–*H*, aromatic); 5.39 (s, 2H, CH_2, benzyl); 4.21 (t, 2H, CH_2, butylimidazolium); 2.36 (t, 2H, CH_2, butylamide); 1.81 (m, 2H, CH_2, butylimidazolium); 1.59 (m, 2H, CH_2, butylamide); 1.34 (m, 2H, CH_2, butylimidazolium); 1.28 (m, 2H, CH_2, butylamide); 0.93 (s, 6H, CH_3, butyl amide and imidazolium). ^{13}C NMR (DMSO-d_6): 171.91 (*C*O); 140.27, 129.36, 129.26, 119.63 (aromatic); 136.34 (*C*–H, imidazolium); 123.09, 122.79 (*C*–H, backbone imidazolium); 52.00 (*C*H_2, benzyl); 49.00, 31.62, 22.15 (*C*H_2, butylimidazolium); 36.42, 27.58, 19.16 (*C*H_2, butylamide); 14.10 (*C*H_3, butylimidazolium); 13.63 (*C*H_3, butylamide). Anal. Calcd. for $C_{19}H_{28}ON_3Cl$ (MW = 349.883): C, 65.22; H, 8.07; N, 12.00. Found: C, 65.25; H, 8.09; N, 11.95.

5.17. {1-Butyl-3-(4-butylamidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene} chloro rhodium (I)

Yield: 1.06 g (94.45%). ^{1}H NMR (CD_2Cl_2): 7.53 (pd, 3H, N–*H* and C–*H* aromatic); 7.34 (pd, 2H, C–*H*, aromatic); 6.87 (d, 1H, C–*H*, backbone imidazolin, J = 2.00); 6.67 (d, 1H, C–*H*, backbone imidazolin, J = 2.00); 5.97 (d, 1H, CH_2 (benzyl), J = 14.40); 5.47 (d, 1H, CH_2 (benzyl), J = 14.40); 4.94 (m, 2H, C–*H*, cod); 4.50 (m, 2H, CH_2, *n*-butylimidazolin); 3.32 (broad, 2H, C–*H*, cod); 2.40 (m, 2H, CH_2, butylamide); 2.33 (m, 4H, CH_2, cod); 1.89 (m, 6H, CH_2, cod and *n*-butylimidazolin); 1.66 (m, 2H, CH_2, butylamide); 1.49 (m, 2H, CH_2, *n*-butylimidazole); 1.38 (m, 2H, CH_2, *n*-butylamide); 1.04 (t, 3H, CH_3, *n*-butylimidazolin); 0.94 (t, 3H, CH_3, *n*-butylamide). ^{13}C NMR (CD_2Cl_2): 183.07 (N*C*N, $J_{Rh–C}$ = 51.31); 172.25 (*C*O); 139.18, 132.80, 129.67, 120.56 (aromatic); 121.49, 121.04 (*C*–H, backbone imidazolin); 98.82 (t, *C*–H, cod), 69.29 (*C*–H, cod, $J_{Rh–C}$ = 14.46); 68.56 (*C*–H, cod, $J_{Rh–C}$ = 14.46); 51.34 (*C*H_2, benzyl); 38.07, 29.41, 23.15 (*C*H_2, *n*-butylimidazolin); 29.79, 28.40, 20.89 (CH_2, *n*-butylamide); 33.37, 33.78 (*C*H_2, cod); 14.64 (CH_3, *n*-butylimidazolin); 14.39 (CH_3, *n*-butylamide). Anal. Calcd. for $C_{27}H_{39}ON_3RhCl$ (MW = 559.9645): C, 57.91; H, 7.02; N, 7.50. Found: C, 58.02; H, 7.20; N, 7.41.

*5.18. [{1-Butyl-3-(4-butylamidebenzyl)-imidazolin-2-ylidene}{1,5-cyclooctadiene}{triphenylphosphine} rhodium] trifluoromethanesulfonate (**13**)*

Yield: 0.59 g (70.66%). ^{1}H NMR (CD_2Cl_2): 8.63 (broad, 1H, N–*H*, amide); 7.67 (d, 2H, C–*H*, aromatic benzyl); 7.52, 7.42, 7.28 (m, 15H, C–*H*, aromatic phosphine); 6.93 (pd, 1H, C–*H*, backbone imidazolin, J = 1.60); 6.85 (d, 2H, C–*H*, aromatic benzyl); 6.71 (pd, 1H, C–*H*, backbone imidazolin, J = 2.00); 5.52 (pd, 1H, CH_2 (benzyl), J = 14.80); 4.82, 4.72 (broad, 2H, C–*H*, cod); 4.45 (pd, 1H, CH_2, benzyl, J = 14.40); 4.25 (broad, 2H, C–*H*, cod); 2.38 (m, 10H, CH_2, cod and butylamide); 1.64 (m, 4H, CH_2, butylamide and butylimidazolin); 1.36 (m, 4H, CH_2, butylamide and butylimidazolin); 0.92 (m, 6H, CH_3, butylamide and butylimidazolin). ^{19}F NMR (CD_2Cl_2): −79.34 (s, CF_3, trifluoromethanesulfonate). ^{31}P NMR (CD_2Cl_2): 26.86 (d, phosphine, $J_{Rh–P}$ = 154.56). ^{13}C NMR (CD_2Cl_2): 177.65 (dd, N*C*N, $J_{Rh–C}$ = 49.93, $J_{C–P}$ = 15.22); 173.16 (*C*O); 140.64, 131.49, 129.16, 120.92 (aromatic benzyl); 134.33 (d, aromatic phosphine, $J_{C–P}$ = 11.32); 131.86, 131.82 (*C*–H,

aromatic phosphine), 129.82 (d, aromatic phosphine, J_{C-P} = 9.56); 123.49, 122.27 (*C*–H, imidazolin); 97.97, 97.49 (*C*–H, cod); 95.82 (d, *C*–H, cod, J_{Rh-C} = 7.29), 94.8 (d, *C*–H, cod, J_{Rh-C} = 7.04); 54.98 (*C*F_3, trifluoromethanesulfonate); 51.76 (*C*H_2, benzyl); 37.73, 30.91, 23.13 (*C*H_2, butylimidazolin); 32.61, 28.43, 21.04 (*C*H_2, butylamide); 31.39, 31.06 (*C*H_2, cod); 14.44 (*C*H_3, butylimidazolin); 14.25 (*C*H_3, butylamide). Anal. Calcd. for $C_{46}H_{54}O_4N_3F_3SRh$ (MW = 904.84): C, 61.06; H, 6.02; N, 4.64. Found: C, 58.49; H, 5.93; N, 4.40.

5.19. 2-Butylamide benzyl alcohol

Yield: 1.40 g (83.18%). ^{1}H NMR (CD_2Cl_2): 8.55 (broad, 1H, N–*H*); 7.95 (pd, 1H, C–*H*, aromatic); 7.30 (pt, 1H, C–*H*, aromatic); 7.21 (pd, 1H, C–*H*, aromatic); 7.08 (pt, 1H, C–*H*, aromatic); 4.65 (pd, 2H, CH_2, benzyl); 2.80 (t, 1H, O*H*); 2.35 (t, 2H, CH_2, butylamide); 1.67 (m, 2H, CH_2, butylamide); 1.40 (m, 2H, CH_2, butylamide); 0.95 (t, 3H, CH_3, butylamide). ^{13}C NMR (CD_2Cl_2): 172.78 (*C*O); 138.32, 131.14, 129.68, 129.51, 124.97, 123.29 (aromatic); 64.87 (*C*H_2–OH); 38.30, 28.52, 23.14 (*C*H_2, butylamide); 14.40 (*C*H_3, butylamide). Anal. Calcd. for $C_{12}H_{17}O_2N$ (MW = 207.268): C, 69.54; H, 8.27; N, 6.75. Found: C, 69.31; H, 8.36; N, 6.74.

5.20. 2-Butylamide benzyl chloride

Yield: 0.30 g (61.22%). ^{1}H NMR (CD_2Cl_2): 7.75 (pd, 1H, C–*H*, aromatic); 7.40 (s-broad, 1H, N–*H*); 7.28 (m, 2H, C–*H*, aromatic); 7.08 (pt, 1H, C–*H*, aromatic); 4.55 (s, 2H, CH_2, benzyl); 2.33 (t, 2H, CH_2, butylamide); 1.63 (m, 2H, CH_2, butylamide); 1.35 (m, 2H, CH_2, butylamide); 0.88 (t, 3H, CH_3, butylamide). ^{13}C NMR (CD_2Cl_2): 172.19 (*C*O); 137.46, 130.79, 130.56, 129.40, 125.92, 125.31 (aromatic); 44.99 (CH_2, benzyl); 38.03, 28.44, 23.14 (CH_2, butylamide); 14.35 (CH_3, butylamide). Anal. Calcd. for $C_{12}H_{16}ONCl$ (MW = 225.71): C, 63.86; H, 7.15; N, 6.20. Found: C, 64.03; H, 7.20; N, 6.19.

5.21. 1-Butyl-3-(2-butylamidebenzyl)-imidazolium chloride

Yield: 0.25 g (59.72%). ^{1}H NMR (CD_2Cl_2): 10.34 (s, 1H, N–*H*); 9.66 (s, 1H, C–*H*, imidazolium); 7.55 (s, 1H, C–*H*, backbone imidazolium); 7.42 (s, 1H, C–*H*, backbone imidazolium); 7.36 (pd, 1H, C–*H*, aromatic); 7.27 (m, 2H, C–*H*, imidazolium); 7.10 (pt, 1H, C–*H*, aromatic); 5.57 (CH_2, benzyl); 4.10 (t, 2H, CH_2, butylamide); 2.48 (t, 2H, CH_2, butylimidazolium); 1.74 (m, 2H, CH_2, butylamide); 1.57 (m, 2H, CH_2, butylimidazolium); 1.27 (m, 4H, CH_2, butylamide); 0.86 (m, 6H, CH_3, butylimidazolium and butylamide). ^{13}C NMR (CD_2Cl_2): 207.33 (*C*–H, imidazolium); 174.54 (*C*O); 137.94, 137.29, 131.18, 130.56, 128.65, 127.04 (aromatic); 123.49, 122.46 (C–H, backbone imidazolium); 50.54 (*C*H_2, benzyl); 36.70, 31.37, 23.18 (*C*H_2, butylamide); 32.73, 28.66, 20.19 (*C*H_2, butylimidazolium); 14.54 (*C*H_3, butylamide); 13.94 (*C*H_3, butylimidazolium). Anal. Calcd. for $C_{19}H_{28}ON_3Cl$ (MW = 349.88): C, 65.22; H, 8.07; N, 12.00. Found: C, 59.36; H, 8.14; N, 11.99.

5.22. {1-Butyl-3-(2-butylamidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene} chloro rhodium (I)

Yield: 0.20 g (49.90%). ^{1}H NMR (CD_2Cl_2): 8.51 (s, 1H, N–*H*); 7.79 (d, 1H, C–*H*, aromatic); 7.37 (m, 2H, C–*H*, aromatic); 7.19 (m, 1H, C–*H*, aromatic); 6.83 (pd, 1H, C–*H*, backbone imidazolin, *J* = 2.00); 6.66 (d, 1H, CH_2, benzyl); 6.63 (d, 1H, C–*H*, backbone imidazolin, *J* = 2.00), 5.03 (d, 1H, CH_2, benzyl); 5.01, 4.88 (m, 2H, C–*H*, cod); 3.46, 3.28 (m, 2H, C–*H*, cod); 2.47 (m, 6H, CH_2, butylamide and cod); 2.24 (m, 2H, CH_2, butylimidazolin); 2.03 (m, 2H, CH_2, butylamide); 1.82 (m, 6H, CH_2, butylimidazolin and cod); 1.52 (m, 2H, CH_2, butylamide); 1.32 (m, 2H, CH_2, butylimidazolin); 1.06 (t, 3H, CH_3, butylamide); 0.90 (t, 3H, CH_3, butylimidazolin). ^{13}C NMR (CD_2Cl_2): 182.34 (N*C*N, J_{Rh-C} = 50.81); 173.56 (*C*O); 137.89, 131.73, 129.71, 127.20, 127.06, 125.58 (aromatic); 120.61, 121.27 (*C*–H, backbone imidazolin); 99.26 (d, *C*–H, cod, J_{Rh-C} = 7.04); 98.99 (d, *C*–H, cod, J_{Rh-C} = 6.92); 70.41 (d, *C*–H, cod, J_{Rh-C} = 14.81); 68.41 (d, *C*–H, cod, J_{Rh-C} = 14.54); 51.48 (*C*H_2, benzylic); 36.97, 31.66, 23.16 (*C*H_2, butylamide); 34.42, 33.93 (*C*H_2, cod); 32.76, 28.73, 20.89 (*C*H_2, butylimidazolin); 30.40, 29.10 (*C*H_2, cod); 14.53 (*C*H_3, butylamide); 14.35 (*C*H_3, butylimidazolin). Anal. Calcd. for $C_{27}H_{39}ON_3ClRh$ (MW = 559.96): C, 57.91; H, 7.02; N, 7.50. Found: C, 56.92; H, 6.95; N, 6.97.

5.23. [{1-Butyl-3-(2-butylamidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate (**12**)

Yield: 0.145 g (58.0%). ^{1}H NMR (CD_2Cl_2): 8.72 (broad, 1H, N–*H*); 7.40 (m, 17H, C–*H*, aromatic phosphine and benzyl); 7.08 (m, 1H, C–*H*, aromatic benzyl); 6.94 (s, 1H, C–*H*, backbone imidazolin); 6.78 (s, 1H, C–*H*, backbone imidazolin); 6.44 (d, 1H, C–*H*, aromatic benzyl); 5.79 (d, 1H, CH_2, benzyl); 4.84, 4.74 (broad, 2H, C–*H*, cod); 4.38 (d, 1H, CH_2, benzyl); 4.29, 4.21 (broad, 2H, C–*H*, cod); 2.27 (m, 12H, CH_2, butylamide and imidazolin, and cod); 1.74 (m, 2H, CH_2, butylamide); 1.60 (m, 2H, CH_2, butylimidazolin); 1.45 (m, 2H, CH_2, butylamide); 1.38 (m, 2H, CH_2, butylimidazolin); 0.96 (m, 6H, CH_3, butylamide and imidazolin). ^{31}P NMR (CD_2Cl_2): 27.09 (d, J_{Rh-P} = 155.60). ^{13}C NMR (CD_2Cl_2): 178.50 (dd, N*C*N, J_{Rh-C} = 52.50, J_{C-P} = 14.38); 173.51 (*C*O); 136.53, 132.97, 129.14, 127.84, 127.27, 126.84 (*C*–H, aromatic benzyl); 134.43 (d, *C*–H, aromatic phosphine, J_{C-P} = 11.47); 131.78, 131.64 (*C*–H, aromatic phosphine); 129.67 (d, *C*–H, aromatic phosphine, J_{C-P} = 9.55); 124.57, 122.18 (*C*–H, backbone imidazolin); 98.87, 96.84 (*C*–H, cod), 93.65 (*C*–H, cod); 51.72 (*C*F_3, trifluoromethanesulfonate); 51.57 (*C*H_2, benzyl); 36.94, 29.85, 23.31 (*C*H_2, butylamide); 32.78,

28.63, 21.03 (*C*H_2, butylimidazolin); 31.41, 31.17, 30.16 (CH_2, cod); 14.53 (CH_3, butylamide); 14.26 (CH_3, butylimidazolin). Anal. Calcd. for $C_{46}H_{54}O_4N_3F_3PSRh$ (MW = 935.84): C, 59.04; H, 5.82; N, 4.49. Found: C, 58.91; H, 5.75; N, 4.50.

5.24. 3-Butylsulfonamide benzyl alcohol

3-Butylamide benzyl alcohol (3.25 mmol) and 1-butanesulfonyl chloride (3.25 mmol) were stirring in pyridine (20 ml) at room temperature for 3 h. The solvent was evaporated in vacuo, an oil was gotten, which was purified by column with 1:1 acetone–hexanes as eluent.

Yield: 0.484 g (61.26%). ^{1}H NMR ($CDCl_3$): 0.74 (t, 3H, C*H*$_3$, butyl); 1.24 (m, 2H, C*H*$_2$, butyl); 1.63 (m, 2H, C*H*$_2$, butyl); 2.95 (pt, 2H, C*H*$_2$, butyl); 4.49 (s, 2H, C*H*$_2$, benzyl); 6.97, 7.05, 7.12 (m, 4H, C–*H*, aromatic); 7.87 (s, 1H, N–*H*). ^{13}C NMR ($CDCl_3$): 13.89 (*C*H$_3$, butyl); 21.75, 25.70, 51.72 (*C*H$_2$ butyl); 64.89 (*C*H$_2$ benzyl); 119.14, 119.59, 123.72, 130.09, 137.68, 143.06 (aromatic). Anal. Calcd. for $C_{11}H_{17}O_3NS$ (MW = 243.257): C, 54.31; H, 7.04; N, 5.76. Found: C, 53.62; H, 7.06; N, 5.58.

5.25. 3-Butylsulfonamide benzylchloride

3-Butylsulfonamide (1.64 mmol) and thionyl chloride (1.93 mmol) were stirring in toluene (20 ml) at 40 °C for 2 h. An oil was gotten, which was purified by column with 1:1 acetone–hexanes as eluent.

Yield: 0.316 g (73.41%). ^{1}H NMR ($CDCl_3$): 7.74 (broad, 1H, N–*H*); 7.19 (m, 4H, aromatic); 4.96 (dd, 2H, C*H*$_2$, benzyl); 3.10 (t, 2H, C*H*$_2$, butyl); 1.77 (m, 2H, C*H*$_2$, butyl); 1.37 (m, 2H, C*H*$_2$, butyl); 0.85 (t, 3H, CH_3, butyl). ^{13}C NMR ($CDCl_3$): 138.08, 137.09, 130.39, 125.65, 120.65, 120.41 (aromatic); 64.24 (*C*H$_2$, benzyl); 51.84, 25.70, 21.75 (*C*H$_2$, butyl); 13.91 (*C*H$_3$, butyl). Anal. Calcd. for $C_{11}H_{16}O_2NSCl$ (MW = 261.70): C, 50.49; H, 6.16; N, 5.35. Found: C, 52.78; H, 6.38; N, 5.23.

5.26. 1-Butyl-3-bis-(4-butylsulfonamidebenzyl)-imidazolium chloride

Yield: 0.24 g (81.23%). ^{1}H NMR (acetone-d_6): 10.55 (s, 1H, N–*H*); 10.28 (s, 1H, C–*H*, imidazolium); 7.91 (d, 2H, C–*H*, aromatic); 7.79 (s, 1H, C–*H*, aromatic); 7.53 (pd, 1H, C–*H*, backbone imidazolium); 7.25 (m, 2H, C–*H*, backbone imidazolium and aromatic); 5.66 (s, 2H, C*H*$_2$, benzyl); 4.39 (t, 2H, C*H*$_2$, sulfonamide); 3.14 (m, 2H, C*H*$_2$, imidazolium); 1.91 (m, 2H, CH_2, sulfonamide); 1.73 (m, 2H, C*H*$_2$, imidazolium); 1.36 (m, 2H, C*H*$_2$, sulfonamide); 1.11 (m, 2H, C*H*$_2$, imidazolium); 0.90 (m, 3H, CH_3, sulfonamide); 0.82 (m, 3H, C*H*$_3$, imidazolium). ^{13}C NMR (acetone-d_6): 141.57 (*C*–H, imidazolium); 138.55, 137.04, 130.76, 124.68, 123.95, 123.83, 121.97 (aromatic); 121.97, 121.60 (*C*–H, backbone imidazolium); 53.48 (*C*H$_2$, benzyl); 52.50, 33.13, 22.47 (*C*H$_2$, butylsulfonamide); 50.65, 26.56, 20.49 (*C*H$_2$, butylimidazolium); 33.13 (*C*H$_2$, butylsulfonamide); 14.35 (*C*H$_3$, butylimidazolium); 14.21 (*C*H$_3$, butylsulfonamide). Anal. Calcd. for $C_{18}H_{28}O_2N_3ClS$ (MW = 385.951): C, 56.02; H, 7.31; N, 10.81. Found: C, 53.32; H, 6.95; N, 8.46.

5.27. {1-Butyl-3-(4-butylsulfonamidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene} chloro rhodium (I)

Yield: 0.14 g (39.38%). ^{1}H NMR (CD_2Cl_2): 7.25 (s, 1H, N–*H*); 7.25 (m, 4H, aromatic); 6.91 (s, 1H, *C*–H, backbone imidazolium); 6.73 (s, 1H, C–H, backbone imidazolium); 5.98 (d, 1H, C*H*$_2$, benzyl); 5.50 (d, 1H, C*H*$_2$, benzyl); 4.95 (broad, 2H, C–*H*, cod); 4.51 (broad, 2H, C–*H*, cod); 3.32 (broad, 2H, C*H*$_2$, cod); 3.07 (t, 2H, C*H*$_2$, butylsulfonamide); 2.40 (pd, 2H, C*H*$_2$, butylimidazolin), 2.31(broad, 2H, cod); 1.84 (m, broad, 8H, C*H*$_2$, cod, butylsulfonamide and butylimidazolin); 1.49 (m, 2H, C*H*$_2$, butylsulfonamide); 1.36 (m, 2H, C*H*$_2$, butylimidazolin); 1.04 (t, 3H, C*H*$_3$, sulfonamide); 0.87 (t, 3H, C*H*$_3$, butylimidazoline). ^{13}C NMR (CD_2Cl_2): 183.31 (carbene), J_{Rh-C} = 51.43; 139.32, 138.82, 130.53, 125.01, 121.72, 121.32 (aromatic sulfonamide); 120.93, 120.65 (*C*–H, backbone imidazolin); 99.04 (d, *C*–H, cod, J_{Rh-C} = 6.79); 98.93 (d, *C*–H, cod, J_{Rh-C} = 6.79); 69.26 (d, *C*–H, cod, J_{Rh-C} = 14.46); 68.81 (d, *C*–H, cod, J_{Rh-C} = 14.46); 54.87 (*C*H$_2$, benzyl); 52.28, 31.39, 22.18 (*C*H$_2$, sulfonamide); 51.39, 26.16, 20.89 (CH_2, butylimidazolin); 33.70, 29.58 (*C*–H, cod); 33.70 (*C*H$_2$, butylimidazolin); 14.41 (*C*H$_3$, sulfonamide); 14.09 (*C*H$_3$, butylamide). Anal. Calcd. for $C_{26}H_{40}O_2N_3ClSRh$ (MW = 596.96): C, 52.31; H, 6.75; N, 7.04. Found: C, 52.99; H, 6.76; N, 6.87.

5.28. [{1-Butyl-3-(4-butylsulfonamide benzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate (**16**)

^{1}H NMR (CD_2Cl_2): 7.84 (broad, 1H, N–*H*); 7.41 (m, 17H, C–*H*, aromatic phosphine and benzyl); 7.15 (s, 1H, C–*H*, aromatic benzyl); 6.98 (pd, 1H, C–*H*, backbone imidazolin); 6.87 (pd, 1H, C–*H*, backbone imidazolin); 6.67 (pd, 1H, C–*H*, aromatic sulfonamide); 5.63 (d, 1H, C*H*$_2$, benzyl); 4.85 (broad, 1H, C–*H*, cod); 4.64 (broad, 1H, C–*H*, cod); 4.42 (d, 1H, C*H*$_2$, benzyl); 4.26 (broad, 2H, C–*H*, cod); 3.80, 4.26 (broad, 3H, C*H*$_2$, cod); 3.8 (m, 1H, C*H*$_2$, cod); 3.07 (pt, 2H, C*H*$_2$, sulfonamide); 2.35 (m, 8H, C*H*$_2$, cod and butylimidazolin); 1.75 (m, 2H, C*H*$_2$, sulfonamide); 1.59 (m, 2H, C*H*$_2$, butylimidazolin); 1.36 (m, 4H, C*H*$_2$, sulfonamide and butylimidazolin); 0.90 (q, 6H, C*H*$_3$, sulfonamide and butylimidazolin). ^{19}F NMR (CD_2Cl_2): −79.23 (SO_3CF_3). ^{31}P NMR (CD_2Cl_2): 26.90 (dd, J_{Rh-C} = 153.01). ^{13}C NMR (CD_2Cl_2): 178.07 (dd, N*C*N, J_{Rh-C} = 50.09, J_{C-P} = 14.68); 139.83, 137.11, 130.77, 124.01, 123.41, 122.62 (aromatic benzyl); 120.63, 120.36 (*C*–H, backbone imidazolin); 134.39 (d, aromatic phosphine, J_{P-C} = 11.47); 131.78,

131.41 (aromatic phosphine); 129.78 (d, aromatic phosphine, J_{P-C} = 9.66); 96.03, 95.96, 94.48, 94.41 (*C*–H, cod), 54.26 (*C*F_3, trifluromethanesulfonate), 53.70 (*C*H_2, benzyl); 52.47, 32.57, 22.26 (*C*H_2, sulfonamide); 51.69, 26.03, 21.03 (*C*H_2, butylimidazolin); 31.32, 31.23, 31.04, 30.73 (*C*H_2, cod); 14.09 (*C*H_3, butylsulfonamide); 13.88 (*C*H_3, butylimidazolin). Anal. Calcd. for $C_{45}H_{55}O_5N_3ClF_3S_2PRh$ (MW = 1008.39): C, 53.60; H, 5.50; N, 4.17. Found: C, 55.27; H, 5.63; N, 4.15.

5.29. N-(4-hydroxybutyl)benzamide

Yield: 1.58 g (79.46%). ^{1}H NMR ($CDCl_3$): 7.6 (m, 2H, aromatic); 7.2 (m, 3H, aromatic); 6.7 (broad, 1H, N–*H*); 3.5 (m, 2H, C*H*$_2$, butyl); 3.25 (m, 2H, C*H*$_2$, butyl), 2.9 (broad, 1H, O*H*); 1.5 (m, 4H, C*H*$_2$, butyl). ^{13}C NMR ($CDCl_3$): 168.26 (*C*O); 134.98, 131.77, 128.90, 127.33 (aromatic); 62.62, 40.25, 30.19, 26.62 (CH_2, butyl). Anal. Calcd. for $C_{11}H_{15}O_2N$ (MW = 193.24): C, 68.37; H, 7.82; N, 7.24. Found: C, 68.18; H, 7.65; N, 7.12.

5.30. N-(4-chlorobutyl)benzamide

Yield: 0.4 g (72.09%). ^{1}H NMR ($CDCl_3$): 7.7 (m, 2H, aromatic); 7.4 (m, 3H, aromatic); 6.2 (broad, 1H, N–*H*); 3.6 (m, 2H, C*H*$_2$, butyl); 3.4 (m, 2H, C*H*$_2$, butyl); 1.8 (m, 4H, C*H*$_2$, butyl). ^{13}C NMR ($CDCl_3$): 168.01 (*C*O), 134.96, 131.90, 129.02, 127.22 (aromatic); 45.04, 39.63, 30.28, 27.52 (*C*H_2, butyl). Anal. Calcd. for $C_{11}H_{14}ONCl$ (MW = 211.683): C, 62.41; H, 6.67; N, 6.61. Found: C, 62.55; H, 6.66; N, 6.48.

5.31. 1-Butyl-3-(4-benzylamidebutyl)-imidazolium chloride

^{1}H NMR ($CDCl_3$): 10.03 (broad, 1H, C–*H*, imidazolium); 8.64 (t, 1H, N–*H*); 7.96 (pd, 2H, aromatic); 7.62 (s, 1H, C–*H*, backbone imidazolium); 7.29 (m, 4H, C–*H*, aromatic and backbone imidazolium); 4.30 (t, 2H, C*H*$_2$, butylamide); 4.10 (t, 2H, C*H*$_2$, butylimidazolin); 3.40 (m, 2H, C*H*$_2$, butylamide); 1.89 (m, 2H, C*H*$_2$, butylamide); 1.73 (m, 2H, C*H*$_2$, butylamide); 1.61 (m, 2H, C*H*$_2$, butylimidazolium); 1.22 (m, 2H, CH_2, butylimidazolium); 0.82 (t, 3H, CH_3, butylimidazolium). ^{13}C NMR ($CDCl_3$): 168.04 (*C*O); 137.63 (*C*–H, imidazolium); 134.48, 131.63, 128.70, 128.08 (aromatic); 123.18, 122.04 (*C*–H, backbone imidazolium); 50.29, 38.44, 28.04, 26.00 (*C*H_2, butylamide); 49.74, 32.54, 19.84 (*C*H_2, butylimidazolium); 13.83 (*C*H_3, butylimidazolium). Anal. Calcd. for $C_{18}H_{26}ON_3Cl$ (MW = 335.856): C, 64.37; H, 7.80; N, 12.51. Found: C, 58.52; H, 8.30; N, 11.60.

5.32. {1-Butyl-3-(4-benzylamidebutyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene} chloro rhodium (I)

Yield: 0.07 g (84.44%). ^{1}H NMR (CD_2Cl_2): 7.89 (m, 2H, aromatic benzyl); 7.57 (t, 1H, N–*H*); 7.40 (m, 3H, aromatic benzyl); 6.89 (s, 2H, C–*H*, backbone imidazolin); 5.05 (m, 1H, C*H*$_2$, butylamide); 4.88 (broad, 2H, C–*H*, cod); 4.5 (m, 2H, C*H*$_2$, butylamide); 4.01 (m, 1H, C*H*$_2$, butylamide); 3.67 (m, 2H, C*H*$_2$, butylimidazolin); 3.35, 3.27 (broad, 2H, C–*H*, cod); 2.42 (m, 4H, C*H*$_2$, cod); 1.82 (m, 10H, C*H*$_2$, cod, butylamide and butylimidazolin); 1.48 (m, 2H, CH_2, butylimidazolin); 1.04 (t, 3H, CH_3, butylimidazolin). ^{13}C NMR (CD_2Cl_2): 181.58 (N*C*N, J_{Rh-C} = 51.06); 167.89 (*C*O); 134.60, 131.21, 120.87, 120.83 (aromatic); 128.63, 127.80 (*C*–H, backbone imidazolin); 98.69, 98.59, 69.09, 68.45 (C–H, cod); 51.13, 49.80, 38.61, 33.66 (CH_2, cod); 33.29, 33.00, 31.96, 29.68, 28.89, 25.74, 20.56 (CH_2, butylimidazolin and butylamide); 14.22 (CH_3, butylimidazolin and butylamide). Anal. Calcd. for $C_{27}H_{39}ON_3Cl_3RhCH_2Cl_2$ (MW = 630.889); C, 51.40; H, 6.23; N, 6.66. Found: C, 53.25; H, 6.30; N, 6.98.

5.33. [{1-Butyl-3-(4-benzylamidebutyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate (**14**)

^{1}H NMR ($CDCl_3$): 8.01 (m, 2H, aromatic amide); 7.91 (t, 1H, N–*H*); 7.47, 7.40 (m, 12H, aromatic amide and phosphine); 7.20 (m, 7H, aromatic phosphine); 7.29, 6.89 (backbone imidazolium); 4.71 (m, 2H, C–*H*, cod); 4.22 (m, 4H, C–H cod and CH_2, *n*-butyl); 3.67, 3.46 (m, 4H, CH_2, butyl); 2.4 (m, 10H, CH_2, cod and butyl); 1.73, 1.50 (m, 4H, CH_2, butyl); 1.31 (m, 4H, CH_2, butyl); 0.92 (t, 3H, CH_3, butyl). ^{19}F NMR ($CDCl_3$): −78.65 (SO_3CF_3). ^{31}P NMR ($CDCl_3$): 26.85 (J_{Rh-P} = 155.44). ^{13}C NMR ($CDCl_3$): 175.99 (dd, N*C*N, J_{Rh-C} = 49.43, J_{P-C} = 15.72); 168.08 (*C*O); 134.73, 131.03, 128.68, 127.86 (aromatic amide); 123.12, 121.70 (backbone imidazole); 133.80 (d, aromatic phosphine, J_{C-P} = 11.70); 131.41, 131.36 (aromatic phosphine); 129.39 (d, aromatic phosphine, J_{C-P} = 9.68); 97.60, 96.57 (C–H, cod); 95.08 (d, C–H, cod, J = 6.29); 93.78 (d, CH, cod, J = 6.67); 51.15 (SO_3CF_3), 50.95, 39.61, 32.16, 31.32, 27.72, 27.03, 20.65 (CH_2, butyl); 31.03, 30.94, 30.75, 30.48 (CH_2, cod); 14.06 (CH_3, butyl).

5.34. 3-(N-butyl)amide benzyl chloride

Yield: 0.91 (38.11%). ^{1}H NMR ($CDCl_3$): 7.7 (s, 1H, C–*H*, aromatic); 7.6 (pd, 1H, C–*H*, aromatic); 7.4 (pd, 1H, C–*H*, aromatic); 7.3 (pt, 1H, C–*H*, aromatic); 6.1 (s, 1H, broad, N–*H*); 4.5 (s, 2H, C*H*$_2$–Cl); 3.4 (m, 2H, C*H*$_2$, butylamide); 1.5 (m, 2H, C*H*$_2$, butylamide); 1.4 (m, 2H, C*H*$_2$, butylamide); 0.9 (t, 3H, C*H*$_3$, butylamide). ^{13}C NMR ($CDCl_3$): 167.36 (carbonyl); 138.41, 135.87, 131.81, 129.45, 127.53, 127.11 (aromatic); 46.05 (*C*H_2–Cl); 40.29, 32.13, 20.57 (*C*H_2); 14.21 (*C*H_3). Anal. Calcd. for $C_{12}H_{16}ONCl$ (MW = 225.72): C, 63.85; H, 7.15; N, 6.21. Found: C, 63.61; H, 7.15; N, 6.08.

5.35. 1-Butyl-3-(4-(N-butyl)amidebenzyl)-imidazolium chloride

Yield: 0.16 g (42.38%). ^{1}H NMR ($CDCl_3$): 10.40 (broad, 1H, C–*H*, imidazolium); 8.53 (broads, 1H, broad, N–*H*); 8.31

(s, 1H, C–*H*, aromatic); 7.84 (d, 1H, C–*H*, aromatic); 7.72 (s, 1H, C–H, backbone imidazolium); 7.50 (d, 1H, C–*H*, aromatic); 7.24 (m, 2H, C–*H*, backbone imidazolium and aromatic); 5.58 (s, 2H, CH_2, benzyl); 4.14 (m, 2H, CH_2–NH); 3.32 (m, 2H, CH_2, butylimidazolium); 1.93 (m, 2H, CH_2, butylamide); 1.55 (m, 2H, CH_2, butylimidazolium); 1.26 (m, 4H, CH_2, butylamide and butylimidazolium); 0.82 (m, 6H, CH_3, butylamide and butylimidazolium). ^{13}C NMR ($CDCl_3$): 167.02 (*C*O); 133.81 (*C*–H, imidazolium); 137.45, 136.31, 131.73, 129.63, 129.37, 128.55 (aromatic benzyl); 123.03, 122.25 (*C*–H, backbone imidazolium); 53.29 (*C*H_2, benzyl); 50.26, 32.32, 20.67 (*C*H_2, imidazolium); 40.31, 31.35, 19.82 (*C*H_2, amide); 14.23 (*C*H_3, imidazolium); 13.77 (*C*H_3, amide). Anal. Calcd. for $C_{19}H_{28}ON_3Cl$ (MW = 349.88): C, 65.22; H, 8.07; N, 12.00. Found: C, 62.43; H, 8.02; N, 11.33.

5.36. {1-Butyl-3-(4-(N-butyl)amidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene} chloro rhodium (I)

Yield: 0.166 g (94.20%). ^{1}H NMR (CD_2Cl_2): 8.10 (s, 1H, N–*H*); 7.86, 7.51, 7.42 (m, 4H, aromatic benzyl); 6.91 (d, 1H, C–*H*, backbone imidazolin, $J_{H–H}$ = 2.00); 6.77 (d, 1H, C–*H*, imidazolin, $J_{H–H}$ = 2.00); 6.41 (d, 1H, CH_2, benzyl, $J_{H–H}$ = 14.40); 5.07 (d, 1H, CH_2, benzyl, $J_{H–H}$ = 14.40; 4.97 (m, 2H, C–*H*, cod); 4.56 (t, 2H, CH_2, amide); 3.40, 3.32 (m, 4H, C–*H*, cod and CH_2–N imidazolin); 2.42 (m, 4H, CH_2, cod); 1.91, 1.87 (m, 6H, CH_2, cod and amide); 1.53 (m, 4H, CH_2, imidazolin and amide); 1.35 (m, 2H, CH_2, imidazolin); 1.05 (t, 3H, CH_3, imidazolin); 0.90 (t, 3H, CH_3, amide). ^{13}C NMR (CD_2Cl_2): 182.96 (d, carbene, $J_{Rh–C}$ = 51.56); 167.02 (*C*O); 137.62, 136.21, 130.77, 129.29, 128.59, 127.36 (aromatic benzyl); 122.19, 121.26 (*C*–H, backbone imidazolin); 99.57 (d, *C*–H, cod, $J_{Rh–C}$ = 6.79); 99.29 (d, *C*–H, cod, $J_{Rh–C}$ = 6.84); 69.38 (dd, *C*–H, cod, $J_{Rh–C}$ = 14.68); 51.44 (*C*H_2, benzyl); 40.38, 29.74, 21.02 (*C*H_2, butylamide); 33.79, 33.55 (*C*H_2, cod); 29.74, 29.46, 20.89 (*C*H_2, amide); 14.43 (*C*H_3, butylamide); 14.37 (*C*H_3, butylimidazolin). Anal. Calcd. for $C_{27}H_{39}ON_3ClRh$ (MW=559.96): C, 57.91; H, 7.02; N, 7.50. Found: C, 57.62; H, 7.03; N, 7.31.

*5.37. [{1-Butyl-3-(4-(N-butyl)amidebenzyl)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate (**15**)*

^{1}H NMR (CD_2Cl_2): 7.75 (1H, N–*H*); 7.76 (m, 1H, aromatic amide); 7.34, 7.43 (m, 3H, aromatic amide); 7.51, 7.43, 7.31 (m, 15H, aromatic phosphine); 6.98 (d, 1H, C–*H*, backbone imidazolin, $J_{H–H}$ = 2.00); 6.86 (d, 1H, C–*H*, backbone imidazolin, $J_{H–H}$ = 2.00); 7.04, 6.89 (m, 2H, C–*H*, cod); 4.85, 4.68 (broad, 2H, C–*H*, cod); 5.69 (d, 1H, CH_2, benzyl, J_{gem} = 15.00); 4.65 (d, 1H, CH_2, benzyl, J_{gem} = 15.00); 3.39, 2.40, 1.59, 1.40, 1.36 (m, 12H, CH_2, imidazolin and amide); 2.44, 2.23 (m, 8H, CH_2, cod); 0.95 (pt, 6H, CH_3, imidazolin and amide). ^{19}F NMR (CD_2Cl_2): −79.04. ^{31}P NMR (CD_2Cl_2): 26.76 ($J_{Rh–P}$ = 146.16). ^{13}C NMR (CD_2Cl_2): 178.04 (dd, N*C*N, $J_{Rh–C}$ = 50.05, $J_{P–C}$ = 14.34; 167.19 (*C*O); 136.97, 135.92, 130.36, 129.88, 127.87, 127.85 (aromatic amide); 134.34 (d, aromatic phosphine, $J_{C–P}$ = 11.44); 131.78, 131.48 (aromatic phosphine); 129.79 (d, aromatic phosphine, $J_{C–P}$ = 9.68); 124.02, 122.50 (backbone imidazolin); 97.98, 97.63 (*C*–H, cod); 96.21 (d, *C*–H, cod, *J* = 7.32); 94.46 (d, *C*–H, cod, *J* = 7.31); 54.96 (*C*H_2, benzyl); 51.71, 32.58, 21.02 (*C*H_2, butylimidazolin); 31.52, 31.07, 30.95, 30.85 (*C*H_2, cod); 40.55, 32.38, 20.95 (*C*H_2, butylamide); 14.36 (*C*H_3, butylimidazolin); 14.22 (*C*H_3, butylamide). Anal. Calcd. for $C_{46}H_{54}O_4N_3F_3SPRhCH_2Cl_2$ (MW = 1020.818): C, 55.30; H, 5.53; N, 4.12. Found: C, 56.51; H, 5.61; N, 4.19.

5.38. 4-Butyl(N-methyl)amide benzyl alcohol

^{1}H NMR ($CDCl_3$): 7.33 (pt, 1H, aromatic), 7.27 (pd, 1H, aromatic), 7.14 (s, 1H, aromatic), 7.01 (pd, 1H, aromatic); 4.67 (s, 2H, CH_2 benzyl); 3.18 (s, 3H, N–CH_3); 2.00, 1.47, 1.13 (CH_2, butyl); 0.73 (CH_3, butyl). ^{13}C NMR ($CDCl_3$): 173.88 (*C*O); 144.80, 143.52, 130.15, 126.60, 126.39, 125.87 (aromatic); 64.79 (*C*H_2–OH); 37.75, 28.06, 22.75 (*C*H_2, butyl); 34.18 (N–*C*H_3); 14.17 (*C*H_3, butyl). Anal. Calcd. for $C_{13}H_{19}O_2N$ (MW = 221.299): C, 70.56; H, 8.65; N, 6.33. Found: C, 69.10; H, 8.71; N, 6.15.

5.39. [{1-Butyl-3-(4-butyl, N-methylamide)-imidazolin-2-ylidine}{1,5-cyclooctadiene}{triphenylphosphine} rhodium (I)] trifluoromethanesulfonate

^{1}H NMR ($CDCl_3$): 7.43, 7.35, 7.22, 7.07 (m, 19H, aromatic phosphine and benzyl); 7.03, 6.77 (d, 2H, C–*H*, backbone imidazolin); 5.55, 4.66 (d, 2H, CH_2, benzyl); 4.76, 4.66, 4.17 (broad, 4H, C–*H*, cod); 3.09 (broad, 3H, N–CH_3); 3.68, 1.55, 1.28 (m, 6H, CH_2, butylimidazolin); 1.89, 1.45, 1.15 (broad, 6H, CH_2, butylamide); 0.84 (pt, 3H, CH_3, butylimidazolin); 0.75 (broad, 3H, CH_3, butylamide). ^{31}P NMR ($CDCl_3$): 26.89 ($J_{Rh–P}$ = 153.29). ^{19}F NMR ($CDCl_3$): −78.52 (SO_3CF_3). ^{13}C NMR (CD_2Cl_2): 175.01 (*C*O); 146.11, 131.71, 131.38, 127.04, 123.43, 122.89 (aromatic benzyl); 134.30 (pd, aromatic phosphine, $J_{P–C}$ = 11.44); 131.92 (s, aromatic phosphine); 129.85 (pd, aromatic phosphine, $J_{P–C}$ = 9.68); 123.13, 120.58 (*C*–H, backbone imidazolin); 97.66, 97.58, 95.87, 95.27 (*C*–H, cod); 51.81 (*C*H_2, benzyl); 34.61, 31.31, 23.17 (*C*H_2, butylimidazolin); 32.56 (N–*C*H_3); 31.00, 30.79 (CH_2, cod); 29.85, 28.24, 21.02 (*C*H_2 butylamide); 14.40 (CH_3, butylimidazolin); 14.22 (CH_3, butylamide). Anal. Calcd. for $C_{47}H_{56}O_4N_3F_3PSRhCH_2Cl_2$ (MW = 1034.844): C, 55.71; H, 5.65; N, 4.06. Found: C, 53.92; H, 5.43; N, 3.95.

5.40. Control experiments (Table 12)

All manipulations were done under inert atmosphere. (1) Entry 1: *n* = 0.01. 0.65 mmol of each substrate was added to a round Schlenk and dissolved in 3 ml of dried THF, then 0.0065 mmol of catalyst **9**, 0.0065 mmol of sodium tetrafluoroborate and 5 ml of dried THF were added and refluxed

for 20 min. The solvent was evaporated and 0.024 of 1,3,5 tri-*tert*-butyl-benzene as internal standard was used. (2) Entry 2: $n = 0.005$. The procedure was the same as in the last case, but 1.30 mmol of each substrate and 0.013 mmol of catalyst were used. (3) Entry 3: $n = 0.003$. Following the same procedure 1.96 mmol of each substrate and 0.0196 mmol of catalyst were used.

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