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Chiral Oxazoline-NHC Ligands with and without CR_2 Bridges: A Comparative Study in Rhodium Hydrosilylation Catalysis

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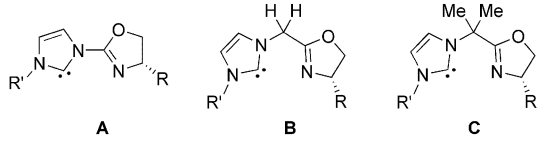
A series of bidentate oxazoline-NHC ligands has been synthesized in which the two heterocycles are connected by a CH_2 linker. The corresponding rhodium(I) complexes were prepared by direct deprotonation of the imidazolium halide salts followed by the addition of a solution of $[Rh(nbd)Cl]_2$ at low temperature. The cationic square planar rhodium complexes were generated by halide abstraction via addition of an excess of KPF_6 in a CH_2Cl_2/water solvent system. Alternatively, the deprotonation of the imidazolium hexafluorophosphates and reaction with $[Rh(nbd)Cl]_2$ directly gave the complex cations. These as well as oxazoline-NHC systems, in which the two heterocycles are directly connected or through a CMe_2 bridge, were investigated in the rhodium-catalyzed hydrosilylation of acetophenone. The comparison of the three ligand families showed that the catalysts obtained by direct coupling of oxazolines and N-heterocyclic carbenes, generating highly rigid chelate ligands, remain the most efficient systems giving the secondary alcohols in high enantioselectivity.

Introduction

N-Heterocyclic carbenes[1] are excellent "anchor" units for late transition metals which form strong metal–carbon bonds[2] and have thus been widely applied in homogeneous catalysis.[3] Since among all the stereoinducing elements used for the design of efficient chiral ligands, the oxazoline ring has become one of the most commonly employed,[4] N-heterocyclic carbenes (NHC) may be combined with such ligating units to develop efficient asymmetric catalysis.[5,6] The first example of such a combination was provided by Herrmann et al. who reported the bidentate ligand **B** in which the two heterocycles are connected by a methylene bridge (Scheme 1).[7] Preliminary investigations of the corresponding Rh^I complexes established their activity as catalysts in the hydrosilylation of ketones, albeit with low enantioselectivities (*ee* values up to 11%).[8] More recently, Pfaltz et al. developed an alternative synthesis of such ligands; their Ir^I complexes were tested in alkene hydrogenations and gave moderate to high enantioselectivities (*ee* values up to 90%).[9] We reported the direct coupling of oxazolines and N-heterocyclic carbenes generating highly rigid type **A** chelate ligands.[10] This strategy provided the key to a highly efficient class of catalysts for the asymmetric hydrosilylation of ketones[11] and confirmed the considerable potential of combining a N-heterocyclic carbene with oxazoline. However, this class of ligands imposes a rather constrained geometry upon coordination which limits its applicability for a broad range of transition metals.[12]



Scheme 1.

Recently, we reported the synthesis of the NHC-oxazoline ligands **C** in which the two heterocycles are connected by a (dimethyl)methylene bridge.[13] In comparison with the **B**-type ligands, the methyl groups on the methylene bridge were found to kinetically stabilize the bridge under the conditions of molecular catalysis. However, these systems display low activity in catalytic hydrosilylations of ketones. In the light of the recent results reported by Pfaltz et al., we decided to (re)investigate the potential of the **B**-type ligand by generating a library of such ligands. Three alternative syntheses of **B** have been employed to allow the introduction of a range of substituents on the imidazolyl ring or to vary the nature of the counter-anion. We report herein the synthesis and coordination of chiral carbene precursors of type **B** NHCs as well as the results of a comparative study into their use in the catalytic hydrosilylation of acetophenone.

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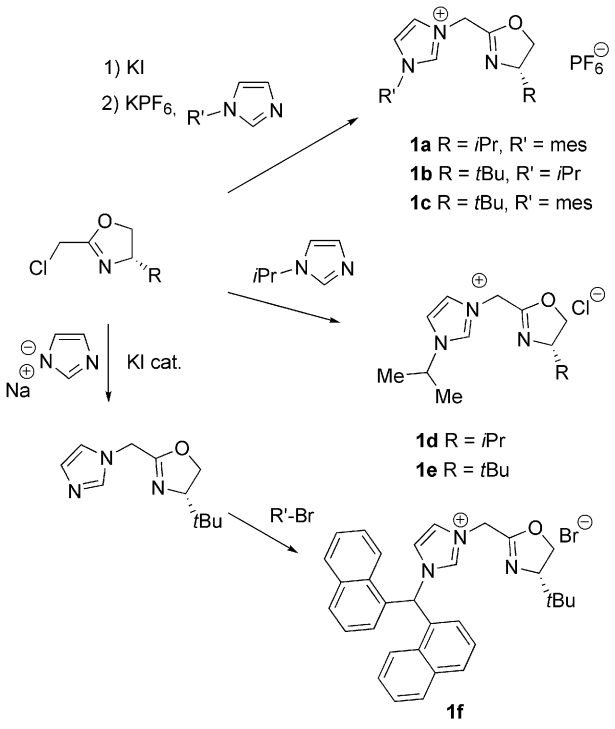
Results and Discussion

Synthesis of the Ligand Precursors

In order to generate a library of type **B** carbene ligands, three different synthetic procedures have been employed (Scheme 2), the key reactant being chloromethyl oxazoline, which is obtained by condensation of chloroacetyl chloride and the chiral amino alcohol [(*S*)-valinol or (*S*)-*tert*-leucinol], followed by ring closure using Burgess' reagent.[9,14]



Scheme 2. General synthesis of the imidazolium salts.

After its conversion to the corresponding iodomethyl oxazoline via a Finkelstein reaction, the coupling with substituted imidazoles in the presence of KPF_6, led to the imidazolium salts **1a**–**c**. Chloromethyl oxazoline derivatives also react directly with several substituted imidazoles to give the imidazolium salts **1d**,**e**. Alternatively, a chiral imidazole derivative was first prepared by reaction with sodium imidazolide in presence of a catalytic amount of potassium iodide. The neutral compound was then converted into the imidazolium salt **1f** upon coupling with bromobis(1-naphthyl)-methane (R′-Br in Scheme 2). Further, Pfaltz et al. have reported the analogous BARF salts of **1b**, **1c** and **1e**.[9] All imidazolium salts **1a**–**f** were isolated as air-sensitive white powders. The ^1H and ^{13}C NMR spectra are consistent with the proposed structure of the molecule, with the typical downfield shifted signal of the C2-*H* proton of the imidazolium ring [for example, δ = 8.93 (**1c**); 11.25 (**1e**); 9.91 (**1f**)]. Remarkable is the dependence of the chemical shift of this signal on the counterion. While the presumably weakly coordinating counterion hexafluorophosphate gives rise to a proton signal in the expected region for aromatic protons, the smaller chloride ion causes the signal of the C2-*H* proton to shift to lower field. In a sample of **1e** the exchange of chloride in favour of hexafluorophosphate, which yields **1b**, showed a difference between the shifts of $\Delta\delta$ = 2.08 ppm. Similar observations were encountered during the investigation of ionic liquids.[15] Intense molecular ion peaks $[M - \text{counter anion}]^+$ were observed in the mass spectra of all compounds, whilst the IR vibrational bands $\nu_{(C=N)}$ of the oxazoline units were found between 1691–1675 cm^{-1}. Suitable crystals for an X-ray diffraction analysis of **1d**′ (**1d** with PF_6^- as counterion instead of Cl^-) were obtained to establish its structural details (Figure 1). There are two independent molecules in the unit cell which differ mainly in the rotational orientation of the isopropyl groups. The planar imidazole and oxazoline rings are almost orthogonal to each other [angles between normals to planes 83.8(1) and 81.6(2)°].

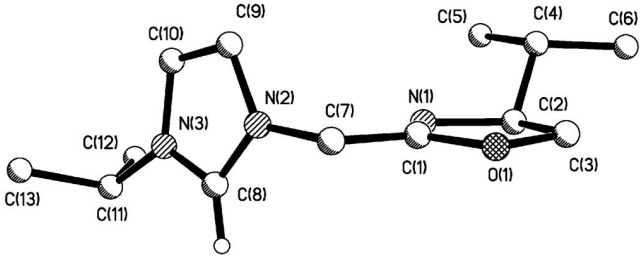
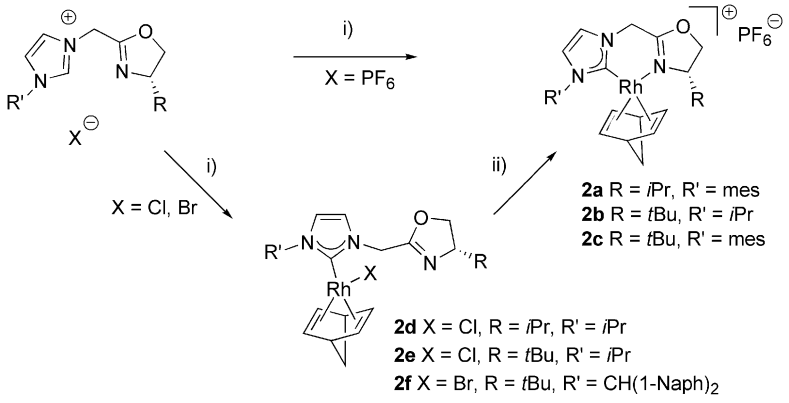


Figure 1. Molecular structure of the imidazolium salt **1d**′ [counterion PF_6^- and hydrogen atoms, except for C(8)–H, are omitted for clarity]. Selected bond lengths [Å] and angles [°] (values in square brackets refer to the second cation): N(2)–C(8) 1.322(3) [1.337(3)], N(3)–C(8) 1.328(4) [1.319(4)], N(1)–C(1) 1.247(4) [1.247(4)], N(2)–C(8)–N(3) 109.0(3) [108.4(3)], C(8)–N(2)–C(7)–C(1) 93.7(3) [–98.2(3)], N(2)–C(7)–C(1)–N(1) –2.6(4) [4.9(4)].

Preparation and Structure of the Rhodium Complexes

The protioligands **1a**–**f** were metallated with rhodium norbornadiene (nbd) derivatives which had previously been found to give rise to more active catalysts in the hydrosilylation of ketones than their cyclooctadiene analogues (Scheme 3).[11] The complexes could be obtained by direct deprotonation of the imidazolium halide salt by KHMDS followed by the addition of a solution of $[Rh(nbd)Cl]_2$ at low temperature. All complexes were isolated as pure solids, fully characterized by elemental analysis and NMR spectroscopy, and were found to be relatively stable in air. Diagnostic for the formation of the carbene complexes was the observation of the ^{13}C NMR signals of the carbene carbon nuclei at δ = 188–175 ppm with coupling constants $J_{Rh\text{-}C}$ of ca. 58 Hz.

The rhodium complexes display fluxional behaviour on the NMR time scale at 295 K, and their complete NMR characterization was thus performed at 263 K, only one set of signals being observed at that temperature. For complexes **2d**–**f**, the resonances of the oxazolinyl ring protons and the N*C*O ^{13}C nuclei have chemical shifts similar to those observed in the corresponding imidazolium salt which indicates that the oxazoline is probably not coordinated to



Scheme 3. Synthesis of neutral and cationic rhodium(I) complexes.

the metal centre in solution at 263 K. In contrast to the NHC-resonances, which are exchange broadened at 295 K, the oxazolyl signals are sharp indicating a free rotation around the methylene bridge. The broad signals of the NHC protons at 295 K are a consequence of the hindered rotation of the bis(α-naphthyl)substituents, which influences the chemical shifts of the norbornadiene unit by an aromatic ring current effect. In case of the isopropyl and *tert*-butyl derivatives **2d** and **2e** the NHC-resonances appear sharp, while the nbd-signals are broadened. In the IR spectrum the vibrational band at 1678 cm^{-1} is assigned to the $\nu_{C=N}$ stretching mode of a non-coordinated oxazoline. The monomolecular structure is confirmed by the intense MS-molecular peaks $[M - Br]^+$, $[M - nbd - Br]^+$ and $[M - Cl]^+$ as well.

The molecular structure of **2e**, established by X-ray diffraction, confirms a monodentate coordination of the NHC/oxazoline carbene ligand (Figure 2). No less than four independent molecules are found in the monoclinic unit cell of **2e**. The structural differences between the individual molecules can be characterized by (i) a 180° rotation of the N-heterocyclic carbene ligand around the Rh–C(carbene) bond and (ii) a much smaller intra-ligand rotation centered on the methylene group which joins the two heterocycles.

The coordination geometry around the metal centre is approximately square planar, as observed in other structures of neutral NHC-Rh^I complexes,[16] with the CC vectors of the norbornadiene carbon carbon double bonds perpendicular to the coordination plane. The observed minor distortion is attributed to the rigidity and the small bite angle of the nbd ligand. To minimize steric hindrance, the imidazolyl rings in all independent molecules are twisted by almost 90° out of the coordination plane. The $C_{carbene}$–Rh bond lengths range from 2.025(4) to 2.036(4) Å and agree well with data reported in the Cambridge Structural Database[17] for NHC-Rh^I complexes (mean distance $C_{carbene}$–Rh^I = 2.035 Å for 163 entries). As expected, the Rh–C_{nbd} distances *trans* to the carbene carbon atom in **2e** are longer

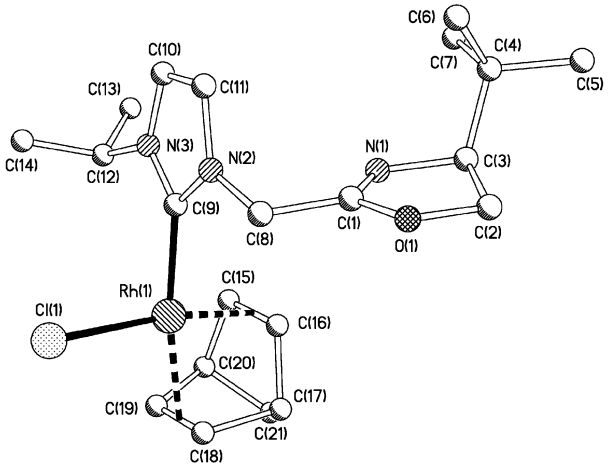


Figure 2. Molecular structure of neutral rhodium complex **2e** (hydrogen atoms are omitted for clarity). Selected average bond lengths [Å] and angles [°]: Rh(1)–Cl(1) 2.357, Rh(1)–C(9) 2.029, Rh(1)–C(15) 2.076, Rh(1)–C(16) 2.087, C(15)–C(16) 1.376, Rh(1)–C(18) 2.207, Rh(1)–C(19) 2.202, C(18)–C(19) 1.404, C(9)–Rh(1)–Cl(1) 91.8, Cl(1)–Rh(1)–C(18)/C(19) 98.6, C(9)–Rh(1)–C(15)/C(16) 98.0, C(15)/C(16)–Rh1–C(18)/C(19) 71.5, N(2)–C(9)–N(3) 104.1.

than those *trans* to the halide (average values are 2.203 vs. 2.086 Å). This *trans* influence is also reflected in the difference in the C=C bond lengths of the coordinated nbd ligand (average values 1.404 vs. 1.376 Å).

The cationic square planar rhodium complexes were generated by halide abstraction via addition of an excess of KPF_6 in a CH_2Cl_2/water solvent system. Alternatively, the deprotonation of the imidazolium hexafluorophosphates and reaction with $[Rh(nbd)Cl]_2$ directly gave the complex cations. The ^1H-, and ^{13}C-NMR spectra were found to be very similar to those of neutral complexes and do not provide direct evidence for the generation of the cationic complex, the generation of which is established by its analytical data. The infrared spectra display a vibrational band at 1663–1654 cm^{-1} (for **2a**–**c**), which is assigned to $\nu_{C=N}$ stretching mode of a coordinated oxazoline unit (in com-

parison to those observed for the imidazolium salts 1691–1679 cm^{-1}, **1a**–**e**). Several attempts to obtain suitable crystals of **2a**–**c** for X-ray diffraction were unsuccessful. However, the complexes are expected to have the same structural features as other cationic Rh complexes with **A**–**C** type oxazoline-NHC ligands.[7,16]

Catalysis

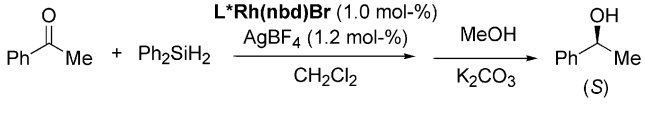
To investigate the potential of these complexes in the asymmetric hydrosilylation of ketones, acetophenone was employed as a reference substrate. The neutral complexes were first allowed to react with one equivalent of silver salt to generate the active cationic square-planar catalysts (catalyst loading: 1.0 mol-%). Even upon varying the nature of the silane, of the counter-anion, the temperature or the solvent, the catalysts displayed relatively poor activity and selectivity, some representative examples being listed in Table 1. Reasonable activities were observed at room temperature however the enantioselectivities remained extremely low (close to racemic), whilst lowering the temperature resulted to a significant decrease of activity.

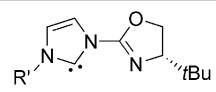
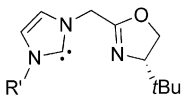
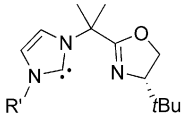
Table 1. Hydrosilylation of acetophenone with precatalysts **2a**–**c** and **2f**.

Precatalyst[a]	Temp. /°C	Time /h	% Yield[b]	% *ee*[c]
2a	0	6.5	97	–7 (*R*)
	–40	6.5	trace	–
2b	room temp.	6	89	0
	0	5	58	25 (*S*)
	–20	6	32	26 (*S*)
	–40	6	trace	–
2c	–10	4	5	31 (*S*)
	–40	4	no reaction	–
2f[d]	room temp.	4	99	2 (*S*)
	–40	7	trace	–

[a] Reaction conditions: 1 mol-% cat., Ph_2SiH_2 (1.1 equiv.), solvent CH_2Cl_2. Work-up: K_2CO_3/MeOH. [b] Isolated yield. [c] Determined by GC. [d] 1.1 mol-% of $AgPF_6$ was added.

Table 2. Hydrosilylation of acetophenone with rhodium complexes L·Rh(nbd)Br.[a]



	L*	r.t.[b] *ee* (yield)	–40 °C[c] *ee* (yield)
A		**26** (88)	**91** (83)
B		**2** (100)	– (trace)
C		**–4** (*R*) (8)	no reaction

[a] R′ = $(\alpha\text{-Np})_2CH$. [b] Reaction time: 4 h. [c] Reaction time: 7 h.

Finally, Table 2 displays the results of hydrosilylation of acetophenone with ligands type **A**–**C** bearing the substituents R′ = $(\alpha\text{-Np})_2CH$ and R = *t*Bu, which allows a direct comparison of the three systems. At room temperature, systems **A** and **B** showed good activity while **C** remained almost inactive (8% yield). Lowering the temperature to –40 °C resulted in a dramatic drop of activity for the **B** system, while system **A** remains highly active (83% yield) and GC analysis revealed an 91% enantiomeric excess of the alcohol. From these results, it appears that even after prolonged optimisations, the **B**- and **C**-type catalysts are unlikely to supersede the **A**-type catalyst.

Conclusions

In conclusion, a series of different oxazoline-NHC ligands has been synthesized and investigated in the rhodium-catalyzed hydrosilylation of ketones. Although these systems were found to be active at room temperature, we failed to obtain significant enantioselectivities for catalysts bearing ligands in which the two heterocycles are connected by a CH_2 or CMe_2 bridge. The comparison of the three ligand families showed that the direct coupling of oxazolines and N-heterocyclic carbenes generating highly rigid type **A** chelate ligands remains the most efficient system for the reaction we studied. Notably, this system remains active even at low temperature therefore giving rise to high enantiocontrol.

Experimental Section

General Experimental Procedures: All manipulations of air and moisture-sensitive materials were performed under an inert atmosphere of dry argon using standard Schlenk techniques. Solvents were purified and dried by standard methods. (4*S*)-isopropyl-2-(chloromethyl)oxazoline, (4*S*)-*tert*-butyl-2-(chloromethyl)oxazoline[9] and $[Rh(nbd)Cl]_2$[18] were synthesized according to reported procedures. Acetophenone was purified by bulb-to-bulb distillation prior to use. All other reagents were obtained commercially and used as received. ^1H, ^{13}C and ^{15}N spectra were recorded on Bruker Avance 400 and 600 NMR spectrometers and were referenced using the residual protio solvent (^1H) or solvent (^{13}C) resonances or externally to $^{15}NH_3$. Infrared spectra were recorded on a Varian 3100 FT-IR spectrometer. Mass spectra and elemental analyses were obtained by the analytical service of the Heidelberg Chemistry Department. Gas chromatographic analysis were carried out on a Finnigan Focus GC apparatus equipped with a chiral capillary column (Chiraldex B-PM, β-cyclodextrin, permethylated, 50 m × 0.25 mm): T_{inj} = 200 °C, T_{det} = 200 °C (flame ionization detector, FID), carrier gas: helium.

Preparation of the Compounds

1-{1-[(4*S*)-Isopropyl-4,5-dihydrooxazol-2-yl]methyl}-3-mesitylimidazolium Hexafluorophosphate (1a): Potassium iodide (226 mg, 1.36 mmol) was placed in a Schlenk tube, suspended in acetone (2 mL) and treated with (4*S*)-isopropyl-2-(chloromethyl)oxazoline

(220 mg, 1.36 mmol). The resulting yellow suspension was stirred for one hour at ambient temperature, filtered, and concentrated in vacuo. The yellow residue was subsequently dissolved in CH_3CN (5 mL), followed by addition of potassium hexafluorophosphate (250 mg, 1.36 mmol) and 1-mesitylimidazole (254 mg, 1.36 mmol). The resulting solution was stirred for two days at 60 °C. After removal of the solvent in vacuo the resulting brown residue was washed with Et_2O (3 × 20 mL) and dried in vacuo to yield **1a** as a white powder (496 mg, YIELD 80%). ^{1}H NMR (600 MHz, $CDCl_3$, 296 K): δ = 8.84 (s, 1 H, CH_{imid}), 7.68 (t, ^3J = 1.7 Hz, 1 H, CH_{imid}), 7.17 (t, ^3J = 1.7 Hz, 1 H, CH_{imid}), 7.00 (s, 2 H, CH_{Mes}), 5.28 (dd, ^2J = 17.4, ^5J = 1.0 Hz, 1 H, NCH_2), 5.24 (dd, ^2J = 17.4, ^5J = 1.7 Hz, 1 H, NCH_2), 4.40 (dd, ^3J = 9.6, ^2J = 8.6 Hz, 1 H, C$H_{2\ oxa}$), 4.06 (t, $^{2/3}J$ = 8.4 Hz, 1 H, C$H_{2\ oxa}$), 3.84 (q, ^3J = 8.3 Hz, 1 H, CH_{oxa}), 2.34 (s, 3 H, C$H_{3\ p\text{-}Mes}$), 2.06 (s, 6 H, C$H_{3\ o\text{-}Mes}$), 1.65 [o, ^3J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$], 0.87 [d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.83 [d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 296 K): δ = 160.2 (N*C*O), 141.5 (*C*$_{Mes}$), 138.1 (*C*H$_{imid}$), 134.5, 130.5 (*C*$_{Mes}$), 129.8 (*C*H$_{Mes}$), 124.4, 122.8 (*C*H$_{imid}$), 72.4 (*C*H$_{2\ oxa}$), 72.2 (*C*H$_{oxa}$), 46.5 (N*C*H$_2$), 32.6 [*C*H(CH$_3$)$_2$], 21.1 (*C*H$_{3\ p\text{-}Mes}$), 18.7 [CH(*C*H$_3$)$_2$], 18.5 [CH(*C*H$_3$)$_2$], 17.2 (*C*H$_{3\ p\text{-}Mes}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{19}H_{26}N_3O^+$ [M – PF_6]$^+$ 312.207; found 312.211 (100). FT-IR (KBr): $\tilde{\nu}$ = 1685 cm^{-1} (m, $\nu_{(C=N)}$). $C_{19}H_{26}F_6N_3OP$ (457.40): calcd. C 49.89, H 5.73, N 9.19; found C 49.95, H 5.75, N 9.15.

1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]methyl}-3-isopropylimidazolium Hexafluorophosphate (1b):[9] The same procedure as the one used for **1a** was followed. Reacting (4*S*)-*tert*-butyl-2-chloromethyloxazoline (240 mg, 1.36 mmol), potassium iodide (226 mg, 1.36 mmol), isopropylimidazole (150 mg, 1.36 mmol) and potassium hexafluorophosphate (250 mg, 1.36 mmol) yielded **1b** as a white powder (318 mg, yield 60%). ^{1}H NMR (600 MHz, $CDCl_3$, 296 K): δ = 8.90 (s, 1 H, CH_{imid}), 7.41 (t, ^3J = 1.8 Hz, 1 H, CH_{imid}), 7.32 (t, ^3J = 1.8 Hz, 1 H, CH_{imid}), 5.06 (dd, ^2J = 16.9, ^5J = 1.4 Hz, 1 H, NCH_2), 5.03 (dd, ^2J = 16.9, ^5J = 1.0 Hz, 1 H, NCH_2), 4.66 (sept, ^3J = 6.7 Hz, 1 H, C$H_{i\text{Pr}}$), 4.31 (dd, ^3J = 10.1, ^2J = 8.9 Hz, 1 H, C$H_{2\ oxa}$), 4.15 (t, $^{2/3}J$ = 8.6 Hz, 1 H, C$H_{2\ oxa}$), 3.88 (dd, ^3J = 10.0, ^3J = 8.4 Hz, 1 H, CH_{oxa}), 1.60 (d, ^3J = 6.7 Hz, 6 H, C$H_{3\ i\text{Pr}}$), 0.85 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 296 K): δ = 159.5 (N*C*O), 135.7, 123.4, 119.6 (*C*H$_{imid}$), 75.7 (*C*H$_{oxa}$), 70.2 (*C*H$_{2\ oxa}$), 53.8 (N*C*H$_{i\text{Pr}}$), 46.1 (N*C*H$_2$), 33.5 [*C*(CH$_3$)$_3$], 25.7 [C(*C*H$_3$)$_3$], 22.7 (*C*H$_{3\ i\text{Pr}}$) ppm. HR-MS (FAB+) *m*/*z* (%) calcd. for $C_{14}H_{24}N_3O^+$ [M – PF_6]$^+$ 250.191; found 250.191 (100). FT-IR (KBr): $\tilde{\nu}$ = 1691 cm^{-1} (m, $\nu_{(C=N)}$). $C_{14}H_{24}F_6N_3OP$ (395.32): calcd. C 42.53, H 6.12, N 10.63; found C 42.61, H 6.14, N 10.58.

1-{1[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]methyl}-3-mesitylimidazolium Hexafluorophosphate (1c):[9] The same procedure as the one used for **1a** was followed. Reacting (4*S*)-*tert*-butyl-2-(chloromethyl)-oxazoline (240 mg, 1.36 mmol), potassium iodide (226 mg, 1.36 mmol), 1-mesitylimidazole (254 mg, 1.36 mmol) and potassium hexafluorophosphate (250 mg, 1.36 mmol) yielded **1c** as a white powder (443 mg, yield 70%). ^{1}H NMR (600 MHz, $CDCl_3$, 296 K): δ = 8.93 (s, 1 H, CH_{imid}), 7.73 (s, 1 H, CH_{imid}), 7.20 (s, 1 H, CH_{imid}), 7.02 (s, 2 H, CH_{Mes}), 5.32 (s, 2 H, NCH_2), 4.34 (t, $^{2/3}J$ = 9.4 Hz, 1 H, C$H_{2\ oxa}$), 4.18 (t, $^{2/3}J$ = 8.6 Hz, 1 H, C$H_{2\ oxa}$), 3.86 (t, ^3J = 9.2 Hz, 1 H, CH_{oxa}), 2.35 (s, 3 H, C$H_{3\ p\text{-}Mes}$), 2.08 (s, 6 H, C$H_{3\ o\text{-}Mes}$), 0.82 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 296 K): δ = 160.2 (N*C*O), 141.4 (*C*$_{Mes}$), 138.1 (*C*H$_{imid}$), 134.5, 130.5 (*C*$_{Mes}$), 129.8 (*C*H$_{Mes}$), 124.5, 122.8 (*C*H$_{imid}$), 75.5 (*C*H$_{oxa}$), 70.5 (*C*H$_{2\ oxa}$), 46.5 (N*C*H$_2$), 33.4 [*C*(CH$_3$)$_3$], 25.7 [C(*C*H$_3$)$_3$], 21.1 (*C*H$_{3\ p\text{-}Mes}$), 17.2 (*C*H$_{3\ o\text{-}Mes}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{20}H_{28}N_3O^+$ [M – PF_6]$^+$ 326.224; found 326.223 (100). FT-IR (KBr): $\tilde{\nu}$ = 1685 cm^{-1} (m, $\nu_{(C=N)}$). $C_{20}H_{28}F_6N_3OP$ (471.42): calcd. C 50.96, H 5.99, N 8.91; found C 51.11, H 6.07, N 8.89.

1-{1[(4*S*)-Isopropyl-4,5-dihydrooxazol-2-yl]methyl}-3-isopropylimidazolium Chloride (1d): In a Schlenk tube (4*S*)-isopropyl-2-(chloromethyl)oxazoline (300 mg, 1.86 mmol) and isopropylimidazole (230 mg, 2.08 mmol) were dissolved in CH_3CN (10 mL) and stirred for six hours at 60 °C. The resulting mixture is left at ambient temperature and after one week a white solid precipitated. The solvent was removed in vacuo, and the remaining residue was washed with Et_2O (3 × 30 mL) to yield **1d** as a white powder (203 mg, yield 41%). Suitable crystals for an X-ray diffraction study of **1d′** (counterion PF_6^-) were obtained by addition of 1 equiv. KPF_6 to a solution of **1d** in CH_2Cl_2, filtration after 30 min and slow diffusion of Et_2O into the filtrate. ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 10.97 (s, 1 H, CH_{imid}), 7.47 (s, 1 H, CH_{imid}), 7.43 (s, 1 H, CH_{imid}), 5.52 (dd, ^2J = 16.8, ^5J = 1.2 Hz, 1 H, CH_2), 5.31 (d, ^2J = 16.8 Hz, 1 H, CH_2), 4.84 (sept, ^3J = 6.8 Hz, 1 H, C$H_{i\text{Pr}}$), 4.34 (t, $^{2/3}J$ = 9.2 Hz, 1 H, C$H_{2\ oxa}$), 4.02 (t, $^{2/3}J$ = 8.4 Hz, 1 H, C$H_{2\ oxa}$), 3.88 (q, ^3J = 8.0 Hz, 1 H, CH_{oxa}), 1.70 [o, ^3J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$], 1.62 (d, ^3J = 6.4 Hz, 6 H, C$H_{3\ i\text{Pr}}$), 0.90 [d, 3 H, ^3J = 6.4 Hz, CH(CH_3)$_2$], 0.83 [d, 3 H, ^3J = 6.4 Hz, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 296 K): δ = 160.1 (N*C*O), 138.1, 123.0, 119.4 (*C*H$_{imid}$), 72.4 (*C*H$_{2\ oxa}$), 71.7 (*C*H$_{oxa}$), 53.6 (*C*H$_{i\text{Pr}}$), 46.1 (N*C*H$_2$), 32.6 [*C*H(CH$_3$)$_2$], 23.2 (*C*H$_{3\ i\text{Pr}}$), 18.9, 18.4 [CH(*C*H$_3$)$_2$] ppm. MS (FAB+): *m*/*z* (%) = 236.2 (100) [M – Cl]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1679 cm^{-1} (s, $\nu_{(C=N)}$).

1-{1[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]methyl}-3-isopropylimidazolium Chloride (1e):[9] The same procedure as the one used for **1d** was followed. Reacting 1-isopropylimidazole (130 mg, 1.18 mmol) and (4*S*)-*tert*-butyl-2-(chloromethyl)oxazoline (176 mg, 1.06 mmol) yielded **1e** as a white solid (124 mg, yield 41%). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 11.25 (s, 1 H, CH_{imid}), 7.41 (t, ^3J = 1.6 Hz, 1 H, CH_{imid}), 7.29 (t, ^3J = 1.6 Hz, 1 H, CH_{imid}), 5.52 (dd, ^2J = 16.8, ^5J = 1.2 Hz, 1 H, NCH_2), 5.31 (d, ^2J = 16.8 Hz, 1 H, NCH_2), 4.85 (sept, ^3J = 6.8 Hz, 1 H, C$H_{i\text{Pr}}$), 4.29 (dd, ^3J = 10.0, ^2J = 9.2 Hz, 1 H, C$H_{2\ oxa}$), 4.14 (t, $^{2/3}J$ = 8.8 Hz, 1 H, C$H_{2\ oxa}$), 3.88 (dd, ^3J = 10.0, ^3J = 8.4 Hz, 1 H, CH_{oxa}), 1.64 (d, ^3J = 6.8 Hz, 6 H, C$H_{3\ i\text{Pr}}$), 0.86 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 296 K): δ = 159.9 (N*C*O), 138.8, 122.7, 119.0 (*C*H$_{imid}$), 75.9 (*C*H$_{2\ oxa}$), 70.1 (*C*H$_{oxa}$), 53.6 (N*C*H$_{i\text{Pr}}$), 46.1 (N*C*H$_2$), 33.7 [*C*(CH$_3$)$_3$], 25.9 [C(*C*H$_3$)$_3$], 23.2 (*C*H$_{3\ i\text{Pr}}$) ppm. MS (FAB+) *m*/*z* (%) = 250.2 (100) [M – Cl]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1689 cm^{-1} (m, $\nu_{(C=N)}$).

1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]methyl}imidazole: NaH (60 w/w in mineral oil, 323 mg, 8.1 mmol) was placed in a Schlenk tube and dissolved in CH_3CN (10 mL). At 0 °C, a solution of imidazole (555 mg, 8.1 mmol) in CH_3CN (5 mL) was added drop wise and the reaction mixture was allowed to react at room temperature for 24 h. After removal of the solvent in vacuo, the formed sodium imidazolide was dissolved in THF (10 mL). At 0 °C, a solution of (4*S*)-*tert*-butyl-2-(chloromethyl)oxazoline (1.4 g, 8.2 mmol) in THF (5 mL) and KI (catalytic amount) were added and the reaction mixture was allowed to react for three days at room temperature. The formed yellow suspension was filtered through celite and concentrated in vacuo. The resulting orange oil was then purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3) to give the product as a colourless oil (1.32 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, 296 K): δ = 7.50 (m, 1 H, CH_{imid}), 7.02 (m, 1 H, CH_{imid}), 6.95 (m, 1 H, CH_{imid}), 4.69 (s, 2 H, NCH_2), 4.18 (dd, ^2J = 8.7, ^3J = 10.3 Hz, 1 H, C$H_{2\ oxa}$), 4.04 (dd, ^2J = 8.7, ^3J = 7.9 Hz, 1 H, 1 H, C$H_{2\ oxa}$), 3.85 (dd, ^3J = 10.3, ^3J = 7.9 Hz, 1 H, 1 H, CH_{oxa}), 0.82 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,

296 K): δ = 161.4 (N*C*O), 137.7, 129.7, 119.6 (*C*H$_{imid}$), 75.9 (*C*H$_{oxa}$), 69.6 (*C*H$_{2\,oxa}$), 43.9 (N*C*H$_2$), 33.6 [*C*(CH$_3$)$_3$], 25.7 [C(*C*H$_3$)$_3$] ppm. MS (FAB) *m/z* (%): 226.1 [M + H$_3$O]$^+$ (30), 208.1 [M + H]$^+$ (100). FT-IR (KBr): $\tilde{\nu}$ = 1675 cm^{-1} (s, $\nu_{(C=N)}$). $C_{11}H_{17}N_3O_2$ (223.27): calcd. C 63.74, H 8.27, N 20.27; found C 63.60, H 8.21, N 20.12.

1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]methyl}-3-[bis(α-naphthyl)methyl]imidazolium Bromide (1f): The imidazole derivative (553 mg, 2.7 mmol) and bromodinaphthalen-1-ylmethane (926 mg, 2.7 mmol) were placed in a Schlenk tube and dissolved in CH_3CN (15 mL). After reacting for 12 h at 60 °C, the solvent was evaporated and the resulting solid was washed with Et_2O (2 × 5 mL) and pentane (5 mL) and dried in vacuo to yield the imidazolium salt **1f** as an air-sensitive white powder (1.24 g, 84%). ^{1}H NMR (600 MHz, CD_2Cl_2, 296 K): δ = 9.91 (br. s, 1 H, C*H*$_{imid}$), 9.02 (s, 1 H, C*H*Np$_2$), 8.18 (m, 2 H, C*H*$_{Np}$), 7.94–7.93 (m, 5 H, 4C*H*$_{Np}$ + C*H*$_{imid}$), 7.50–7.37 (m, 7 H, 4C*H*$_{Np}$ + C*H*$_{imid}$), 6.97 (m, 2 H, C*H*$_{Np}$), 5.34 (d, ^2J = 16.2 Hz, 1 H, NC*H*$_2$), 5.32 (d, ^2J = 16.2 Hz, 1 H, NC*H*$_2$), 4.22 (dd, ^2J = 9.3, ^3J = 9.3 Hz, 1 H, C*H*$_{2\,oxa}$), 4.08 (dd, ^2J = 8.5, ^3J = 8.5 Hz, 1 H, C*H*$_{2\,oxa}$), 3.79 (dd, ^3J = 9.1, ^3J = 9.1 Hz, 1 H, C*H*$_{oxa}$), 0.78 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 296 K): δ = 160.1 (N*C*O), 139.7 (N$_2$*C*), 134.1, 132.6, 132.5, 132.0, 130.4, 130.4 (*C*$_{Np}$), 130.3, 129.0, 127.6, 126.8, 126.3, 126.3, 125.3 (*C*H$_{Np}$), 123.9 (*C*H$_{imid}$), 123.5 (*C*H$_{Np}$), 122.0 (*C*H$_{imid}$), 75.5 (*C*H$_{oxa}$), 70.3 (*C*H$_{2\,oxa}$), 61.5 (*C*HNp$_2$), 46.3 (N*C*H$_2$), 33.4 [*C*(CH$_3$)$_3$], 25.5 [C(*C*H$_3$)$_3$] ppm. ^{15}N NMR (60 MHz, CD_2Cl_2, 296 K): δ = 232.8 (*N*$_{oxa}$), 189.6, 173.5 (*N*$_{imid}$) ppm. HR-MS (FAB+) *m/z* (%): calcd. for $C_{32}H_{32}N_3O$ ([M – Br]$^+$) 474.254; found 474.254 (100). FT-IR (KBr): $\tilde{\nu}$ = 1680 cm^{-1} (s, $\nu_{(C=N)}$). $C_{32}H_{32}BrN_3O$ (554.52): calcd. C 69.31, H 5.82, N 7.58; found C 69.18, H 5.75, N 7.40.

(η^4-2,5-Norbornadiene)(1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]methyl}-3-mesitylimidazole-2-ylidene)rhodium(I) Hexafluorophosphate (2a): To a solution of the imidazolium salt **1a** (146 mg, 0.32 mmol) in THF (5 mL) was added a solution of KHMDS (70 mg, 0.33 mmol) in THF (5 mL) at –78 °C. The resulting yellow solution was stirred for 30 min and a solution of [Rh(nbd)Cl]$_2$ (74 mg, 0.16 mmol) in THF (3 mL) was added. The mixture was stirred and warmed to ambient temperature for 12 h. The orange-red solution was then filtered and the volatiles were removed in vacuo. The resulting orange solid was washed twice with an Et_2O/CH_2Cl_2 mixture (5:1, 2 × 5 mL) and hexane (5 mL) to yield **2a** as a yellow solid (164 mg, yield 82%). ^{1}H NMR (600 MHz, CD_2Cl_2, 263 K): δ = 7.29 (d, ^3J = 1.9 Hz, 1 H, C*H*$_{imid}$), 7.07 (s, 1 H, C*H*$_{Mes}$), 6.92 (s, 1 H, C*H*$_{Mes}$), 6.80 (d, ^3J = 1.8 Hz, 1 H, C*H*$_{imid}$), 5.25 (d, ^2J = 17.8 Hz, 1 H, NC*H*$_2$), 4.98 (d, ^2J = 17.8 Hz, 1 H, NC*H*$_2$), 4.74 (br. s, 1 H, C*H*$_{nbd}$), 4.49 (t, $^{2/3}J$ = 9.5 Hz, 1 H, C*H*$_{2\,oxa}$), 4.45 (dd, ^2J = 9.4, ^3J = 5.3 Hz, 1 H, C*H*$_{2\,oxa}$), 4.37 (br. s, 1 H, C*H*$_{nbd}$), 3.95 (br. s, 1 H, C*H*$_{nbd}$), 3.76 (br. s, 1 H, C*H*$_{nbd}$), 3.58 (ddd, ^3J = 9.6, $^{3,3}J$ = 5.0 Hz, 1 H, C*H*$_{oxa}$), 3.55 (br. s, 1 H, C*H*$_{nbd}$), 2.52 (br. s, 1 H, C*H*$_{nbd}$), 2.34 (s, 3 H, C*H*$_{3\,p\text{-Mes}}$), 2.09 (s, 3 H, C*H*$_{3\,o\text{-Mes}}$), 1.92 (s, 3 H, C*H*$_{3\,p\text{-Mes}}$), 1.23 (br. s, 2 H, C*H*$_{2\,nbd}$), 0.89 [d, ^3J = 7.0 Hz, 3 H, CH(C*H*$_3$)$_2$], 0.70 [d, ^3J = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 263 K): δ = 174.6 [d, $^1J(^{103}Rh^{13}C)$ = 58 Hz, N$_2$*C*], 164.7 (N*C*O), 139.8, 136.0, 134.5, 134.2 (*C*$_{Mes}$), 129.0, 128.9 (*C*H$_{Mes}$), 122.9, 121.8 (*C*H$_{imid}$), 80.7 [d, $^1J(^{103}Rh^{13}C)$ = 5.1 Hz, *C*H$_{nbd}$], 73.2 (*C*H$_{nbd}$), 71.4 (*C*H$_{2\,oxa}$), 68.9 (*C*H$_{oxa}$), 67.7 (*C*H$_{2\,nbd}$), 60.8 [d, $^1J(^{103}Rh^{13}C)$ = 10.4 Hz, *C*H$_{nbd}$], 60.1 [d, $^1J(^{103}Rh^{13}C)$ = 8.8 Hz, *C*H$_{nbd}$], 52.8 (*C*H$_{nbd}$), 51.9 (*C*H$_{nbd}$), 46.9 (N*C*H$_2$), 31.7 [*C*H(CH$_3$)$_2$], 20.9 (*C*H$_{3\,p\text{-Mes}}$), 18.2 (*C*H$_{3\,o\text{-Mes}}$), 17.8 [CH(*C*H$_3$)$_2$], 17.3 (*C*H$_{3\,o\text{-Mes}}$), 14.8 [CH(*C*H$_3$)$_2$] ppm. HR-MS (FAB+) *m/z* (%): calcd. for $C_{26}H_{33}N_3ORh^+$ ([M – PF$_6$]$^+$) 506.167; found 506.174 (100). FT-IR (KBr): $\tilde{\nu}$ = 1663 cm^{-1} (m, $\nu_{(C=N)}$). $C_{26}H_{33}F_6N_3OPRh$ (651.43): calcd. C 47.94, H 5.11, N 6.45; found C 47.66, H 5.51, N 6.30.

(η^4-2,5-Norbornadiene)(1-{1-[(4*S*)-*tert*-butyl-4,5-dihydrooxazol-2-yl]methyl}-3-isopropylimidazole-2-ylidene)rhodium(I) Hexafluorophosphate (2b): Similar procedure as the one for **2a**. Reacting the imidazolium salt **1b** (127 mg, 0.32 mmol), [RhCl(nbd)]$_2$ (74 mg, 0.16 mmol) and KHMDS (70 mg, 0.33 mmol) yielded a crude product, which was diluted in CH_2Cl_2, filtered through celite, and dried under vacuum to give **2b** as a yellow solid (137 mg, yield 96%). ^{1}H NMR (600 MHz, CD_2Cl_2, 296 K): δ = 7.08 (d, ^3J = 1.6 Hz, 1 H, C*H*$_{imid}$), 6.94 (d, ^3J = 1.6 Hz, 1 H, C*H*$_{imid}$), 5.32 (br. s, 1 H, NC*H*$_2$), 4.92 (br. s, 1 H, NC*H*$_2$), 4.88 (s, 1 H, C*H*$_{nbd}$), 4.59 (m, 2 H, C*H*$_{i\text{Pr}}$+C*H*$_{nbd}$), 4.46 (br. s, 1 H, C*H*$_{nbd}$), 4.43 (t, ^3J = 9.6 Hz, 1 H, C*H*$_{2\,oxa}$), 4.23 (br. s, 1 H, C*H*$_{2\,oxa}$), 4.07 (s, 1 H, C*H*$_{nbd}$), 3.91 (s, 1 H, C*H*$_{nbd}$), 3.88 (s, 1 H, C*H*$_{nbd}$), 3.53 (br. s, 1 H, C*H*$_{oxa}$), 1.47 (d, ^3J = 8.0 Hz, 1 H, C*H*$_{2\,nbd}$), 1.41 (m, 4 H, C*H*$_{3\,i\text{Pr}}$+C*H*$_{2\,nbd}$), 1.33 (d, ^3J = 3.4 Hz, 3 H, C*H*$_{3\,i\text{Pr}}$), 0.85 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 296 K): δ = 188.3 (m, N$_2$*C*), 165.6 (N*C*O), 122.6, 117.7 (*C*H$_{imid}$), 80.6 (*C*H$_{nbd}$), 74.0 (*C*H$_{2\,oxa}$), 73.5 (*C*H$_{oxa}$), 72.2 (*C*H$_{nbd}$), 65.7 (*C*H$_{2\,nbd}$), 56.2 (*C*H$_{nbd}$), 52.3 (N*C*H$_{i\text{Pr}}$/*C*H$_{nbd}$), 47.7 (N*C*H$_2$), 33.9 [*C*(CH$_3$)$_3$], 25.4 [C(*C*H$_3$)$_3$], 24.4, 23.4 (*C*H$_{3\,i\text{Pr}}$) ppm. HR-MS (FAB+) *m/z* (%): calcd. for $C_{21}H_{31}N_3ORh^+$ ([M – PF$_6$]$^+$) 444.152; found 444.152 (100). FT-IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1} (m, $\nu_{(C=N)}$). $C_{21}H_{31}F_6N_3OPRh{\cdot}0.5CH_2Cl_2$ (631.83): calcd. C 40.87, H 5.10, N 6.65; found C 40.79, H 5.40, N 6.89.

(η^4-2,5-Norbornadiene)(1-{1-[(4*S*)-*tert*-butyl-4,5-dihydrooxazol-2-yl]methyl}-3-mesitylimidazole-2-ylidene)rhodium(I) Hexafluorophosphate (2c): Similar procedure as the one for **2a**. Reacting the imidazolium salt **1c** (147 mg, 0.32 mmol), [RhCl(nbd)]$_2$ (74 mg, 0.16 mmol) and KHMDS (70 mg, 0.33 mmol) yielded **2c** as a yellow solid (154 mg, yield 80%). ^{1}H NMR (600 MHz, $CDCl_3$, 296 K): δ = 7.33 (d, ^3J = 18.6 Hz, 1 H, C*H*$_{imid}$), 7.08 (s, 1 H, C*H*$_{Mes}$), 6.92 (s, 1 H, C*H*$_{Mes}$), 6.74 (d, ^3J = 18.6 Hz, 1 H, C*H*$_{imid}$), 5.48 (d, ^2J = 18.2 Hz, 1 H, NC*H*$_2$), 5.00 (d, ^3J = 18.2 Hz, 1 H, NC*H*$_2$), 4.92 (t, ^3J = 3.7 Hz, 1 H, C*H*$_{nbd}$), 4.56 (d, ^3J = 6.7 Hz, 2 H, C*H*$_{2\,oxa}$), 4.39 (t, ^3J = 3.9 Hz, 1 H, C*H*$_{nbd}$), 3.96 (dd, ^3J = 5.8, ^3J = 5.8 Hz, 1 H, C*H*$_{nbd}$), 3.84 (br. s, 1 H, C*H*$_{nbd}$), 3.50 (br. s, 1 H, C*H*$_{nbd}$), 3.39 (t, ^3J = 6.7 Hz, 1 H, C*H*$_{oxa}$), 2.50 (br. s, 1 H, C*H*$_{nbd}$), 2.37 (s, 3 H, C*H*$_{3\,p\text{-Mes}}$), 2.10 (s, 3 H, C*H*$_{3\,o\text{-Mes}}$), 1.92 (s, 3 H, C*H*$_{3\,o\text{-Mes}}$), 1.25 (br. s, 2 H, C*H*$_{2\,nbd}$), 0.93 [s, 9 H, C(C*H*$_3$)$_3$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 296 K): δ = 175.5 [d, $^1J(^{103}Rh^{13}C)$ = 58 Hz, N$_2$*C*], 165.5 (N*C*O), 139.6, 135.7, 134.6, 134.5 (*C*$_{Mes}$), 129.2, 129.0 (*C*H$_{Mes}$), 122.8, 122.1 (*C*H$_{imid}$), 82.6 [d, $^1J(^{103}Rh^{13}C)$ = 6.6 Hz, *C*H$_{nbd}$], 74.4 [d, $^1J(^{103}Rh^{13}C)$ = 5.8 Hz, *C*H$_{nbd}$], 72.9 (*C*H$_{oxa}$), 71.8 (*C*H$_{2\,oxa}$), 64.9 (*C*H$_{2\,nbd}$), 58.6 [d, $^1J(^{103}Rh^{13}C)$ = 10.7 Hz, *C*H$_{nbd}$], 58.8 [d, $^1J(^{103}Rh^{13}C)$ = 11.1 Hz, *C*H$_{nbd}$], 52.6, 51.6 (*C*H$_{nbd}$), 47.1 (N*C*H$_2$), 33.7 [*C*(CH$_3$)$_3$], 25.2 [C(*C*H$_3$)$_3$], 21.2 (*C*H$_{3\,p\text{-Mes}}$), 18.3, 17.5 (*C*H$_{3\,o\text{-Mes}}$) ppm. HR-MS (FAB+) *m/z* (%): calcd. for $C_{27}H_{35}N_3ORh^+$ ([M – PF$_6$]$^+$) 520.183; found 520.183 (100). FT-IR (KBr): $\tilde{\nu}$ = 1654 cm^{-1} (m, $\nu_{(C=N)}$).

Chloro(η^4-2,5-Norbornadiene)(1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]methyl}-3-isopropylimidazole-2-ylidene)rhodium(I) (2d): Similar procedure as the one for **2a**. Reacting the imidazolium salt **1d** (85 mg, 0.30 mmol), [RhCl(nbd)]$_2$ (69 mg, 0.15 mmol) and KHMDS (66 mg, 0.33 mmol) gives a crude product that is crystallized from a CH_2Cl_2/pentane mixture to yield **2d** as a yellow solid (110 mg, yield 85%). ^{1}H NMR (600 MHz, $CDCl_3$, 263 K): δ = 6.96 (s, 1 H, C*H*$_{imid}$), 6.82 (s, 1 H, C*H*$_{imid}$), 5.72 (sept, ^3J = 6.8 Hz, 1 H, NC*H*$_{i\text{Pr}}$), 5.49 (br. s, 1 H, NC*H*$_2$), 5.44 (br. s, 1 H, NC*H*$_2$), 4.82 (br. s, 2 H, C*H*$_{nbd}$), 4.33 (t, $^{2/3}J$ = 9.1 Hz, 1 H, C*H*$_{2\,oxa}$), 4.07 (t, $^{2/3}J$ = 8.2 Hz, 1 H, C*H*$_{2\,oxa}$), 3.98 (q, ^3J = 7.8 Hz,

1 H, CH_{oxa}), 3.79 (s, 2 H, CH_{nbd}), 3.58 (br. s, 2 H, CH_{nbd}), 1.81 [o, ^3J = 6.8 Hz, 1 H, CH(CH_3)$_2$], 1.46 (d, ^3J = 6.8 Hz, 6 H, NC$H_{3\ iPr}$), 1.34 (s, 2 H, C$H_{2\ nbd}$), 0.97 [d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$], 0.89 [d, 3 H, CH(CH_3)$_2$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 263 K): δ = 184.2 [d, ^1J(^{103}Rh^{13}C) = 59 Hz, N_2C], 162.5 (NCO), 121.4, 116.9 (CH_{imid}), 72.2 (CH_{oxa}), 70.7 (C$H_{2\ oxa}$), 63.5 (C$H_{2\ nbd}$), 52.4 (NCH_{iPr}), 51.0 (CH_{nbd}), 47.7 (NCH_2), 32.4 [CH(CH$_3$)$_2$], 23.8, 26.7 (NC$H_{3\ iPr}$), 18.8, 17.9 [CH(CH_3)$_2$] ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{20}H_{29}N_3ORh^+$ ([M – Cl]$^+$) 430.136; found 430.136 (100). FT-IR (KBr): $\tilde{\nu}$ = 1676 cm^{-1} (m, $\nu_{(C=N)}$). $C_{20}H_{29}ClN_3ORh$ (465.83): calcd. C 51.57, H 6.27, N 9.02; found C 51.50, H 6.47, N 8.89.

Chloro(η^4-2,5-Norbornadiene)(1-{1-[(4*S*)-*tert*-butyl-4,5-dihydrooxazol-2-yl]methyl}-3-isopropylimidazole-2-ylidene)rhodium(I) (2e): Similar procedure as the one for **2a**. Reacting the imidazolium salt **1e** (124 mg, 0.22 mmol), [RhCl(nbd)]$_2$ (100 mg, 0.22 mmol) and KHMDS (88 mg, 0.44 mmol) yielded **2e** as a yellow solid (165 mg, yield 80%). Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of pentane into a solution of **2e** in CH_2Cl_2. ^{1}H NMR (600 MHz, CD_2Cl_2, 295 K): δ = 6.98 (d, ^3J = 1.8 Hz, 1 H, CH_{imid}), 6.87 (d, ^3J = 1.8 Hz, 1 H, CH_{imid}), 5.70 (sept, ^3J = 6.7 Hz, 1 H, NCH_{iPr}), 5.40 (br. s, 2 H, NCH_2), 4.74 (s, 2 H, CH_{nbd}), 4.27 (t, $^{2/3}J$ = 9.6 Hz, 1 H, C$H_{2\ oxa}$), 4.13 (t, $^{2/3}J$ = 8.2 Hz, 1 H, C$H_{2\ oxa}$), 3.91 (t, ^3J = 9.1 Hz, 1 H, CH_{oxa}), 3.77 (s, 1 H, CH_{nbd}), 3.56 (br. s, 1 H, CH_{nbd}), 1.44 (d, ^3J = 6.2 Hz, 6 H, C$H_{3\ iPr}$), 1.35 (d, ^2J = 8.2 Hz, 1 H, C$H_{2\ nbd}$), 1.29 (d, ^2J = 8.2 Hz, 1 H, C$H_{2\ nbd}$), 0.88 [s, 9 H, C(CH_3)$_3$] ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 295 K): δ = 185.0 [d, ^1J(^{103}Rh^{13}C) = 58 Hz, N_2C], 162.6 (NCO), 122.1, 117.3 (CH_{imid}), 79.6, 79.5 (CH_{nbd}), 76.5 (CH_{oxa}), 69.9 (C$H_{2\ oxa}$), 63.4 (C$H_{2\ nbd}$), 53.0 (CH_{iPr}), 51.6, 48.9, 48.8 (CH_{nbd}), 47.6 (NCH_2), 34.1 [C(CH$_3$)$_3$], 26.1 [C(CH_3)$_3$], 23.9 (C$H_{3\ iPr}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{21}H_{31}N_3ORh^+$ ([M – Cl]$^+$) 444.152; found 444.155 (100). FT-IR (KBr): $\tilde{\nu}$ = 1677 cm^{-1} (s, $\nu_{(C=N)}$). $C_{21}H_{31}ClN_3ORh{\cdot}0.2CH_2Cl_2$ (479.9+0.2 × 84.9): calcd. C 51.25, H 6.37, N 8.46; found C 51.36, H 6.56, N 8.42.

Bromo(η^4-2,5-norbornadiene)(1-{1-[(4*S*)-*tert*-butyl-4,5-dihydrooxazol-2-yl]methyl}-3-[bis(α-naphthyl)methyl]imidazol-2-ylidene)rhodium(I) (2f): To a solution of the imidazolium salt **1f** (225 mg, 0.4 mmol) in THF (5 mL) was added a solution of KHMDS (90 mg, 0.44 mmol) in THF (5 mL) at –78 °C. The resulting yellow solution was stirred for 30 min and a solution of [Rh(nbd)Cl]$_2$ (93 mg, 0.2 mmol) in THF (3 mL) was added. The mixture was stirred and warmed to ambient temperature for 12 h. The orange-red solution was then filtered and the volatiles were removed in vacuo. The resulting orange solid was washed twice with an Et_2O/CH_2Cl_2 mixture (5:1, 2 × 5 mL) and hexane (5 mL) to yield **2f** as a yellow solid (162 mg, yield 53%). ^{1}H NMR (600 MHz, $CDCl_3$, 263 K): δ = 9.13 (s, 1 H, CHNp$_2$), 8.97 (m, 1 H, CH_{Np}), 8.19 (m, 1 H, CH_{Np}), 8.10–7.80 (m, 4 H, CH_{Np}), 7.76–7.43 (m, 5 H, CH_{Np}), 7.24 (m, 1 H, CH_{Np}), 7.12–6.81 (m, 3 H, CH_{Np} + CH_{imid}), 6.55 (m, 1 H, CH_{imid}), 6.15 (m, 1 H, CH_2), 4.88 (m, 1 H, CH_2), 4.78 (m, 1 H, CH_{nbd}), 4.48 (m, 1 H, CH_{nbd}), 4.32 (m, 1 H, C$H_{2\ oxa}$), 4.18 (m, 1 H, C$H_{2\ oxa}$), 3.91 (m, 1 H, CH_{oxa}), 3.70 (m, 1 H, CH_{nbd}), 3.59 (m, 1 H, CH_{nbd}), 2.25 (m, 1 H, CH_{nbd}), 1.78 (m, 1 H, CH_{nbd}), 1.01–0.72 [m, 11 H, C(CH_3)$_3$ + C$H_{2\ nbd}$] ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 263 K): δ = 188.1 [d, ^1J(^{103}Rh^{13}C) = 53.0 Hz, N_2C], 160.2 (NCO), 138.1, 133.8, 133.8, 131.6, 131.2 (C$_{Np}$), 129.9, 128.7, 128.7, 128.7, 128.3, 128.3, 128.0 (CH_{Np}), 127.1 (C$_{Np}$), 126.5, 125.9, 125.3, 124.9, 124.8, 124.8, 124.2 (CH_{Np}), 121.5, 120.5 (CH_{imid}), 78.4, 76.8 (CH_{nbd}), 75.6 (CH_{oxa}), 69.5 (C$H_{2\ oxa}$), 63.7 (C$H_{2\ nbd}$), 61.3 (CHNp$_2$), 52.3, 50.8, 50.4, 49.8 (CH_{nbd}), 48.1 (CH_2), 33.9 [C(CH$_3$)$_3$], 25.7 [C(CH_3)$_3$] ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{39}H_{39}N_3ORh$ ([M – Br]$^+$) 668.215; found 668.218 (100); calcd. for $C_{32}H_{31}N_3ORh$ ([M – C_7H_8 – Br]$^+$) 576.152; found 576.159 (85). FT-IR (KBr): $\tilde{\nu}$ = 1678 cm^{-1} (s, $\nu_{(C=N)}$). $C_{39}H_{39}BrN_3ORh$ (748.57): calcd. C 62.58, H 5.25, N 5.61; found C 62.48, H 5.21, N 5.50.

General Procedure for the Hydrosilylation of the Acetophenone: In a glove box, the silver salt (1.1 mol-%) was added to a solution of the desired neutral rhodium complex (1 mol-%) in CH_2Cl_2 (4 mL). The resulting mixture was stirred for about 5 min under exclusion of light and then filtered through a pad of celite and rinsed with additional CH_2Cl_2 (4 mL). Alternatively the cationic complexes were just dissolved in CH_2Cl_2 (8 mL). The orange-red solution was divided into four equal parts (for four different catalytic runs; 2 mL each), and each vial was topped with a septum and taken out of the glove box. After addition of the acetophenone (117 μL, 1.0 mmol) at ambient temperature, the reaction mixture was cooled to the catalysis temperature and the silane (1.1 mmoL) was added drop wise. The bright yellow mixture was stirred at the defined temperature for the desired amount of time. A solution of K_2CO_3 in methanol (0.1%, 2 mL) was added and the resulting mixture was stirred for at least 4 h at room temperature. After evaporation of the solvents, the product was purified by flash column chromatography (SiO_2, hexane/Et_2O, 85:15) to yield the *sec*-phenylethyl alcohol as a colourless oil. Conversions are determined by ^{1}H-NMR spectroscopy before quenching. Yields refer to isolated yields of compounds estimated to be > 95% pure. The *ee* values of the product were determined by GC analysis using a Chiraldex B-PM column. GC method: carrier-cas pressure: 170 kPa, initial temp.: 40 °C, final temp.: 120 °C, 5 °C/min, hold time at 120 °C: 14 min; (*R*)-*sec*-phenethyl alcohol: *t* = 25.82 min, (*S*)-*sec*-phenethyl alcohol: *t* = 26.54 min. Conversions, yields and *ee* values are the average of at least two corroborating runs.

Table 3. Details of the crystal structure determinations of **1d′** and **2e**.

	1d′	**2e**
Formula	$C_{13}H_{22}F_6N_3OP$	$C_{21}H_{31}ClN_3ORh$
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a /Å	12.214(3)	10.8741(9)
b /Å	10.791(2)	15.8065(13)
c /Å	13.605(3)	25.414(2)
β /°	101.271(4)	92.231(2)
V /Å^3	1758.5(6)	4364.9(6)
Z	4	8
M_r	381.31	479.85
d_c /Mgm^{-3}	1.440	1.460
F(000)	792	1984
μ(Mo-K_α) /mm^{-1}	0.221	0.920
Max., min. transmission factors	0.7464, 0.6956	0.7463, 0.6274
θ range /°	2.1 to 30.5	0.8 to 30.5
Index ranges (indep. set) *h*,*k*,*l*	–17... 17, –15... 15, 0... 19	–15... 15, –22... 22, 0... 36
Reflections measured	42861	104433
Reflections unique [R_{int}]	10568 [0.0496]	26608 [0.0597]
Reflections observed [$I \geq 2\sigma(I)$]	7919	19927
Parameters refined	441	994
R indices [$F>4\sigma(F)$] *R*(*F*), *wR*(F^2)	0.0552, 0.1584	0.0430, 0.0903
R indices (all data) *R*(*F*), *wR*(F^2)	0.0766, 0.1714	0.0689, 0.0996
GooF on F^2	1.185	1.072
Absolute structure parameter	–0.05(11)	–0.01(2)
Largest residual peaks /e Å^{-3}	0.879, –0.357	1.283, –0.867

X-ray Crystal Structure Determinations: Crystal data and details of the structure determinations are listed in Table 3. Intensity data were collected at 100 K with a Bruker AXS Smart 1000 CCD diffractometer (Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å). Data were corrected for for air and detector absorption, Lorentz and polarization effects;[19] absorption by the crystal was treated with a semiempirical multiscan method.[20,21] The structures were solved by conventional direct methods[22,23] (for **1d′**) or by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors[24] (for **2e**) and refined by full-matrix least-squares methods based on F^2 against all unique reflections. All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions and refined with a riding model.[23,25]

CCDC-708216 (for **1d′**) and -708217 (for **2e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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