Cationic and Neutral Rhodium(I) Oxazolinylcarbene Complexes

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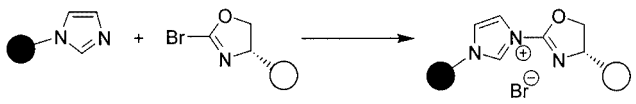
Reaction of $[Rh(\mu\text{-}O\textit{t}Bu)(diene)]_2$ [diene = 1,5-cyclooctadiene (COD) or bicyclo[2.2.1]hepta-2,5-diene (NBD)] with the oxazolinylcarbene ligand precursor 2-(4,4-dimethyl)oxazolinylimidazolium bromide ("$Me_2carboxH^+Br^-$", **2**) yielded the five-coordinate complexes [RhBr(Me_2carbox)(diene)] [diene = COD (**3**), NBD (**4**)]. Single-crystal X-ray structure analyses established a distorted trigonal bipyramidal configuration for **3**, whereas the molecular structure of **4** is distorted square pyramidal. The dynamic properties of these five-coordinate complexes have been investigated by variable temperature ^1H NMR spectroscopy, indicating polytopal rearrangements of the five-coordinate complexes. The two compounds were converted into the square-planar cationic complexes $[Rh(Me_2carbox)(diene)]^+$ (**5** and **6**, respectively), which have been isolated and fully characterised. The rhodium complex [RhBr(Me_2carbox)(CO)] (**7**) was obtained in high yield in a one-step reaction of the ligand precursor **2** and [Rh(acac)-$(CO)_2$] (acac = acetylacetonate).

Introduction

The combination of ligand donor units with very different coordination properties in a di- or polydentate spectator ligand ("hetero-donor ligands") may permit a stereoelectronic control of the reactivity at the remaining coordination sites in a transition metal complex. This has been an underlying principle in the development of many phosphane-heteroatom-based polydentate ligands employed in molecular catalysts.[1]

In recent years, *N*-heterocyclic carbenes have emerged as a new class of spectator ligands in transition metal complexes with ever increasing potential in homogeneous catalysis.[2] They are strong σ-donors and in many respects resemble phosphorus-donor ligands rather than classical Fischer- or Schrock-type carbenes.[3] In this regard, they may replace phosphane units in heterodonor ligands in combination with more "classical" ligand functionalities.[4,5] Among these novel chelating ligand systems, *N*-functionalised carbene complexes have recently received much attention and have given rise to exciting results in homogeneous catalysis.[5,6]

We previously reported the direct coupling of oxazolines and *N*-heterocyclic carbenes, and this new class of C,N-donor ligands (**A**) has been successfully employed in various catalytic reactions.[6] The ligand synthesis is modular, assembling both units in a single coupling step, which was thought to be an efficient strategy in the development of novel catalysts.



(A)

The rigidity of the bidentate ligand **A** allows for the modeling of a well-defined active space in its molecular catalysts. In this paper we report a number of new complexes of rhodium(I) containing a type **A** ligand which is derived from a 2-(4,4-dimethyl)oxazolinylimidazolium salt. A detailed structural study was intended to provide insight into the nature of precursors and active rhodium catalysts based on these systems.[6b]

Results and Discussion

Synthesis and Structural Characterization of the Bromo{1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-ylidene}rhodium(I) Complexes 3 and 4

As described in a previous paper,[6a] the imidazolium salt **2** is readily obtained from 1-mesityl-1*H*-imidazole and commercially available 4,5-dihydro-4,4-dimethyloxazole. Following the procedure reported by Meyers and Novachek, the reaction of the lithiated oxazole (*t*BuLi, THF, −78 °C) with 1,2-dibromotetrafluoroethane gave the corresponding

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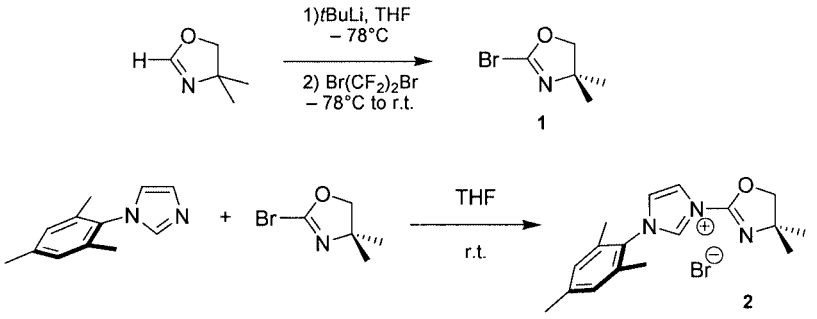


Scheme 1. Synthesis of the 2-bromooxazoline **1** and the oxazolinyl imidazolium salt **2** as ligand precursor

2-bromo-4,5-dihydro-4,4-dimethyloxazole **1** in 65−70% yield (Scheme 1).[7] Treatment of **1** with 1-mesityl-1*H*-imidazole in THF at 50 °C gave the ligand precursor, the 2-(4,4-dimethyloxazolinyl)imidazolium salt (Me_2oxcarb-H^+Br^-) **2**, in about 80% yield (Scheme 1).[6a]

All attempts to generate the free carbene Me_2oxcarb by reaction of **2** with an external base were unsuccessful and led to the nonspecific degradation of the compound. We therefore chose to generate the corresponding rhodium complexes by using precursors that already contain an anionic ligand with sufficient basicity and are capable of in situ deprotonation of the imidazolium salt. Following a general procedure first reported by Herrmann and co-workers,[8] we prepared the rhodium(I) alkoxide precursor [Rh(μ-O*t*Bu)(diene)]$_2$ in situ by reaction of [Rh(COD)Cl]$_2$ or [Rh(NBD)Cl]$_2$ with potassium *tert*-butoxide at room temperature in THF. The resulting solution was then slowly added to a suspension of the imidazolium salt **2** at −78 °C and the mixture was allowed to warm slowly to room temperature overnight. Using this procedure, we obtained the rhodium complexes [Rh(Me_2oxcarb)(COD)Br] (**3**) and [Rh(Me_2oxcarb)(NBD)Br] (**4**) as orange, air-stable solids in 86% and 84% yield, respectively (Scheme 2).

The formation of the carbene complexes was confirmed by ^{13}C NMR spectroscopy. Signals characteristic of N-heterocyclic carbene carbon nuclei[4,5] at δ = 177.2 ppm ($J_{Rh,C}$ = 53 Hz) and at δ = 183.6 ppm ($J_{Rh,C}$ = 55 Hz) were observed for complexes **3** and **4**, respectively Furthermore, a significant coordination shift of the *C*(=N)O ^{13}C NMR resonances in both cases (**3**: δ = 158.8 ppm; **4**: δ = 155.6 ppm) in comparison with the ligand precursor **2** (δ = 148.8 ppm) indicates the coordination of the oxazoline ring. The latter is also supported by the oxazoline ν(C=N) vibrational band which is shifted to lower wavenumbers (**3**: 1677 cm^{-1}; **4**: 1664 cm^{-1}) compared to the free oxazoline in **2** (1691 cm^{-1}). The details of the molecular structure of both complexes were determined by single-crystal X-ray

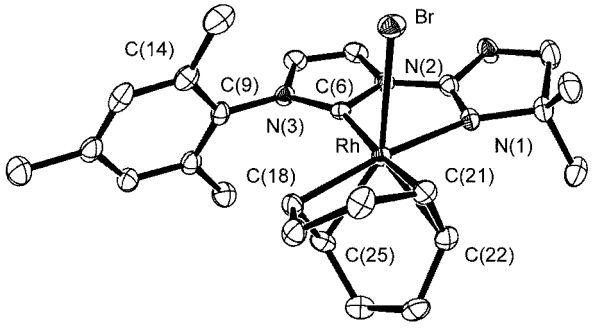
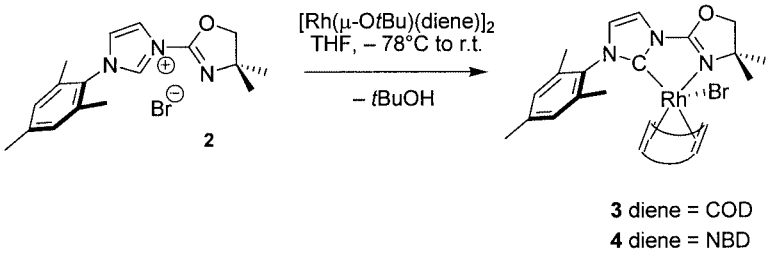


Figure 1. Molecular structure of **3**; selected bond lengths (Å) and angles (°): Rh−Br 2.7545(3), Rh−N(1) 2.255(2), Rh−C(6) 2.022(2), Rh−C(18) 2.090(3), Rh−C(25) 2.096(3), Rh−C(21) 2.223(2), Rh−C(22) 2.251(2), C(21)−C(22) 1.371(4), C(18)−C(25) 1.428(4); C(6)−Rh−N(1) 77.47(9), C(6)−Rh−Br 86.98(7), N(1)−Rh−Br 81.89(6)(4)

diffraction studies and are depicted in Figure 1 and 2, along with the principal bond lengths and interbond angles.

The X-ray structure analyses confirm the bidentate nature of the oxazolinylcarbene ligand in these rhodium complexes. The coordination geometry of **3** around the metal center is best approximated by a distorted trigonal bipyramidal arrangement with C(6), C(21) and C(22) occupying the apical positions whereas the coordination geometry of **4** is essentially square pyramidal. A steric interaction between the COD ligand and the mesityl ring seems to be the origin of the trigonal bipyramidal arrangement of **3**. The mesityl rings are oriented almost orthogonally to the imidazolyl rings [dihedral angle for **3**: C(14)−C(9)−N(3)−C(6) 80.0°; dihedral angle for **4**: C(10)−C(9)−N(2)−C(1) 78.6°].



Scheme 2. Synthesis of the five-coordinate complexes [RhBr(ligand)(diene)] **3** and **4**

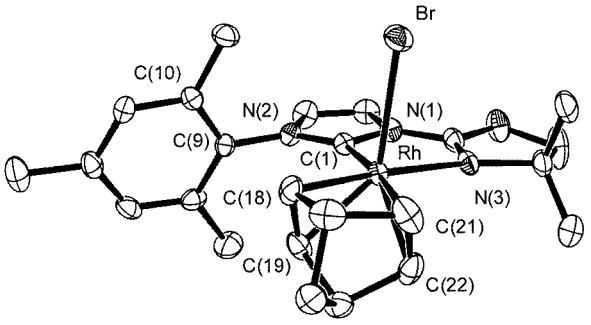


Figure 2. Molecular structure of **4**; selected bond lengths (Å) and angles (°): Rh−Br 2.7615(3), Rh−N(3) 2.178(2), Rh−C(1) 2.016(2), Rh−C(18) 2.070(2), Rh−C(19) 2.105(3), Rh−C(21) 2.192(2), Rh−C(22) 2.177(2), C(21)−C(22) 1.357(5), C(18)−C(19) 1.401(4); C(1)−Rh−Br 95.13(7), C(1)−Rh−N(3) 77.49(8), N(3)−Rh−Br 89.12(5)

As expected, the $Rh-C_{COD}$ distances in **3**, which are *trans* to the carbene carbon atom, are longer than the $Rh-C_{COD}$ bond lengths *trans* to the oxazoline [2.223(2)−2.251(2) Å versus 2.090(3)−2.096(3) Å]. This pronounced *trans* influence[5j,9] is also reflected in the difference in the C=C double bond distances of the coordinated COD ligand. For the double bond *trans* to the carbene a C=C bond length of 1.371(4) Å is found, in comparison with the value of 1.428(4) Å for the double bond *trans* to the oxazoline *N*-atom. In contrast, due to the more rigid conformation and smaller bite angle of the NBD ligand in complex **4**, compared to COD, the *trans* influence of the *N*-heterocyclic carbene in **4** on the Rh−C bond lengths of the diolefin is less pronounced [2.192(2)−2.178(2) Å versus 2.105(3)−2.070(2) Å *trans* to the oxazoline unit]. The distances between the rhodium and the carbene carbon atoms are 2.022(2) Å and 2.016(2) Å for **3** and **4**, respectively, and are similar to those found in related structures.[4b,10]

Signals attributable to the COD ligand are not observed in the ^{1}H NMR spectrum (recorded at 300 MHz) of **3** at 25 °C, indicating a coalescence phenomenon and thus a dynamic process. Upon lowering the temperature to −60 °C, four broad signals between δ = 1.5 and 2.5 ppm appear, which correspond to the -CH_2- groups, while two resonances for the olefin protons are observed at δ = 3.6 and 5.3 ppm. This exchange process has a free activation enthalpy $\Delta G^{\ddagger}$ of about 54 kJ/mol. The fact that only two signals of the four olefin protons are observed at low temperature, in spite of their chemical inequivalence, suggests that a second fast-exchange process takes place which has a low activation barrier (vide infra).

In the ^{1}H NMR spectrum of complex **4**, recorded at 25 °C, only one signal for the olefin protons is observed (δ = 3.59 ppm) indicating fast exchange at that temperature.[11] At −22 °C, this resonance coalesces, and two signals at δ = 4.67 ppm and at δ = 2.67 ppm are detected at −70 °C, as shown in Figure 3. The estimated $\Delta G^{\ddagger}$ of the exchange process associated with this coalescence is ca. 46 kJ/mol. The mechanism operating in the dynamic processes observed for **3** and **4** has to explain the rapid exchange of the two inequivalent C=C double-bond positions in the molecular structures of both complexes. In line with the ubiquitous dynamic processes observed for pentacoordinate molecules, we propose a sequence of Berry pseudorotations as displayed in Scheme 3.

One possible pathway interconverting the two square-pyramidal complexes **A** and **B** (each with a "marked" C=C double bond) involves the intermediates **I**−**III**, which are connected by Berry-type polytopal rearrangements. However, in the low-temperature-limit spectra of both **3** and **4** the (four inequivalent) olefin hydrogen atoms give rise to two signals and not four, as expected. This may be due to fast Br^- exchange even at these low temperatures. Dissociation and the subsequent reassociation of the anion to the ionic planar intermediate, combined with the Berry rearrangements of the pentacoordinate complexes, would indeed lead to the equilibration of the four olefin protons in both complexes. This rapid bromide dissociation and association mechanism is supported by the observed fast intermolecular bromide exchange between **3** and **4** and the respective square-planar complex cations, as discussed in the following section

Synthesis and Structural Characterization of the Cationic {1-(4,4-Dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-ylidene}(diolefin)rhodium(I) Complexes 5 and 6

The bromo ligand in the pentacoordinate complex **3** can be removed by the addition of an excess of KPF_6 in dichloromethane (Scheme 4). The cationic complex [Rh(Me_2-carbox)(COD)](PF_6) (**5**) was isolated in nearly quantitative yield as a red solid. In the same fashion, the analogous cationic complex [Rh(Me_2carbox)(NBD)](BF_4) (**6**) derived from **4** was obtained by addition of an excess of $NaBF_4$ in a dichloromethane/water solvent system.

The formulation of compounds **5** and **6** was substantiated by their analytical data, and the molecular structures displayed in Scheme 4 are consistent with the resonance patterns in the NMR spectra. The ^{1}H NMR spectra of complexes **5** and **6**, recorded at room temperature, display two signals for the olefin protons since both square-planar complexes possess C_s symmetry. In the ^{13}C NMR spectra of **5** and **6** the carbene signals are observed at δ = 174.2 ppm ($J_{C,Rh}$ = 54 Hz) and δ = 175.3 ppm ($J_{C,Rh}$ = 59 Hz), respectively.

In order to establish the details of their molecular structures, both compounds were characterized by single-crystal X-ray diffraction which confirmed the expected square-planar arrangement of the ligands around the metal centre (Figure 4 and 5). As for complexes **3** and **4**, the mesityl ring is oriented almost orthogonally to the imidazolyl ring [dihedral angle for **5**: C(10)−C(9)−N(3)−C(8) 99.3°; dihedral angle for **6**: C(14)−C(9)−N(3)−C(8) 87.4°]. Both the Rh−C distances [Rh−C(8) = 2.037(7) Å for **5** and Rh−C(8) = 2.039(6) Å for **6**] and the nitrogen to rhodium distances [Rh−N(1) = 2.136(3) Å and Rh−N(1) = 2.120(5) Å] are within the expected range.[5a][5l][5m] A *trans* influence of the carbene ligand is also found, but appears to be less pronounced than for the pentacoordinate neutral complexes. This is also reflected in the C=C double-bond

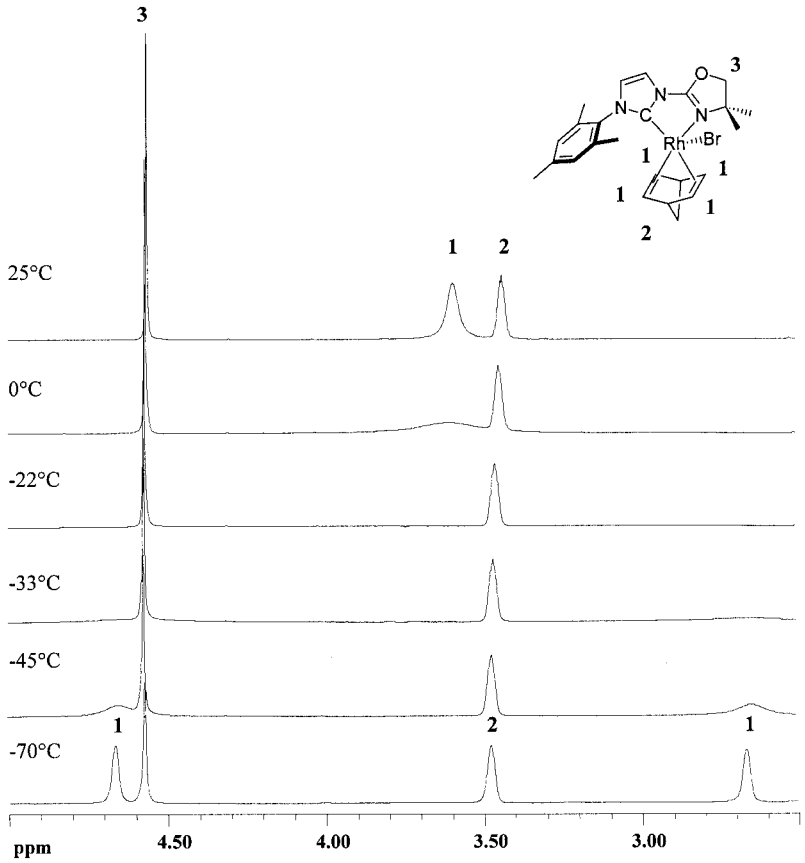
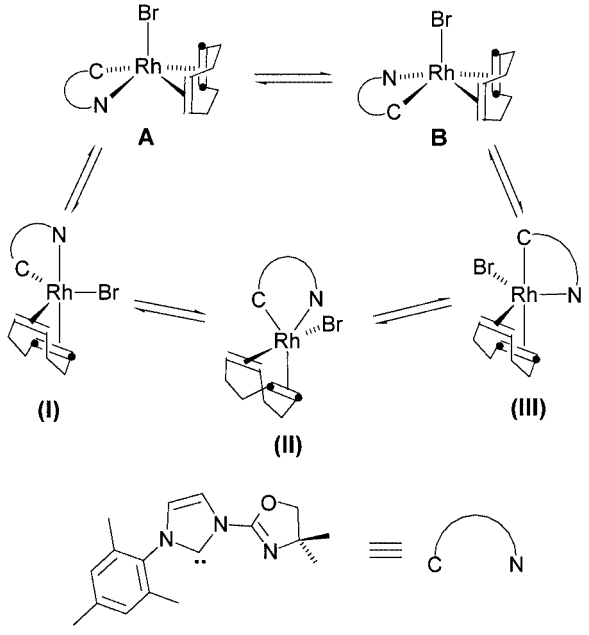


Figure 3. Variable temperature ^{1}H NMR spectra of **4** in the region δ = 2.5−5.0 ppm (recorded in CD_2Cl_2)



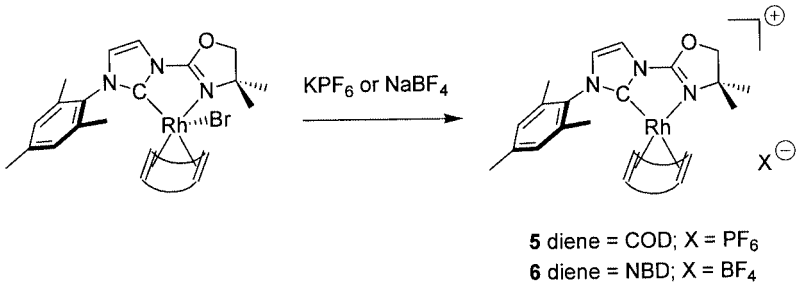
Scheme 3. A sequence of Berry pseudo-rotations leading to the exchange of the positions of the C=C double bonds in the chelating diolefin ligands relative to the C,N bidentate ligand. This process, together with the dissociation and re-association of Br^-, explains the exchange pattern observed in the variable temperature ^{1}H NMR spectra of **3** and **4**

lengths. In complex **5**, for instance, the bond length of the double bond *trans* to the carbene is 1.357(8) Å, compared with the value of 1.371(7) Å for the double bond *trans* to the oxazoline N-atom [1.371(4) Å and 1.428(4) Å in the neutral compound **3**].

The rapid dissociative Br^- exchange postulated for compounds **3** and **4** is supported by the observation of rapid intermolecular bromide exchange between these pentacoordinate complexes and their corresponding square-planar cations **5** and **6**. The ^{1}H NMR spectrum of a 1:1 mixture of the neutral complex **4** and the ionic complex **6**, dissolved in CD_2Cl_2, shows an average resonance pattern of those of **4** and **6**, instead of the spectra of separate species. The same average resonance is observed at −70 °C and is compared in Figure 6 with those of **4** and **6** recorded at the same temperature. This implies fast intermolecular exchange at low temperature (Scheme 5) and indicates that such a dissociative mechanism is probably at the origin of the low energy fluxional process in the neutral pentacoordinate complexes.

Synthesis and Structural Characterization of the Square-Planar Complex Bromo{1-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-3-mesitylimidazol-2-ylidene}(carbonyl)rhodium(I) (7)

Both the square-planar complexes **5** and **6** are cations. As a neutral analogue we synthesized a rhodium carbonyl derivative by direct reaction of the imidazolium precursor **2** with [Rh(acac)(CO)$_2$] (Scheme 6).[12] The complex



Scheme 4. Synthesis of the cationic four-coordinate complexes [Rh(ligand)(diene)]$^+$ **5** and **6**

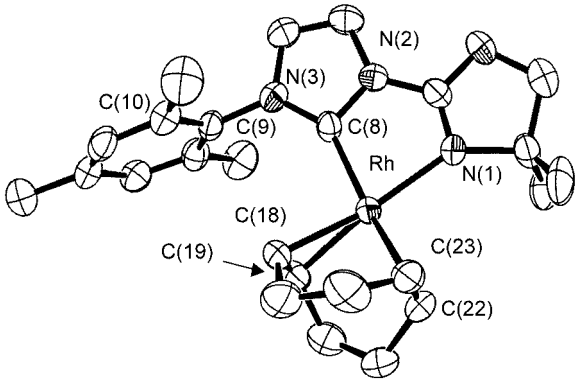


Figure 4. Molecular structure of **5**; selected bond lengths (Å) and angles (°): Rh−N(1) 2.136(3), Rh−C(8) 2.037(7), Rh−C(18) 2.122(4), Rh−C(19) 2.116(4), Rh−C(22) 2.226(5), Rh−C(23) 2.206(5), C(18)−C(19) 1.371(7), C(22)−C(23) 1.357(8); C(8)−Rh−N(1) 78.7(2), C(18)−Rh−C(23) 81.5(2)

[RhBr(Me$_2$carbox)(CO)] (**7**) was obtained in high yield by reacting the two components in THF at room temperature. The synthesis is based on the protonation of the acetylacetonate by the imidazolium precursor and trapping the resulting carbene by coordination to the rhodium(I) centre. The $\nu_{(C=O)}$ band of the carbonyl ligand is observed in the IR spectrum at 1974 cm^{-1} and the detection of a signal at δ = 184.0 ppm in the ^{13}C NMR spectrum, with a characteristic $J_{C,Rh}$ coupling constant of 60 Hz, established the formation of the carbene complex.

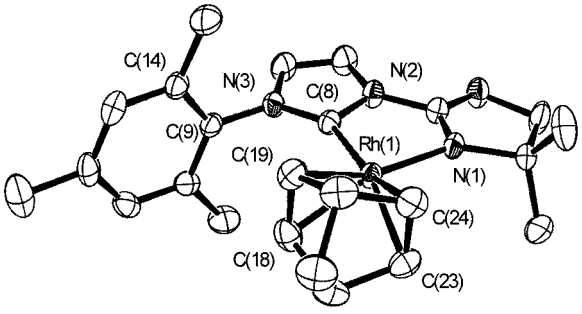


Figure 5. Molecular structure of **6**; selected bond lengths (Å) and angles (°): Rh(1)−C(8) 2.039(6), Rh(1)−N(1) 2.120(5), Rh(1)−C(18) 2.098(7), Rh(1)−C(19) 2.106(7), Rh(1)−C(23) 2.196(7), Rh(1)−C(24) 2.189(7), C(18)−C(19) 1.38(1), C(23)−C(24) 1.35(1); C(8)−Rh−N(1) 78.2(2), C(19)−Rh−C(24) 67.1(3)

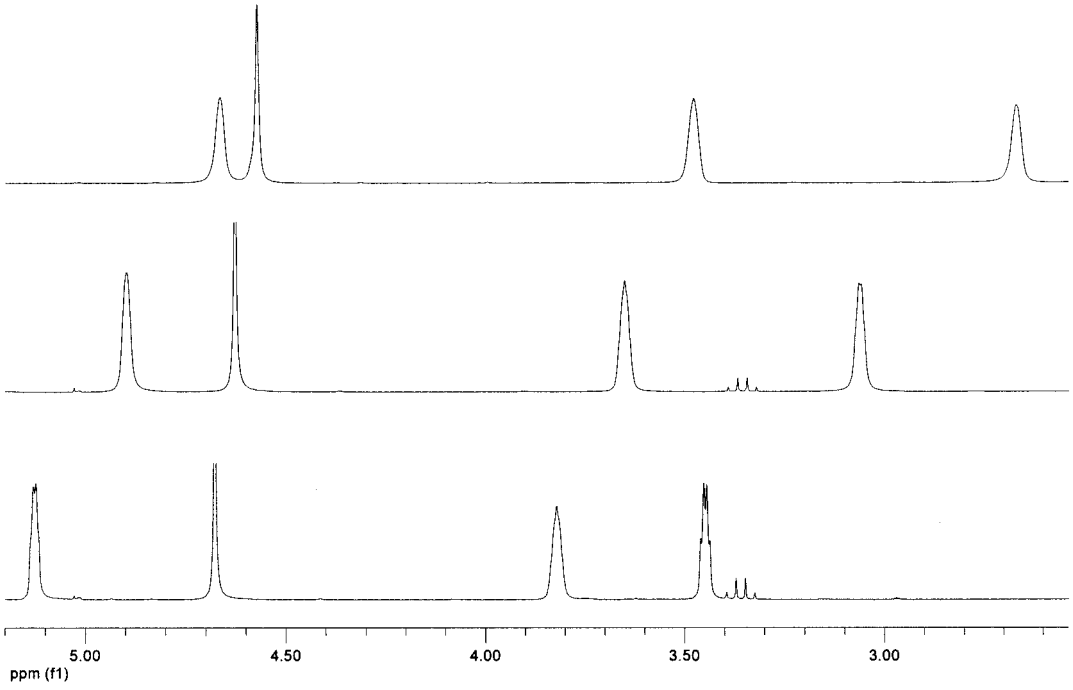
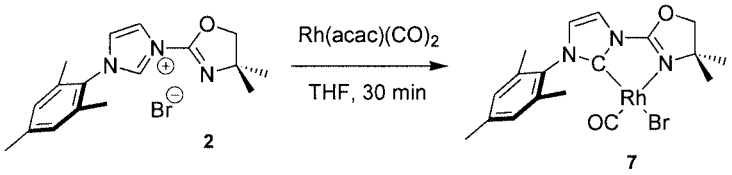


Figure 6. ^{1}H NMR spectra of complex **4** (top), a 1:1 mixture of **4** and **6** (middle) and **6** (bottom) recorded in CD_2Cl_2 at 203 K

Scheme 5. Rapid intermolecular Br^- exchange between complexes **4** and **6**



Scheme 6. Synthesis of the neutral four-coordinate complexes [RhBr(ligand)(CO)] (**7**)

The single-crystal X-ray diffraction study of compound **7** confirmed the square-planar coordination geometry (Figure 7). The carbonyl ligand is disposed *trans* to the oxazoline unit whereas the bromide is coordinated *trans* to the carbene. The rhodium−carbene distance [Rh−C(2) = 1.950(4) Å] and the rhodium−nitrogen distance [Rh−N(3) = 2.143(3) Å]) are within the expected range.[13]

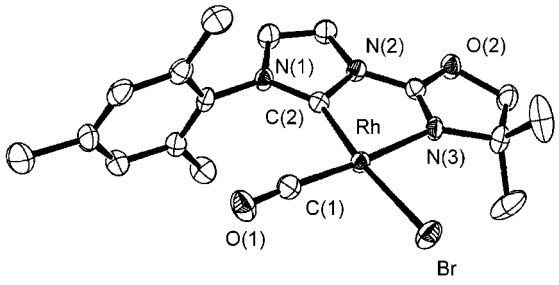


Figure 7. Molecular structure of **7**; selected bond lengths (Å) and angles (deg): Rh−Br 2.5072(5), Rh−C(1) 1.807(4), Rh−C(2) 1.950(4), Rh−N(3) 2.143(3), C(1)−O(1) 1.152(4); Br−Rh−C(1) 90.1(1), Br−Rh−C(2) 173.0(1), C(2)−Rh−N(3) 78.4(1).

It is interesting to compare the C−Rh−N bite angles of the chelating oxazolinylcarbene ligand in the molecular structures of compounds **3**−**7**. The values found for the five-coordinate complexes **3** and **4** are 77.47(9)° and 77.49(8)°, respectively, while the corresponding data of the square-planar cations **5** and **6** are 78.7(2)° and 78.2(2)°, respectively. In the neutral complex **7** this value is 78.4(1)°. The rigidity of the ligand upon coordination to a metal centre thus imposes very well defined metric data, with little variation, regardless of the coordination number or charge of the complex.

Conclusion

The direct condensation of a 2-bromooxazoline derivative with an imidazole provides a modular bidentate ligand precursor which readily coordinates to rhodium(I) complex fragments. The rigidity of the ligand allows for only small variations of the metal−ligand bond lengths and angles, regardless of the coordination number or charge of the complex. The structural details concerning the binding of this class of oxazolinylcarbene ligands have been established in this work. They provide the basis for a systematic use of these functionalised *N*-heterocyclic carbene ligands in catalysis. The first results in catalysis, which we obtained recently, indicate their considerable potential.[6]

Experimental Section

All manipulations were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques or by working in a glove box. THF and diethyl ether were distilled from sodium/benzophenone. Pentane was distilled from a sodium/potassium alloy, dichloromethane was dried over CaH_2 and subsequently distilled. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 NMR spectrometer at 300 MHz and 75 MHz and were referenced to the residual proton solvent peak. Infrared spectra were obtained on a FT-IR Perkin−Elmer 1600 spectrometer and the mass spectra were recorded by the "service de spectrométrie de masse de l'Université Louis Pasteur" on an Autospec HF mass spectrometer. The elemental analyses were performed by the analytical services of the Strasbourg and Heidelberg Chemistry Departments. $[RhCl(COD)]_2$ and $[RhCl(nbd)]_2$ were prepared according to literature procedures.[14] $[Rh(acac)(CO)_2]$ was synthesized by reacting $[RhCl(CO)_2]_2$ with Na(acac) in THF. Potassium *tert*-butoxide was sublimed prior to use. $RhCl_3{\cdot}3H_2O$ was provided by BASF AG (Ludwigshafen). All other reagents were commercially available and used as received.

2-Bromo-4,5-dihydro-4,4-dimethyloxazole (1): *t*BuLi (17.7 mL, 1.7 M in pentane, 30.0 mmol) was added dropwise to a solution of 4,5-dihydro-4,4-dimethyloxazole (3.0 mL, 27.3 mmol) in anhydrous THF (80 mL) at −78 °C over a period of 5 min. The resulting yellow solution was stirred for an additional 15 min prior to the addition of 1,2-dibromo-1,1,2,2-tetrafluoroethane (4.84 mL, 36.8 mmol). The solution was allowed to warm to ambient temperature overnight and was subsequently concentrated to about 15 mL. The brown crude product was purified by a short bulb-to-

bulb distillation to yield a colorless solution of the expected bromo-oxazoline in THF (concentration of about 18% w/w) (2.58 g of pure compound, 53%). ^{1}H NMR ($CDCl_3$): δ = 4.12 (s, 2 H, oxa CH_2), 1.34 (s, 6 H, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 141.4 (N*C*O), 76.3 (*C*H), 71.6 (*C*H_2), 25.5 (*C*H_3) ppm.

1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-3-mesitylimidazolium Bromide (2): 1-Mesityl-1*H*-imidazole (1.11 g, 5.96 mmol) was added to a solution of **1** (1.11 g, 6.23 mmol) in THF (ca. 1.0 M) and the mixture was heated at 50 °C for 2 hours. A white solid precipitated during this period of time. After cooling, diethyl ether (10 mL) was added to complete the precipitation. The product was filtered, washed with diethyl ether (2 × 10 mL) and dried in vacuo to yield 1.80 g (82%) of **2** as a white powder. ^{1}H NMR ($CDCl_3$): δ = 10.57 (t, ^4J = 1.5 Hz, 1 H, NC*H*N), 8.14 (dd, ^3J = 2.1, ^4J = 1.5 Hz, 1 H, 4,5-imidazolium C*H*), 7.60 (dd, ^3J = 2.1, ^4J = 1.5 Hz, 1 H, 4,5-imidazolium C*H*), 7.00 (s, 2 H, mesityl C*H*), 4.53 (s, 2 H, CH_2), 2.32 (s, 3 H, *para* CH_3), 2.16 (s, 6 H, *ortho* CH_3), 1.45 (s, 6 H, oxazoline CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 148.8 (*C*NO), 142.2 (mesityl *C*), 138.3 (N$_2$*C*), 134.4, 130.5 (mesityl *C*), 130.4 (mesityl *C*H), 125.8, 121.3 (imidazolium *C*H), 83.2 (*C*H_2), 68.7 (oxazoline *C*^{4}), 28.4 (*ortho* *C*H_3), 21.5 (*para* *C*H_3), 18.4 (oxazoline *C*H_3) ppm. MS (FAB): *m*/*z* (%) = 284.0 [M]$^+$ (100), 187.0 [M − C_5H_8NO]$^+$ (22). FT-IR (KBr): $\tilde{\nu}$ = 1691 cm^{-1} (s, $\nu_{C=N}$). $C_{17}H_{22}BrN_3O$ (364.29): calcd. C 56.05, H 6.09, N 11.54; found C 55.66, H 6.08, N 11.49.

Bromo(η^4-1,5-cyclooctadiene){1-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-3-mesitylimidazol-2-ylidene}rhodium(I) (3): [RhCl(1,5-COD)]$_2$ (48 mg, 0.098 mmol) and KO*t*Bu (24 mg, 2.2 equiv.) were stirred in THF (5 mL) for 30 min at room temperature. The resulting dark yellow solution was then slowly added to a suspension of the imidazolium salt **2** (72 mg, 2.0 equiv.) in THF (10 mL) at −78 °C. The mixture was allowed to warm to room temperature overnight. The bright yellow solution was centrifuged, the supernatant was separated and the solvents evaporated to give a yellow powder which was washed with pentane (2−3 mL) and dried in vacuo to yield compound **3** (97 mg, 86%). Suitable crystals for an X-ray diffraction studies were obtained by slow diffusion of Et_2O into a solution of **3** in CH_2Cl_2. ^{1}H NMR ($CDCl_3$, 298 K): δ = 7.69 (d, ^3J = 2.1 Hz, 1 H, 4/5-im C*H*), 6.96 (s, 2 H, mes C*H*), 6.82 (d, ^3J = 2.1 Hz, 1 H, 5/4-im C*H*), 4.66 (s, 2 H, oxa CH_3), 2.29 (s, 3 H, *para* CH_3), 2.12 (br, 4 H, COD CH_2), 2.08 (s, 6 H, *ortho* CH_3), 1.74 (br, 4 H, COD CH_2), 1.49 (s, 6 H, oxa CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 177.2 (d, $^1J^{103}_{Rh,}{}^{13}_{C}$ = 53 Hz, N$_2$*C*), 158.8 (N*C*O), 140.4 (*C*$_{mes}$), 134.5 (*C*$_{mes}$), 133.6 (*C*$_{mes}$), 129.5 (*C*H$_{mes}$), 125.2 (*C*H$_{im}$), 118.8 (*C*H$_{im}$), 84.3 (oxa *C*H$_2$), 67.8 (oxa *C*^{4}), 30.5 (br, COD *C*H$_2$), 27.8 (oxa *C*H$_3$), 21.2 (*para* *C*H$_3$), 18.1 (*ortho* *C*H$_3$) ppm. MS (ESI): *m*/*z* (%) = 486.09 (22) [M − Br − COD + 2CH$_3$CN + H$_2$O]$^+$, 527.12 (100) [M − Br − COD + 3CH$_3$CN + H$_2$O]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1677 cm^{-1} (s, $\nu_{C=N}$). $C_{25}H_{33}BrN_3ORh$ (574.36): calcd. C 52.28, H 5.79, N 7.32; found C 51.82, H 5.66, N 7.38.

Bromo{1-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-3-mesitylimidazol-2-ylidene}(η^4-2,5-norbornadiene)rhodium(I) (4): Solid [RhCl(nbd)]$_2$ (86 mg, 0.186 mmol) and KO*t*Bu (46 mg, 0.41 mmol, 2.2 equiv.) were weighed and placed in a Schlenk tube. THF (6 mL) was then added and the reaction mixture was stirred for 30 minutes at ambient temperature. The solution thus obtained was slowly added to a suspension of the imidazolium salt **2** (136 mg, 0.373 mmol, 2.0 equiv.) in THF (12 mL) at −78 °C. The mixture was allowed to warm to ambient temperature overnight and was centrifuged. The resulting orange-red supernatant was separated and the solvents evaporated in vacuo. The crude solid was washed two or three times with pentane (5 mL). Complex **4** was obtained as an orange powder (175 mg, 84%). Crystallization from CH_2Cl_2/Et_2O gave small orange crystals suitable for an X-ray diffraction study. ^{1}H NMR ($CDCl_3$): δ = 7.30 (d, ^3J = 2.1 Hz, 1 H, 4/5-im C*H*), 6.95 (s, 2 H, C*H*$_{mes}$), 6.62 (d, ^3J = 2.1 Hz, 1 H, 4/5-im C*H*), 4.52 (s, 2 H, oxa CH_2), 3.58 (br. m, 4 H, 2/3/5/6-nbd C*H*), 3.45 (m, 2 H, 1/4-nbd C*H*), 2.30 (s, 3 H, *para* CH_3), 2.20 (s, 6 H, *ortho* CH_3), 1.45 (s, 6 H, oxa CH_3), 0.98 (s, 2 H, CH_{2nbd}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 183.6 (d, $^1J^{103}_{Rh,}{}^{13}_{C}$ = 55 Hz, N$_2$*C*), 155.6 (N*C*O), 139.5 (*C*$_{mes}$), 135.6 (*C*$_{mes}$), 133.6 (*C*$_{mes}$), 128.8 (*C*H$_{mes}$), 123.5 (*C*H$_{im}$), 115.6 (*C*H$_{im}$), 84.6 (oxa *C*H$_2$), 67.3 (oxa *C*^{4}), 60.1 (nbd *C*H$_2$), 49.2 (1/4-*n*bd *C*H), 28.5 (oxa *C*H$_3$), 21.1 (*para* *C*H$_3$), 18.6 (*ortho* *C*H$_3$) ppm. MS (ESI): *m*/*z* (%) = 478.13 (100) [M − Br]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1664 cm^{-1} (s, $\nu_{C=N}$). $C_{24}H_{29}BrN_3ORh$ (558.32): calcd. C 51.63, H 5.23, N 7.53; found C 51.11, H 5.19, N 7.34.

(η^4-1,5-Cyclooctadiene){1-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-3-mesitylimidazol-2-ylidene}rhodium(I) Hexafluorophosphate (5): Solid KPF_6 (34 mg, 0.185 mmol, 1.5 equiv.) was added to an orange solution of **3** (70 mg, 0.122 mmol) in CH_2Cl_2 (5 mL). Degassed water (5 mL) was subsequently added and the mixture was stirred vigorously for 30 minutes. The organic layer was decanted and the aqueous layer was washed with an additional 5 mL of CH_2Cl_2. The organic layers were combined, dried over Na_2SO_4 and the volatiles were removed in vacuo. After washing with Et_2O (5 mL) and drying, an orange powder was isolated (76 mg, 98%). Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a saturated solution of **5** in CH_2Cl_2/Et_2O. ^{1}H NMR ($CDCl_3$): δ = 7.50 (d, ^3J = 2.1 Hz, 1 H, 4/5-im CH), 6.96 (s, 2 H, C*H*$_{mes}$), 6.75 (d, ^3J = 2.1 Hz, 1 H, 4/5-im C*H*), 5.32−5.29 (m, 2 H, COD C*H*), 4.70 (s, 2 H, oxa CH_2), 3.66−3.64 (m, 2 H, COD C*H*), 2.33 (s, 3 H, *para* CH_3), 2.33−2.10 (m, 4 H, COD CH_2), 2.10 (s, 6 H, *ortho* CH_3), 1.98−1.92 (m, 2 H, COD CH_2), 1.82−1.76 (m, 2 H, COD CH_2), 1.49 (s, 6 H, oxa CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ = 174.2 (d, $^1J^{103}_{Rh,}{}^{13}_{C}$ = 54 Hz, N$_2$*C*), 160.2 (N*C*O), 140.8, 134.2, 133.0 (*C*$_{mes}$), 129.7 (*C*H$_{mes}$), 125.3 (*C*H$_{im}$), 118.2 (*C*H$_{im}$), 97.6 (d, $J^{103}_{Rh,}{}^{13}_{C}$ = 7.5 Hz, COD *C*H), 85.1 (oxa *C*H$_2$), 74.4 (d, $J^{103}_{Rh,}{}^{13}_{C}$ = 13 Hz, COD *C*H), 67.9 (oxa *C*^{4}), 31.8, 29.1 (COD *C*H$_2$), 27.4 (oxa *C*H$_3$), 21.2 (*para* *C*H$_3$), 17.6 (*ortho* *C*H$_3$) ppm. MS (ESI): *m*/*z* (%) = 486.09 (100) [RhL(CH$_3$CN)$_2$(H$_2$O)]$^+$, 527.12 (46) [RhL(CH$_3$CN)$_3$(H$_2$O)]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1664 cm^{-1} (s, $\nu_{C=N}$). $C_{25}H_{33}F_6N_3OPRh$ (639.42): calcd. C 46.96, H 5.20, N 6.57; found C 46.9, H 5.35, N 6.65.

{1-(4,5-Dihydro-4,4-dimethyloxazol-2-yl)-3-mesitylimidazol-2-ylidene}(η^4-2,5-norbornadiene)rhodium(I) Tetrafluoroborate (6): Solid $NaBF_4$ (37 mg, 0.340 mmol, 2 equiv.) was added to an orange solution of **4** (95 mg, 0.170 mmol) in CH_2Cl_2 (5 mL). Degassed water (5 mL) was then added and the resulting red mixture was stirred vigorously for 30 min. The organic layer was removed and the aqueous layer was washed with an additional 5 mL of CH_2Cl_2. The organic layers were combined, dried over Na_2SO_4 and the volatiles were removed in vacuo. Crystallization of the crude material from CH_2Cl_2/Et_2O gave reaction product **6** in the form of long, red needles (77 mg, 80%). Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of Et_2O into a saturated solution of **4** in CH_2Cl_2/Et_2O. ^{1}H NMR ($CDCl_3$): δ = 7.52 (d, ^3J = 2.1 Hz, 1 H, 4/5-im C*H*), 6.81 (s, 2 H, C*H*$_{mes}$), 6.67 (d, ^3J = 2.1 Hz, 1 H, 4/5-im C*H*), 5.13 (br, 2 H, nbd C*H*), 4.76 (s, 2 H, oxa CH_2), 3.87 (br, 2 H, nbd C*H*), 3.52 (br, 2 H, 1/4nbd C*H*), 2.26 (s, 3 H, *para* CH_3), 2.07 (s, 6 H, *ortho* CH_3), 1.33 (s, 6 H, oxa CH_3), 1.31 (s, 2 H, nbd CH_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 175.3 (d, $^1J^{103}_{Rh,}{}^{13}_{C}$ = 59 Hz, N$_2$*C*), 161.8 (N*C*O), 140.5, 134.4, 132.5 (*C*$_{mes}$), 129.2 (*C*H$_{mes}$), 124.7 (*C*H$_{im}$), 117.4 (*C*H$_{im}$), 85.8 (oxa *C*H$_2$), 82.2 (oxa *C*^{4}), 66.3, 65.8 (nbd *C*H), 59.0 (nbd *C*H$_2$), 53.9, 53.5 (1/4-nbd

Table 1. X-ray experimental data of compounds **3**−**7**

	3	**4**	**5**	**6**	**7**
Formula	$C_{25}H_{33}BrN_3ORh$	$C_{24}H_{29}BrN_3ORh$	$C_{25}H_{33}BrN_3ORhPF_6$	$C_{72}H_{87}N_9O_3Rh_3{\cdot}3BF_4{\cdot}2CH_2Cl_2{\cdot}H_2O$	$C_{18}H_{21}BrN_3O_2Rh$
Mol. mass	574.38	558.33	639.43	1883.57	494.20
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	*Pbca*	$P12_1/n$ (no. 1)	$C1c$ (no. 1)	$P12_1/c$ (no. 1)	$P12_1/c$ (no. 1)
a (Å)	13.3030(2)	10.8649(1)	11.6730(2)	26.2844(2)	10.6735(3)
b (Å)	18.9492(2)	9.2177(1)	23.2279(5)	11.5110(1)	11.6164(3)
c (Å)	18.6447(3)	22.4762(3)	10.1204(3)	28.0873(2)	16.3699(4)
β (°)		91.557(5)	97.450(5)	97.268(5)	103.738(5)
V (Å^3)	4700.0(1)	2250.15(4)	2720.9(1)	8429.8(1)	1971.60(9)
Z	8	4	4	4	4
$\rho_{calcd.}$ (g·cm^{-3})	1.62	1.65	1.56	1.48	1.66
$F000$	2336	1128	1304	3832	984
μ (mm^{-1})	2.449	2.555	0.751	0.785	2.908
Temperature (K)	173	173	293	294	173
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Number of data meas.	13757	11954	7090	25736	9055
Number of data with $I > 3\sigma(I)$	4481	5853	5347	16749	3680
Number of variables	280	271	332	1039	226
R	0.029	0.030	0.036	0.069	0.029
Rw	0.036	0.054	0.047	0.089	0.049
GOF	1.032	1.028	1.012	1.209	1.026
Largest peak in final difference (e·Å^{-3})	0.509	2.088	0.405	1.482	0.402

*C*H), 27.7 (oxa *C*H$_3$), 21.1 (*para* *C*H$_3$), 17.7 (*ortho* *C*H$_3$) ppm. MS (ESI): *m/z* (%) = 478.12 (24) [M − BF$_4$]$^+$, 510.11 (64) [M − BF$_4$ − nbd + 3CH$_3$CN]$^+$, 537.12 (100). FT-IR (KBr): $\tilde{\nu}$ = 1662 cm^{-1} (s, $\nu_{C=N}$).

Bromo(carbonyl){1-(4,5-dihydro-4,4-dimethyloxazol-2-yl)-3-mesityl-imidazol-2-ylidene}rhodium(I) (7): [Rh(acac)(CO)$_2$] (75 mg, 0.290 mmol) and the imidazolium salt **2** (106 mg, 1.0 equiv.) were placed in a Schlenk tube and dissolved in THF (8 mL). A rapid evolution of a gas (CO) was observed and the solution color immediately turned bright yellow. After stirring for 50 minutes at ambient temperature, the reaction mixture was centrifuged, the supernatant was separated and the solvents evaporated to dryness. The crude product was washed with pentane (2 × 4 mL) to yield the analytically pure compound **7** as a yellow microcrystalline solid (122 mg, 85%). Crystallization from CH_2Cl_2/pentane gave yellow crystals suitable for X-ray diffraction. ^{1}H NMR ($CDCl_3$): δ = 7.28 (d, ^3J = 2.3 Hz, 1 H, 4/5-im C*H*), 7.04 (s, 2 H, C*H*$_{mes}$), 6.70 (d, ^3J = 2.3 Hz, 1 H, 4/5-im C*H*), 4.62 (s, 2 H, oxa C*H*$_2$), 2.32 (s, 3 H, *para* C*H*$_3$), 2.10 (s, 6 H, *ortho* C*H*$_3$), 1.72 (s, 6 H, oxa C*H*$_3$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 187.4 (d, $^1J^{103}_{Rh,}{}^{13}_{C}$ = 78 Hz, *C*O), 184.0 (d, $^1J^{103}_{Rh,}{}^{13}_{C}$ = 60 Hz, N$_2$*C*), 158.5 (N*C*O), 140.4 (*C*$_{mes}$), 135.0 (*C*$_{mes}$), 134.0 (*C*$_{mes}$), 129.4 (*C*H$_{mes}$), 123.5 (*C*H$_{im}$), 114.7 (*C*H$_{im}$), 86.4 (oxa *C*H$_2$), 67.4 (oxa *C*^{4}), 28.2 (oxa *C*H$_3$), 21.2 (*para* *C*H$_3$), 18.0 (*ortho* *C*H$_3$) ppm. FT-IR (KBr): $\tilde{\nu}$ = 1974 cm^{-1} (s, $\nu_{C=O}$), 1670 cm^{-1} (s, $\nu_{C=N}$). $C_{17}H_{21}BrN_3O_2Rh$ (494.19): calcd. C 43.75, H 4.28, N 8.50; found C 42.93, H 4.05, N 8.14.

Intermolecular Br$^-$ Exchange between Complexes 4 and 6: Equal amounts of compounds **4** and **6** (20 μmol) were weighed, placed into an NMR tube and dissolved in CD_2Cl_2 (0.5 mL). In an ^{1}H NMR spectrum, which was recorded at 203 K, the signals of complexes **4** and **6** were not observed separately but a set of resonances at the weighted mean chemical shift indicated a fast intermolecular exchange of bromide between **4** and **6**.

X-ray Crystallographic Study of Compounds 3−7: Suitable crystals of complexes **3**, **4**, **5**, **6** and **7** were obtained by layering concentrated solutions of the compounds in dichloromethane with pentane, hexane or diethyl ether (vide supra) and allowing slow diffusion at room temperature. The crystal data were collected at −100 °C on a Nonius KappaCCD diffractometer and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[15] The structures were solved by direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference Fourier maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C−H: 0.95 Å) and isotropic temperature factors [B(H) = 1.3 B_{eqv}(C) Å^2] but not refined. Full least-square refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from the literature.[16] Crystal data and experimental details for the crystals of compounds **3**−**7** are given in Table 1.

CCDC-229779 ... -229783 (for **3**−**7**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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