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A New Class of Modular Oxazoline-NHC Ligands and Their Coordination Chemistry with Platinum Metals

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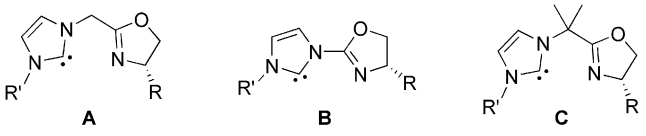
A novel family of enantiomerically pure imidazolium salts $[(NHC\text{-}Ox)H]^+X^-$ (**2a**–**g**) has been generated bearing an oxazoline unit and in which both heterocycles are connected by a (dimethyl)methylene bridge. Deprotonation of the imidazolium salt **2f** and subsequent reaction of the resulting free carbene with $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) afforded the neutral rhodium(I) complex [(NHC-Ox)Rh(nbd)Br] (**3**) in which the ligand was found to be monodentate. Bromide abstraction lead to the air-stable cationic complex [(NHC-Ox)-Rh(nbd)]PF_6 (**4**) with the expected bidentate coordination mode of the ligand. Reaction of the imidazolium salt **2d** with Karstedt's catalyst and one equivalent of KO*t*Bu gave the trigonal planar platinum(0) complex [(NHC-Ox)Pt(dvtms)] (**5**) (dvtms = divinyltetramethylsiloxane), which was oxidized by $CsBr_3$ to give the square planar platinum(II) complex [(NHC-Ox)$PtBr_2$] (**6**). Complex [(NHC-Ox)$PtCl_2$] (**7**) was directly prepared by reaction of the imidazolium salt with Ag_2O followed by the addition of $[PtCl_2(1,5\text{-cod})]$.

Introduction

The design of efficient chiral ligands for asymmetric catalysis is usually based on simple concepts and principles such as molecular symmetry, modularity in the assembly of polydentate ligands or the use of "privileged" structural motifs.[1,2] Among all the stereoinducing elements, the oxazoline ring has become one the most commonly employed.[3] Indeed, such chiral enantiopure units are not only easily accessible, but being rigid, quasi-planar five-membered rings they also provide a good control of the first coordination sphere of the transition metal upon *N*-coordination.[4]

N-Heterocyclic carbenes[5] are excellent "anchor" units for late transition metals which form strong metal–carbon bonds[6] and have thus been widely used in homogeneous catalysis.[7] They may be combined with other ligating units by the appropriate functionalization of the N-atoms in their heterocyclic structures.[8] Especially the combination of an *N*-heterocyclic carbene with an oxazoline unit has led to very efficient catalytic systems.[9–11] The first example of such a combination was provided by Herrmann et al. who reported the bidentate ligand **A**, where the two heterocycles are connected by a methylene bridge (Scheme 1).[12] The corresponding Rh^I complexes were employed as catalysts in the hydrosilylation of ketones but afforded low enantioselectivities (*ee* values up to 11%).[13]



Scheme 1.

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%).[14] We described the direct coupling of oxazolines and *N*-heterocyclic carbenes generating highly rigid type **B** chelate ligands.[15] This strategy has provided the key to a highly efficient class of catalysts for the asymmetric hydrosilylation of prochiral ketones[16] 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.[17]

We were therefore interested in NHC-oxazoline ligands **C** in which the two heterocycles are connected by a (dimethyl)methylene bridge. In comparison with the type **A** ligands, the methyl groups on the methylene bridge are expected to kinetically stabilize the bridge under the conditions of molecular catalysis. We report herein the synthesis of chiral carbene precursors of **C** and their first use in the coordination chemistry of platinum(0 or II) as well as rhodium(I).

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Results and Discussion

Synthesis of the Chiral Imidazolium Salts 2a–g

The synthesis of the imidazolium salts **2a**–**g**, which are the precursors of ligand **C** is summarized in Scheme 2, the key step being the final coupling of the chiral imidazole derivatives **1a**,**b** with a series of alkyl halides. The substituted imidazoles **1a**,**b** were obtained in good yield via a three-step synthesis from imidazole, ethyl 2-bromoisobutyrate and the chiral amino alcohol [(*S*)-valinol or (*S*)-*tert*-leucinol].[18]

The corresponding imidazolium salts **2a**–**g** were isolated as relatively air-stable white powders. The ^{1}H and ^{13}C NMR spectra of **2a**–**g** are consistent with the proposed structure of the molecule. The signals of the C2-*H* proton of the imidazolium ring were observed at δ = 11.16–9.80, reflecting the positive electronic charge located in the ring. Intense molecular ion peaks $[M - Br]^+$ were observed in the mass spectra of all compounds, whilst the IR vibrational bands $\nu_{(C=N)}$ of the oxazoline units were found between 1672 and 1661 cm^{-1}. Suitable crystals for an X-ray diffraction analysis of **2e** were obtained to establish its structural details (Figure 1). The molecule crystallizes as a pair of conformers, which are related to one another by a pseudo centre of inversion (disregarding the chiral centre). Both have similar bond lengths and angles and correspond to rotations along the C(13)–C(14), C(13)–C(24) and N(2)–C(7) bonds. The imidazole ring and the oxazoline ring are almost orthogonal to each other (angles between the best planes through the rings are 84 and 82°, respectively).

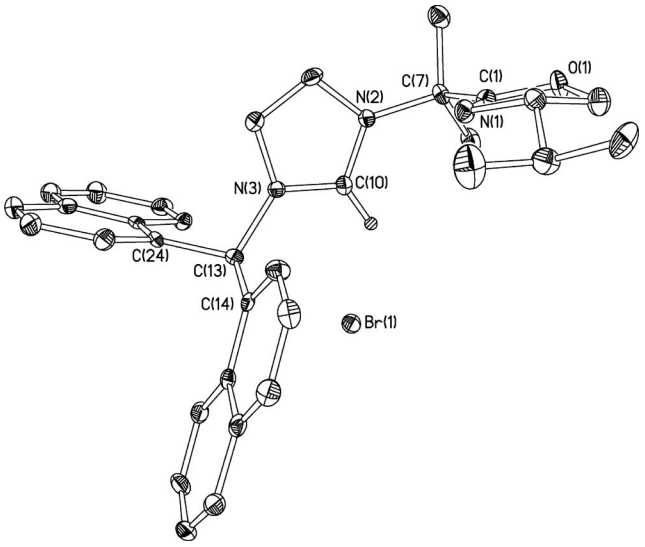
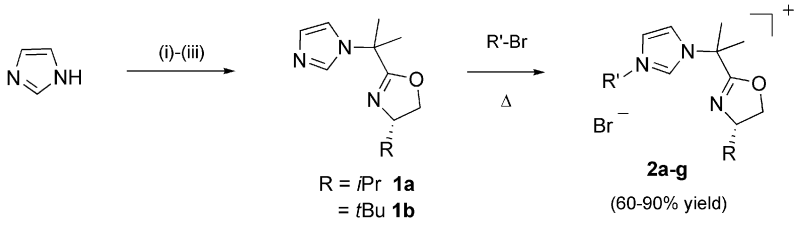
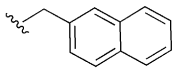
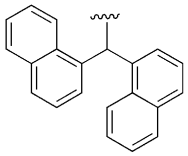


Figure 1. Molecular structure of imidazolium salt **2e** (only one of the two independent moieties is shown, hydrogen atoms, except for C(10)–H, omitted for clarity). Selected bond lengths [Å] and angles [°] (values in square brackets refer to the second cation): C(10)–N(2) 1.326(5) [1.329(5)], C(10)–N(3) 1.325(5) [1.315(5)], C(1)–N(1) 1.248(6) [1.245(5)], N(2)–C(10)–N(3) 108.9(4) [109.0(4)], N(1)–C(1)–C(7)–N(2) –10.3(6) [–0.9(6)], C(1)–C(7)–N(2)–C(10) –89.1(5) [77.5(5)]. Thermal ellipsoids drawn at 25% probability.

The imidazolium salts were readily deprotonated with KHMDS (= potassium hexamethyldisilazide) to afford the corresponding free carbenes, following a procedure reported by Coleman et al.[19] The two carbenes derived from **2e** and **2f** have been characterized spectroscopically in solution. The formation of the free carbenes was confirmed by



	R	R'
2a	*i*Pr	-Me
2b	*i*Pr	-CH_2Ph
2c	*i*Pr	
2d	*i*Pr	

	R	R'
2e	*i*Pr	
2f	*t*Bu	
2g	*t*Bu	

Scheme 2. Synthesis of the imidazolium salts **2a**–**g** (note: the counterion of **2a** is iodide instead of bromide). (i) $BrC(CH_3)_2COOEt$, CH_3CN, reflux, 3 d; (ii) amino alcohol, NaH cat., 120 °C, 4 h; (iii) MsCl, NEt_3, CH_2Cl_2 then NaOH, $MeOH/H_2O$.

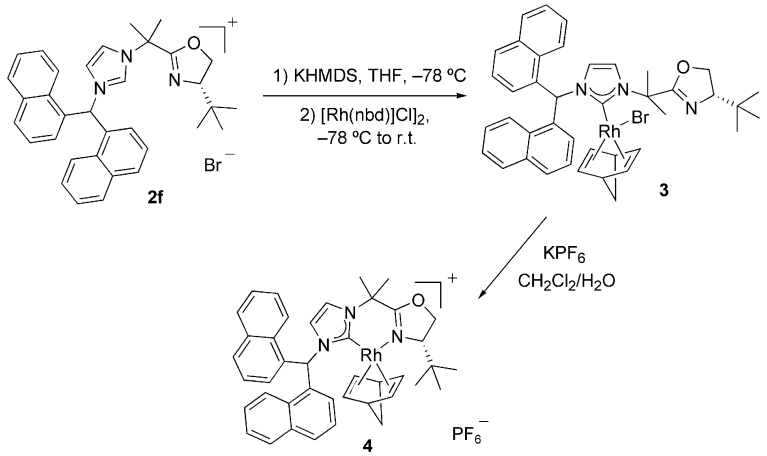
the disappearance of the C2-*H* proton in the ^{1}H NMR spectra, and the typical chemical shift of the carbene carbon at low field (δ = 217.3 in the ^{13}C-NMR spectra for both carbenes).

Synthesis and Structural Characterization of the Rhodium(I) Complexes 3 and 4

In order to study the coordination behavior of the (dimethyl)methylene bridged ligand **C**, neutral and cationic Rh^{I} complexes were prepared. The procedure previously used in our group for the synthesis of the **B**-type rhodium complexes, namely the reaction of the alkoxy-rhodium precursor with the imidazolium salts, could not be applied to **C**, probably due to a different reactivity of the potassium *tert*-butoxide towards the imidazolium salts **2**.[12] However, the latter being cleanly deprotonated by KHMDS and the corresponding free carbene being relatively stable, a procedure similar to the one developed by Lassaletta et al. was chosen (Scheme 3).[20] In a first step, the imidazolium salt **2f** was deprotonated with KHMDS at –78 °C in thf and a solution of [Rh(nbd)Cl]$_2$ in thf was subsequently added. After warming to ambient temperature and workup, complex **3** was isolated as a slightly air-sensitive yellow solid.

The ^{1}H and ^{13}C-NMR spectroscopic data are consistent with the formation of a carbene complex. At room temperature, most of the ^{1}H NMR signals are very broad as a consequence of fluxional processes, and a fully assignable NMR spectrum could be obtained at 263 K. The coordination of the imidazolyl ring to rhodium is confirmed by the coupling of the carbene ^{13}C nuclei with rhodium, $^1J_{(Rh\text{-}C)}$ = 56.1 Hz. The four inequivalent C$H_{2/3/5/6\text{-}nbd}$ protons and the diastereotopic C$H_{2\ nbd}$ protons appear as separate resonances. The ^{15}N-NMR chemical shift of the N_{oxa} resonance at δ = 180.3 is inconclusive as to the role of the oxazoline donor and indicates a probable coordination/decoordination equilibrium of the oxazolinyl ring to the metal center in solution at low temperature. The observed fluxional behaviour at room temperature may be due to rapid coordination/decoordination of the oxazoline ring (vide infra). Another possibility is that the oxazolinyl ring remains coordinated and the metal center undergoes polytopal Berry-type rearrangements similar to those observed in complexes with ligand **B** as well as bromide association/dissociation processes.[21] The characteristic vibrational band of the C=N bond is only slightly shifted from 1669 (**2f**) to 1664 cm^{-1} (**3**), which in turn is consistent with a non-coordinated oxazoline. In order to resolve this structural ambiguity and to establish the molecular structure of compound **3**, an X-ray diffraction study has been carried out (Figure 2). The complex crystallizes with two independent molecules in the unit cell, which are related by a pseudo centre of symmetry (disregarding the oxazoline rings). The two diastereomers roughly correspond to a 180° rotation of the NHC ligand around the Rh–$C_{carbene}$ bond. The coordination geometry around the metal center is approximately square planar as observed in other structures of neutral NHC-Rh^{I} complexes, and the ligand is monodendate.[22] The distortion from an ideal square-planar coordination is due to the rigidity and the small bite angle of the nbd ligand. To minimize the steric hindrance, the imidazolyl ring is twisted by almost 90° out of the coordination plane. The $C_{carbene}$–Rh bond length (2.070(2) and 2.065(2) Å] is within the range reported in the Cambridge Structural Database for NHC-Rh^{I} complexes ($C_{carbene}$–Rh^{I} = 2.035 Å for 163 examples). As expected, the Rh–C_{nbd} distances *trans* to the carbene carbon atom are longer than those *trans* to the bromide (average values are 2.180 vs. 2.121 Å). This *trans* influence is also reflected in the difference in the C=C double bond lengths of the coordinated nbd ligand (average values 1.381 vs. 1.407 Å).

The bromide ligand in **3** could be abstracted by stirring of **3** with an excess of KPF_6 in a CH_2Cl_2/water solvent system (Scheme 3). The cationic complex **4** was isolated from the organic phase as an air-stable red compound. The ^{1}H-, ^{13}C- and ^{15}N-NMR spectra of **4** recorded at 263 K are very similar to those of **3**, and do not show clear evidence for the generation of the cationic complex. The typical signal of the carbene carbon as a doublet is observed at δ = 177.6 with a coupling constant of $^1J_{(Rh\text{–}C)}$ = 56.5 Hz. Finally, the



Scheme 3. Synthesis of the neutral rhodium(I) complex **3** and its cationic derivative **4**.

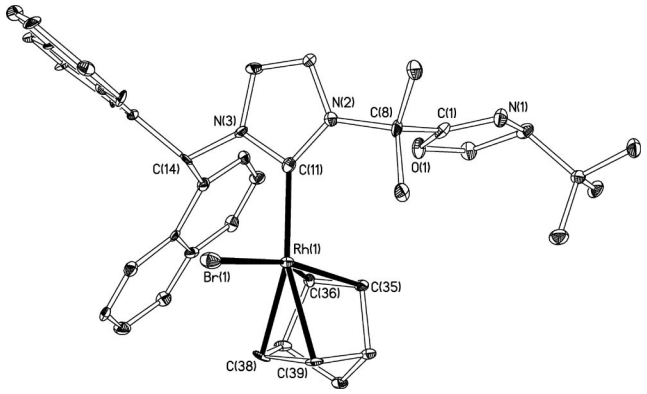


Figure 2. Molecular structure of complex **3** (only one of the two independent molecules is shown, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°] (values in square brackets refer to the second molecule): Rh(1)–C(11) 2.070(2) [2.065(2)], Rh(1)–Br(1) 2.5029(3) [2.5031(4)], Rh(1)–C(35)/C(36) 2.143(2)/2.107(2) [2.115(2)/2.119(2)], Rh(1)–C(38)/C(39) 2.178(2)/2.183(2) [2.169(2)/2.188(2)], C(35)–C(36) 1.363(2) [1.451(3)], C(38)–C(39) 1.377(3) [1.384(3)], C(11)–Rh(1)–Br(1) 91.38(5) [91.03(5)], C(11)–Rh(1)–C(35)/C(36) 101.85(7)/99.10(6) [102.61(7)/101.94(6)], Br(1)–Rh(1)–C(38)/C(39) 94.44(5)/96.01(5) [93.40(6)/96.87(5)], C(35)–Rh(1)–C(39) 67.47(7) [65.92(7)], C(36)–Rh(1)–C(38) 67.69(6) [65.77(7)], N(2)–C(8)–C(1)–N(1) 156.68(2) [137.5(2)]. Thermal ellipsoids drawn at 35% probability.

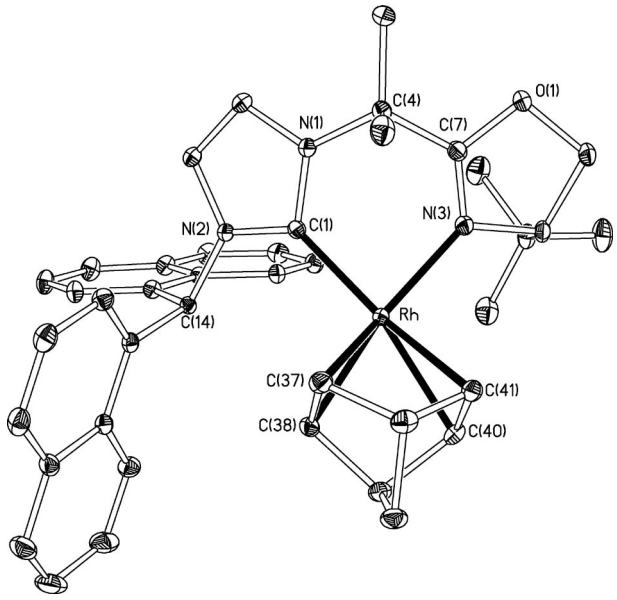


Figure 3. Molecular structure of complex **4** (hydrogen atoms and counterion omitted for clarity). Selected bond lengths [Å] and angles [°]: Rh–C(1) 2.025(1), Rh–N(3) 2.095(1), Rh–C(37)/C(38) 2.100(1)/2.143(1), Rh–C(40)/C(41) 2.240(1)/2.189(2), C(37)–C(38) 1.404(2), C(40)–C(41) 1.383(2), C(1)–Rh–N(3) 84.11(5), C(1)–Rh–C(37)/C(38) 99.77(5)/104.49(5), N(3)–Rh–C(40)/C(41) 105.57(5)/94.89(5), C(37)–Rh–C(41) 67.43(6), C(38)–Rh–C(40) 65.30(6), N(1)–C(4)–C(7)–N(3) –37.3(2). Thermal ellipsoids drawn at 40% probability.

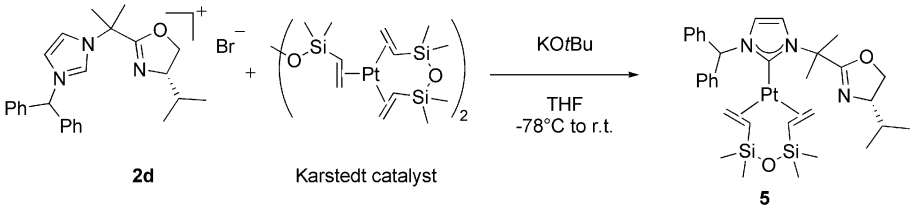
infrared spectrum of **4** displays a vibrational band at 1637 cm^{-1}, which is the signature of the coordination of the oxazoline unit.

Diffraction quality single crystals of **4**·$CDCl_3$ were grown by slow diffusion from pentane/$CDCl_3$. The complex adopts a distorted square-planar geometry where the oxazolinyl/carbene ligand is chelating through both donor functions (Figure 3). As observed in the structure of complex **3**, the distortion is due to the rigidity and the small bite angle of the nbd ligand [C(37)–Rh–C(41) 67.43(6), C(38)–Rh–C(40) 65.30(6)°], but also due to the chelate angle of the oxazolinyl/carbene ligand (C(1)–Rh–N(3) 84.11(5)°]. The imidazolyl and oxazolyl rings are non-coplanar and oriented so that the *tert*-butyl group of the oxazoline points in one direction and the bridging (dimethyl)-methylene in the other and out of the coordination plane [N(1)–C(4)–C(7)–N(3) –37.3°], to form a boat-shaped (Rh–C–N–C–C–N) chelate ring. The nbd ligand is bent away from the ideal coordination plane to avoid unfavorable repulsion with the *tert*-butyl substituent [C(1)–Rh–C(40) 165.51(5)°, N(3)–Rh–C(38) 170.67(5)°]. This arrangement also allows an overlap between the π*-orbital of the $C{=}C_{nbd}$ bonds and the high energy d_{z^2} metal orbital, enhancing back-donation from the electron rich metal center.[23] The $C_{carbene}$–Rh bond length [C(1)–Rh 2.025(1) Å] is within the range reported for NHC–Rh^I complexes and similar to **3**.

Synthesis and Structural Characterization of Platinum(0) and (II) Complexes

The platinum(0) complex [(NHC-Ox)Pt(dvtms)] (**5**) (dvtms = divinyltetramethylsiloxane) was synthesized by reaction of the imidazolium salt **2d** with potassium *tert*-butoxide in presence of Karstedt's catalyst, according to a procedure reported by Markó et al.[24] (Scheme 4). The product was purified by column chromatography and isolated as an air-stable white solid.

The ^1H-, ^{13}C- and ^{15}N-NMR spectra in CD_2Cl_2 solution at 273 K display two sets of signals having the same intensity, which indicates that the complex exists as two conformers in an equimolar ratio. The coordination of the



Scheme 4. Synthesis of the platinum(0) complex **5**.

imidazolyl ring to platinum is confirmed by the large coupling constants of the carbene carbons with ^{195}Pt of $^{1}J_{(Pt\text{-}C)}$ = 1375.7 Hz and 1384.3 Hz. The isopropyl protons have similar environments as indicated by their chemical shifts (δ = 0.97, 0.95, 0.89 and 0.88) and the ^{15}N NMR resonance of N_{oxa} at δ = 259.5, 253.9 is typical for a non-coordinated oxazoline. The characteristic vibrational band of the C=N bond is only slightly shifted from $\tilde{\nu}$ = 1670 (**2d**) to 1663 cm^{-1} (**5**), which is also evidence for non-binding of the oxazoline. The coordination of the dvtms ligand to the metal center is confirmed by the upfield shift of the vinylsilane protons, from δ = 6.1–5.7 for free dvtms to δ = 2.2–1.6 in **5**. Moreover, the ^{195}Pt nuclei couple with several vinyl protons and ^{13}C nuclei: $^{2}J_{(Pt\text{-}H)}$ = 53 Hz for the CH=CH_2 protons, $^{1}J_{(Pt\text{-}C)}$ = 165 Hz for the CH=*C*H$_2$ carbons and $^{1}J_{(Pt\text{-}C)}$ = 120 Hz for the *C*H=CH$_2$ carbons. Another interesting observation is the splitting of the $SiMe_2$ proton resonance into two distinct signals for the *pseudo*-equatorial and *pseudo*-axial positions at δ = 0.3 and –0.5 respectively.[25] This behavior has already been reported for other Pt(0) complexes bearing a chelating dvtms ligand. The two conformers observed in solution may correspond to the two *pseudo*-chair conformations of the dvtms, or to hindered rotations of the (dimethyl)methylene bridge.

The molecule crystallizes as a pair of conformers in the unit cell. Both have similar bond lengths and angles and are related by rotation around the N(1)–C(13) and N(2)–C(4) bonds. The metal center adopts a trigonal planar arrangement which is the characteristic coordination mode of [Pt^0(olefin)$_n$] complexes (Figure 4).[26] This trigonal planar conformation around platinum provides a better overlap between the Pt d-orbitals and the olefinic π* acceptor orbitals, thus enhancing the backbonding.[27] The oxazoline ring is not coordinated to the metal center, whereas the bidentate dvtms ligand adopts a *pseudo*-chair conformation. To minimize interligand repulsion, the NHC ligand is tilted by almost 90° out of the coordination plane spanned by the platinum center and the vinyl carbon atoms. The $C_{carbene}$–Pt bond length [2.06(1) Å] is within the range reported in the Cambridge Crystallographic Structural Database for mono *N*HC–Pt^0 complexes (average of 2.047 Å for 21 examples). The C=C bond lengths of the dvtms ligand (average value 1.43 Å) are halfway between a single and a double bond as a result of the backbonding.

The transformation of the platinum(0) complex **5** into a platinum(II) species leads to the coordination of the oxazoline unit. A clean oxidation of **5** was achieved by stoichiometric reaction with $CsBr_3$, which acts as mild source of Br_2 (Scheme 5).[28,29] The platinum(II) complex **6** was isolated after purification by column chromatography as a white solid in 56% yield.

The oxidation of the platinum is confirmed in the ^{13}C-NMR spectrum by the upfield shift of the carbene carbon resonance from δ = 184.5 (**5**) to 144.2 (**6**).[30] In the ^{1}H NMR spectrum, the oxazolyl ring proton signals are observed downfield compared to the platinum(0) complex (δ = 4.36–3.89 (**5**), 4.52–4.35 (**6**)) and the isopropyl protons show very different chemical shifts (δ = 0.57, 0.07). The

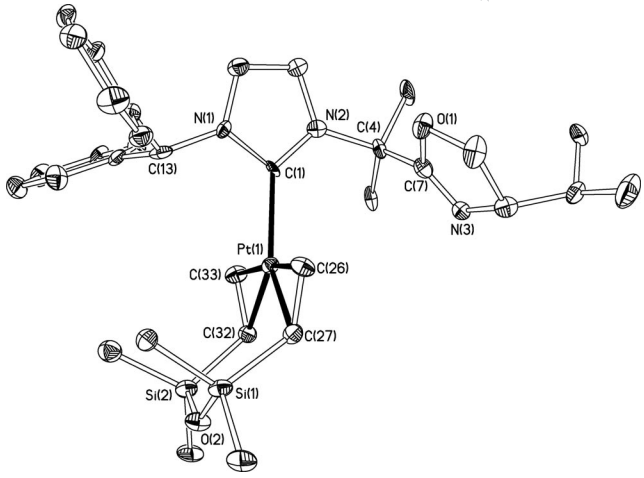
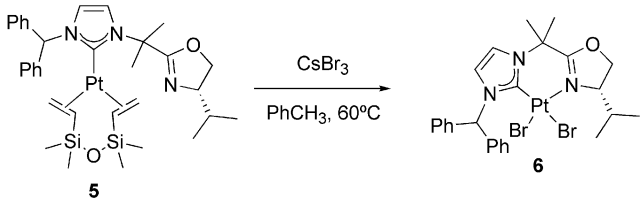


Figure 4. Molecular structure of complex **5** (only one of the two independent molecules is shown, hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°] (values in square brackets refer to the second molecule): Pt(1)–C(1) 2.06(1) [2.06(1)], Pt(1)–C(26)/C(27) 2.11(1)/2.15(1) [2.12(1)/2.15(1)], Pt(1)–C(32)/C(33) 2.16(1)/2.14(1) [2.13(1)/2.1181)], C(26)–C(27) 1.43(2) [1.42(2)], C(32)–C(33) 1.44(2) [1.42(2)], C(1)–Pt(1)–C(27) 132.0(5) [132.3(5)], C(1)–Pt(1)–C(32) 132.5(5) [132.4(5)], N(1)–C(1)–Pt(1)–C(26) –83(1) [85(1)], N(1)–C(1)–Pt(1)–C(33) 94(1) [–91(1)], N(2)–C(4)–C(7)–N(3) 143(1) [61(2)]. Thermal ellipsoids drawn at 25% probability.



Scheme 5. Synthesis of the platinum(II) complex **6** by oxidation of **5** with $CsBr_3$.

^{15}N-NMR resonance of N_{oxa} is shifted from δ = 259.5, 253.9 (**5**) to 189.0 (**6**), and the characteristic vibrational band of the C=N bond from 1663 (**5**) to 1641 cm^{-1} (**6**). All these data indicate that the carbene/oxazolinyl ligand acts as a bidentate ligand.

Suitable crystals for an X-ray structure analysis were grown by vapor diffusion of hexane into a solution of **6** in CH_2Cl_2 (Figure 5). The coordination geometry at the platinum center is distorted square planar. The imidazolyl and oxazolinyl rings are not coplanar and disposed in such a way that the isopropyl group is bent in one direction and the bridging dimethylmethylene group in the other and out of the coordination plane [N(2)–C(7)–C(1)–N(1) 39.4(5)°] to form a boat-shaped (Pt–C–N–C–C–N) chelate ring, similar to the one observed in **4**. The $C_{carbene}$–Pt bond length [C(10)–Pt 1.957(3) Å] is within the range for NHC–Pt^{II} complexes. The strong *trans* influence of the NHC ligand is reflected in the lengthening of the Pt–Br distance in *trans*

disposition to the carbene ligand compared to the Pt–Br distance *trans* to the oxazoline-N donor atom [2.4807(4) vs. 2.4334(4) Å].

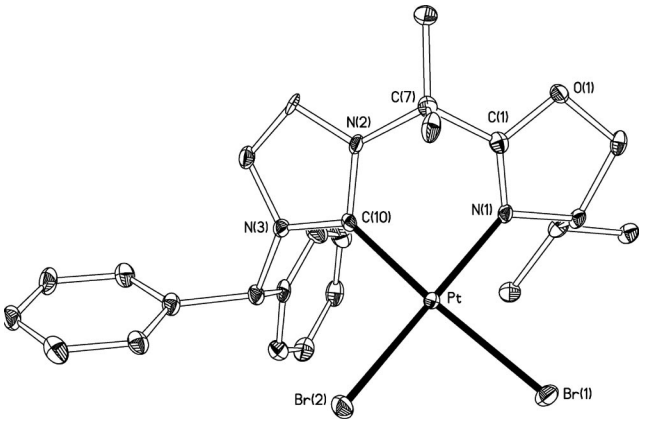
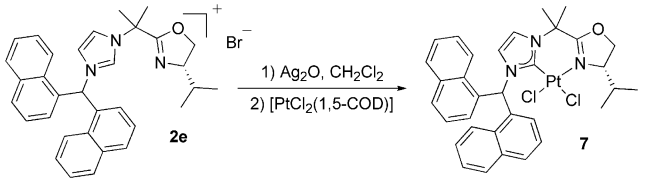


Figure 5. Molecular structure of complex **6** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt–C(10) 1.957(3), Pt–N(1) 2.013(3), Pt–Br(1) 2.4807(4), Pt–Br(2) 2.4334(4), C(1)–N(1) 1.278(4), C(10)–Pt–N(1) 85.21(13), N(1)–Pt–Br(1) 90.49(8), Br(1)–Pt–Br(2) 88.76(1), C(10)–Pt–Br(2) 95.68(9), N(2)–C(7)–C(1)–N(1) –39.4(5). Thermal ellipsoids drawn at 50% probability.

Alternatively, the [(NHC)PtX_2] complexes could be obtained by reaction of the imidazolium salt with Ag_2O and subsequent transmetallation with [PtX_2(1,5-cod)] (X = Cl), according to a procedure previously reported in the literature (Scheme 6).[31] Complex **7** derived from imidazolium salt **2e** has spectroscopic data which are very similar to those of its bromo analogue and was fully characterized by X-ray diffraction. Its molecular structure is represented in Figure 6 along with the main bond lengths and angles.



Scheme 6. Synthesis of the platinum(II) complex **7**.

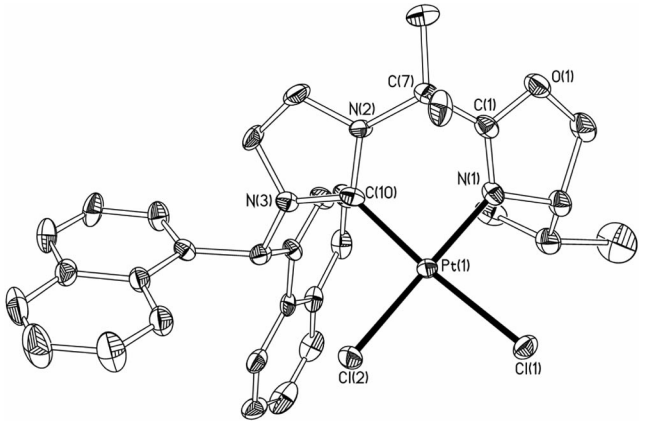


Figure 6. Molecular structure of complex **7** (hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Pt(1)–C(10) 1.983(8), Pt(1)–N(1) 1.977(7), Pt(1)–Cl(1) 2.373(2), Pt(1)–Cl(2) 2.297(2), C(1)–N(1) 1.34(1), C(10)–Pt(1)–N(1) 87.1(3), N(1)–Pt(1)–Cl(1) 89.2(2), C(10)–Pt(1)–Cl(2) 94.2(2), Cl(1)–Pt(1)–Cl(2) 89.16(8), N(2)–C(7)–C(1)–N(1) –38(1). Thermal ellipsoids drawn at 25% probability.

Conclusions

In conclusion, a novel family of mixed carbene/oxazolinyl ligands has been developed. The modular synthetic strategy gives facile access to several new imidazolium salts. The coordination behavior of the corresponding carbenes has been investigated by preparing rhodium and platinum complexes. In general, the ligand readily adapts to the stereoelectronic requirements of the metal center and the methyl groups on the methylene bridge are expected to kinetically stabilize the bridge under the conditions of molecular catalysis and to allow a better control of the steric environment around the metal. To which extent the system at hand will prove useful as a stereodirecting ligand in catalytic transformations is currently being investigated.

Experimental Section

General: 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. (*S*)-valinol,[32] (*S*)-*tert*-leucinol,[33] 1-(1-ethoxycarbonyl-1-methylethyl)imidazole and 1-{1-methyl-1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]ethyl}imidazole (**1a**),[34] bromo(dinaphth-1-yl)methane,[35] [Rh(nbd)Cl]$_2$[36] and [$PtCl_2$(1,5-cod)][37] were synthesized according to reported procedures. KO*t*Bu was purified by sublimation prior to use. Karstedt's catalyst and all other reagents were obtained commercially and used as received. ^{1}H, ^{13}C and ^{15}N spectra were recorded on Bruker Avance 400 and 600 NMR spectrometers and were referenced using the residual protio solvent (^{1}H) 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 recorded by the analytical service of the Heidelberg Chemistry Department.

***N*-[(1*S*)-1-(Hydroxymethyl)-2,2-dimethylpropyl]-2-[(imidazol-1-yl)-methyl]propanamide:** (*S*)-*tert*-leucinol (2.7 g, 22 mmol), 1-(1-ethoxycarbonyl-1-methylethyl)imidazole (4.1 g, 22 mmol) and a catalytic amount of NaH (60% in mineral oil) were placed in a Schlenk tube and heated at 120 °C for 4 h. After removal of the generated ethanol in vacuo, the resulting viscous oil was purified by column chromatography (SiO_2, AcOEt/hexane, 3:1) to yield the reaction product as a white solid (3.16 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (m, 1 H, C*H*$_{imid}$), 7.06 (m, 2 H, C*H*$_{imid}$), 5.74 (d, ^3J = 8.7 Hz, 1 H, N*H*), 4.07 (m, 1 H, O*H*), 3.77–3.66 (m, 2 H, NHC*H* + C*H*$_2$), 3.40 (m, 1 H, C*H*$_2$), 1.78 (s, 3 H, C(C*H*$_3$)$_2$), 1.76 (s, 3 H, C(C*H*$_3$)$_2$), 0.79 (s, 9 H, C(C*H*$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 173.3 (N*C*O), 135.4, 129.7, 117.6 (*C*H$_{imid}$), 62.3 (*C*(CH$_3$)$_2$), 61.5 (*C*H$_2$), 59.1 (NH*C*H), 33.8 (*C*(CH$_3$)$_3$), 26.7 (C(*C*H$_3$)$_3$), 26.5, 26.4 (C(*C*H$_3$)$_2$) ppm. MS (EI): *m*/*z* (%) = 254.3 (100) [M + H]$^+$, 222.3 (20) [M + H – CH_2OH]$^+$, 154.2 (8) [M + 2H – $C_6H_{13}O$]$^+$, 109.2 (51) [M + H – $C_7H_{14}NO_2$]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1668 (s, $\nu_{C=O}$) cm^{-1}. $C_{13}H_{23}N_3O_2$ (253.34): calcd. C 61.63, H 9.15, N 16.59; found C 61.11, H 8.85, N 16.00.

1-{1-[(4*S*)-4-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-imidazole (1b): *N*-[(1*S*)-1-(Hydroxymethyl)-2,2-dimethylpropyl]-2-[(imidazol-1-yl)methyl]propanamide (1.3 g, 5.1 mmol) was dissolved in CH_2Cl_2 (50 mL), and Et_3N (1.8 mL, 12.8 mmol) and mesyl chloride (0.5 mL, 6.4 mmol) were added dropwise at 0 °C. The resulting orange solution was warmed to ambient temperature and was, after two hours, washed with an aqueous solution of NH_4Cl (5%, 20 mL). The organic layer was decanted and the aqueous phase was extracted with additional CH_2Cl_2 (2 × 20 mL). The organic phase was dried with Na_2SO_4 and evaporated to give an orange oil which was directly used in the following reaction. A solution of NaOH (0.45 g, 11.3 mmol) in MeOH/H_2O (1:1, 40 mL) was added to the orange oil and the mixture was refluxed for three hours. After evaporation of methanol, the aqueous phase was extracted with CH_2Cl_2 (4 × 50 mL). The organic phase was dried with Na_2SO_4, concentrated in vacuo and the oily residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3) to give the reaction product **1b** as a colorless oil (778 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (br. s, 1 H, CH_{imid}), 7.03–7.01 (m, 2 H, CH_{imid}), 4.14 (dd, ^2J = 8.8, ^3J = 10.1 Hz, 1 H, C$H_{2\,oxa}$), 4.05 (dd, ^2J = 8.8, ^3J = 7.6 Hz, 1 H, 1 H, C$H_{2\,oxa}$), 3.85 (dd, ^3J = 10.1, ^3J = 7.6 Hz, 1 H, 1 H, CH_{oxa}), 1.81 (s, 6 H, C(CH_3)$_2$), 0.81 (s, 9 H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 167.3 (N*C*O), 135.0, 129.0, 117.0 (*C*H$_{imid}$), 75.5 (*C*H$_{oxa}$), 69.4 (*C*H$_{2\,oxa}$), 56.1 (*C*(CH$_3$)$_2$), 33.7 (*C*(CH$_3$)$_3$), 26.9, 26.8 (C(*C*H$_3$)$_2$), 25.6 (CH(*C*H$_3$)$_3$) ppm. MS (EI): *m*/*z* (%) = 234.2 (100) [M – H]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1669 (s, $\nu_{C=N}$) cm^{-1}. $C_{13}H_{21}N_3O$ (235.33): calcd. C 66.35, H 8.99, N 17.86; found C 66.22, H 8.97, N 17.24.

1-{1-[(4*S*)-Isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-methylimidazolium Iodide (2a): Iodomethane (0.52 g, 3.6 mmol) and **1a** (0.41 g, 1.8 mmol) were placed in a Schlenk tube and dissolved in thf (15 mL). The reaction mixture was stirred at room temperature for 4 h. After evaporation of the solvents in vacuo, the resulting solid was washed with a thf/Et_2O mixture (1:5, 2 × 8 mL), pentane (5 mL) and dried in vacuo to yield the imidazolium salt **2a** as a white powder (0.56 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.31 (dd, ^4J = 1.7, ^4J = 1.7 Hz, 1 H, NC*H*N), 7.43 (dd, ^3J = 1.7, ^4J = 1.7 Hz, 1 H, CH_{imid}), 7.35 (dd, ^3J = 1.7, ^4J = 1.7 Hz, 1 H, CH_{imid}), 4.36 (dd, ^2J = 8.5, ^3J = 9.6 Hz, 1 H, C$H_{2\,oxa}$), 4.22 (s, 3 H, CH_3), 4.06 (dd, ^2J = 8.3, ^3J = 8.0 Hz, 1 H, C$H_{2\,oxa}$), 3.96 (ddd, ^3J = 9.6, ^3J = 7.9, ^3J = 6.1 Hz, 1 H, CH_{oxa}), 2.00 (s, 3 H, C(CH_3)$_2$), 2.00 (s, 3 H, C(CH_3)$_2$), 1.74 (m, 1 H, C*H*(CH$_3$)$_2$), 0.90 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.84 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.1 (N*C*O), 136.4 (N$_2$*C*), 123.7, 120.4 (*C*H$_{imid}$), 72.1 (*C*H$_{oxa}$), 71.6 (*C*H$_{2\,oxa}$), 60.9 (*C*(CH$_3$)$_2$), 37.3 (*C*H$_3$), 32.2 (*C*H(CH$_3$)$_2$), 26.8, 26.7 (C(*C*H$_3$)$_2$), 18.5, 17.9 (CH(*C*H$_3$)$_2$) ppm. HR-MS (ESI) *m*/*z* (%): calcd. for $C_{13}H_{22}N_3O$ ([M – I]$^+$) 236.156, found 236.176 (100); calcd. for $C_{26}H_{44}N_6O_2Cl$ ([2M + Cl – 2I]$^+$) 507.321, found 507.321 (10). FT-IR (KBr): $\tilde{\nu}$ = 1668 (s, $\nu_{C=N}$) cm^{-1}. $C_{13}H_{22}IN_3O$ (363.24): calcd. C 42.99, H 6.10, N 11.57; found C 43.39, H 6.30, N 11.48.

3-Benzyl-1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}imidazolium Bromide (2b): The same procedure as the one described for **2a** was used. Reacting benzyl bromide (237 mg, 1.3 mmol) and imidazole **1a** (150 mg, 0.7 mmol) yielded the imidazolium salt **2b** as a white powder (202 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.09 (dd, ^4J = 1.6, ^4J = 1.6 Hz, 1 H, NC*H*N), 7.55–7.50 (m, 2 H, CH_{Ph}), 7.42–7.35 (m, 3 H, CH_{Ph}), 7.28 (dd, ^3J = 1.9, ^4J = 1.9 Hz, 1 H, CH_{imid}), 7.20 (dd, ^3J = 1.8, ^4J = 1.8 Hz, 1 H, CH_{imid}), 5.78 (s, 2 H, CH_2Ph), 4.34 (dd, ^2J = 8.5, ^3J = 9.7 Hz, 1 H, C$H_{2\,oxa}$), 4.04 (dd, ^2J = 8.4, ^3J = 8.1 Hz, 1 H, C$H_{2\,oxa}$), 3.94 (ddd, ^3J = 9.7, ^3J = 7.9, ^3J = 6.2 Hz, 1 H, CH_{oxa}), 2.02 (s, 3 H, C(CH_3)$_2$), 2.00 (s, 3 H, C(CH_3)$_2$), 1.72 (m, 1 H, C*H*(CH$_3$)$_2$), 0.89 (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 (100 MHz, $CDCl_3$): δ = 165.4 (N*C*O), 137.3 (N$_2$*C*), 133.0 (*C*$_{Ph}$), 129.4, 129.3 (*C*H$_{Ph}$), 121.2, 120.3 (*C*H$_{imid}$), 72.2 (*C*H$_{oxa}$), 71.7 (*C*H$_{2\,oxa}$), 61.1 (*C*(CH$_3$)$_2$), 53.4 (*C*H$_2$Ph), 32.4 (*C*H(CH$_3$)$_2$), 26.8, 26.6 (C(*C*H$_3$)$_2$), 18.5, 18.0 (CH(*C*H$_3$)$_2$ ppm. HR-MS (ESI) *m*/*z* (%): calcd. for $C_{19}H_{26}N_3O$ ([M – Br]$^+$) 312.207, found 312.207 (100); calcd. for $C_{19}H_{28}N_3O_2$ ([M + H_2O – Br]$^+$) 330.217, found 330.217 (10). FT-IR (KBr): $\tilde{\nu}$ = 1665 (s, $\nu_{C=N}$) cm^{-1}. $C_{19}H_{26}BrN_3O$ (392.33): calcd. C 58.17, H 6.68, N 10.71; found C 58.07, H 6.80, N 10.53.

1-{1-[(4*S*)-Isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-[(*R*)-naphth-1-ylmethyl]imidazolium Bromide (2c): Imidazole derivative **1a** (485 mg, 2.2 mmol) and 2-(bromomethyl)naphthalene (533 mg, 2.4 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 **2c** as a white powder (860 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.02 (br. s, 1 H, NC*H*N), 8.04 (br. s, 1 H, CH_{Np}), 7.85–7.75 (m, 3 H, CH_{Np}), 7.61 (dd, ^3J = 8.5, ^4J = 1.8 Hz, 1 H, CH_{Np}), 7.50–7.45 (m, 2 H, CH_{Np}), 7.38 (dd, ^4J = 1.8, ^4J = 1.8 Hz, 1 H, CH_{imid}), 7.29 (dd, ^4J = 1.9, ^4J = 1.9 Hz, 1 H, CH_{imid}), 5.92 (s, 2 H, CH_2Np), 4.30 (dd, ^2J = 8.5, ^3J = 9.7 Hz, 1 H, C$H_{2\,oxa}$), 4.00 (dd, ^2J = 8.3, ^3J = 8.3 Hz, 1 H, C$H_{2\,oxa}$), 3.90 (ddd, ^3J = 9.7 Hz, ^3J = 7.9 Hz, ^3J = 6.2 Hz, 1 H, CH_{oxa}), 1.98 (s, 3 H, C(CH_3)$_2$), 1.96 (s, 3 H, C(CH_3)$_2$), 1.68 (qqd, ^3J = 6.7 Hz, ^3J = 6.7 Hz, ^3J = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 0.84 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.79 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.2 (N*C*O), 136.9 (N$_2$*C*), 133.3, 133.0, 130.4 (*C*$_{Np}$), 129.3, 129.0, 128.1, 127.7, 126.9, 126.7, 126.0, (*C*H$_{Np}$), 121.6, 120.3 (*C*H$_{imid}$), 72.1 (*C*H$_{oxa}$), 71.6 (*C*H$_{2\,oxa}$), 60.9 (*C*(CH$_3$)$_2$), 53.4 (*C*H$_2$Np), 32.3 (*C*H(CH$_3$)$_2$), 26.7, 26.6 (C(*C*H$_3$)$_2$), 18.4, 17.9 (CH(*C*H$_3$)$_2$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{23}H_{28}N_3O$ ([M – Br]$^+$) 362.223, found 362.222 (100). FT-IR (KBr): $\tilde{\nu}$ = 1672 (s, $\nu_{C=N}$) cm^{-1}. $C_{23}H_{28}BrN_3O$ (442.39): calcd. C 62.44, H 6.38, N 9.50; found C 62.58, H 6.45, N 9.41.

3-(Diphenylmethyl)-1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}imidazolium Bromide (2d): The same procedure as the one described for **2c** was followed. Reacting imidazole derivative **1a** (0.90 g, 4.1 mmol) and bromodiphenylmethane (1.31 g, 4.7 mmol) yielded the imidazolium salt **2d** as a white powder (1.65 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.70 (pseudo-t, ^4J = 1.6 Hz, 1 H, NC*H*N), 8.05 (s, 1 H, C*H*Ph$_2$), 7.43 (pseudo-t, J = 1.6 Hz, 1 H, CH_{imid}), 7.40–7.38 (m, 6 H, CH_{Ph}), 7.34–7.30 (m, 4 H, CH_{Ph}), 7.14 (pseudo-t, J = 1.6 Hz, 1 H, CH_{imid}), 4.38 (dd, ^2J = 8.4, ^3J = 9.6 Hz, 1 H, C$H_{2\,oxa}$), 4.07 (dd, ^2J = 8.4, ^3J = 8.4 Hz, 1 H, C$H_{2\,oxa}$), 3.94 (ddd, ^3J = 9.8, ^3J = 8.1, ^3J = 6.4 Hz, 1 H, CH_{oxa}), 2.03 (s, 3 H, C(CH_3)$_2$), 2.02 (s, 3 H, C(CH_3)$_2$), 1.71 (qqd, ^3J = 6.8, ^3J = 6.8, ^3J = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$), 0.89 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.85 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.5 (N*C*O), 137.5 (N$_2$*C*), 136.7 (*C*$_{Ph}$), 129.1, 129.0, 128.4 (*C*H$_{Ph}$), 120.7, 120.3 (*C*H$_{imid}$), 72.1 (*C*H$_{oxa}$), 72.0 (*C*H$_{2\,oxa}$), 66.1 (*C*HPh$_2$), 61.1 (*C*(CH$_3$)$_2$), 32.4 (*C*H(CH$_3$)$_2$), 26.5, 26.4 (C(*C*H$_3$)$_2$), 18.4, 18.1 (CH(*C*H$_3$)$_2$) ppm. ^{15}N NMR (60 MHz, CD_2Cl_2): δ = 235.5 (*N*$_{oxa}$), 194.4, 192.1 (*N*$_{imid}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{25}H_{30}N_3O$ ([M – Br]$^+$) 388.239, found 388.239 (100). FT-IR (KBr): $\tilde{\nu}$ = 1670 (s, $\nu_{C=N}$). $C_{28}H_{30}BrN_3O$ (504.46): calcd. C 64.10, H 6.46, N 8.97; found C 62.77, H 6.45, N 8.59.

3-(Dinaphth-1-ylmethyl)-1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}imidazolium Bromide (2e): Same procedure as the one described for **2c**. Reacting imidazole derivative **1a** (1.14 g,

5.1 mmol) and bromodinaphth-1-ylmethane (1.98 g, 5.6 mmol) yields the imidazolium salt **2e** as a white powder (2.51 g, 86%). Suitable crystals for an X-ray diffraction study were obtained by vapor diffusion of hexane in a solution of **2e** in CH_2Cl_2 at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.04 (dd, ^4J = 1.6, ^4J = 1.6 Hz, 1 H, NC*H*N), 9.33 (s, 1 H, C*H*Np$_2$), 8.41 (m, 2 H, CH_{Np}), 7.90 (m, 2 H, CH_{Np}), 7.88 (m, 2 H, CH_{Np}), 7.57 (m, 2 H, CH_{Np}), 7.52 (m, 2 H, CH_{Np}), 7.32 (m, 2 H, CH_{Np}), 7.32 (m, 1 H, CH_{imid}), 6.91 (dd, ^4J = 1.6, ^4J = 1.6 Hz, 1 H, CH_{imid}), 6.85 (d, ^3J = 7.2 Hz, 2 H, CH_{Np}), 4.34 (dd, ^2J = 8.6, 9.7 Hz, 1 H, C$H_{2\,oxa}$), 4.04 (dd, ^2J = 8.2, ^3J = 8.2 Hz, 1 H, C$H_{2\,oxa}$), 3.93 (ddd, ^3J = 9.7, ^3J = 7.9, ^3J = 6.3 Hz, 1 H, CH_{oxa}), 2.04 (s, 6 H, C(CH_3)$_2$), 1.69 (qqd, ^3J = 6.7, ^3J = 6.7, ^3J = 6.7 Hz, 1 H, C*H*(CH$_3$)$_2$), 0.88 (d, ^3J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 0.84 (d, ^3J = 6.7 Hz, 3 H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.8 (N*C*O), 138.4 (N$_2$*C*), 134.0, 133.2, 130.7 (*C*$_{Np}$), 130.3, 128.6, 128.2, 126.8, 125.6, 124.7, 124.2 (*C*H$_{Np}$), 121.6, 119.5 (*C*H$_{imid}$), 72.1 (*C*H$_{oxa}$), 71.9 (*C*H$_{2\,oxa}$), 61.4 (*C*HNp$_2$), 61.3 (*C*(CH$_3$)$_2$), 32.5 (*C*H(CH$_3$)$_2$), 26.4 (C(*C*H$_3$)$_2$), 18.4, 18.1 (CH(*C*H$_3$)$_2$) ppm. ^{15}N NMR (60 MHz, CD_2Cl_2): δ = 235.2 (*N*$_{oxa}$), 195.7, 189.1 (*N*$_{imid}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{33}H_{34}N_3O$ ([M – Br]$^+$) 488.270, found 488.273 (100). FT-IR (KBr): 1661 cm^{-1} (s, $\nu_{C=N}$). $C_{33}H_{34}BrN_3O$ (568.55): calcd. C 69.71, H 6.03, N 7.39; found C 69.92, H 5.95, N 7.43.

1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-(dinaphth-1-ylmethyl)imidazolium Bromide (2f): The same procedure as the one described for **2c** was followed. Reacting imidazole derivative **1b** (1.40 g, 6.0 mmol) and bromo(dinaphth-1-yl)methane (2.08 g, 6.0 mmol) yielded the imidazolium salt **2f** as a white powder (2.79 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.85 (m, 1 H, NC*H*N), 9.27 (s, 1 H, C*H*Np$_2$), 8.49 (m, 2 H, CH_{Np}), 7.87 (m, 2 H, CH_{Np}), 7.85 (m, 2 H, CH_{Np}), 7.47 (m, 4 H, CH_{Np}), 7.41 (m, 1 H, CH_{imid}), 7.32 (m, 2 H, CH_{Np}), 6.91 (dd, ^3J = 1.7, ^4J = 1.7 Hz, 1 H, CH_{imid}), 6.83 (m, 1 H, CH_{Np}), 6.81 (m, 1 H, CH_{Np}), 4.26 (dd, ^2J = 8.8, ^3J = 10.1 Hz, 1 H, C$H_{2\,oxa}$), 4.10 (dd, ^2J = 8.8, ^3J = 8.0 Hz, 1 H, C$H_{2\,oxa}$), 3.86 (dd, ^3J = 10.1, ^3J = 8.0 Hz, 1 H, CH_{oxa}), 1.98 (s, 3 H, C(CH_3)$_2$), 1.96 (s, 3 H, C(CH_3)$_2$), 0.79 (s, 9 H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.6 (N*C*O), 138.0 (N$_2$*C*), 133.8, 133.0, 130.6, 130.5 (*C*$_{Np}$), 130.1, 128.5, 127.9, 126.6, 126.5, 125.5, 124.7, 124.0, 121.5, 119.8 (*C*H$_{imid}$), 75.4 (*C*H$_{oxa}$), 70.3 (*C*H$_{2\,oxa}$), 61.2 (*C*HNp$_2$), 61.2 (*C*(CH$_3$)$_2$), 33.6 (*C*(CH$_3$)$_3$), 26.3, 26.2 (C(*C*H$_3$)$_2$), 25.5 (C(*C*H$_3$)$_3$) ppm. ^{15}N NMR (60 MHz, CD_2Cl_2): δ = 234.0 (*N*$_{oxa}$), 195.8, 189.0 (*N*$_{imid}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{34}H_{36}N_3O$ ([M – Br]$^+$) 502.286, found 502.286 (100). FT-IR (KBr): $\tilde{\nu}$ = 1669 (s, $\nu_{C=N}$) cm^{-1}. $C_{34}H_{36}BrN_3O$ (582.57): calcd. C 70.10, H 6.23, N 7.21; found C 70.07, H 6.42, N 6.84.

1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-(diphenylmethyl)imidazolium Bromide (2g): Same procedure as the one described for **2c**. Reacting imidazole derivative **1b** (400 mg, 1.7 mmol) and bromodiphenylmethane (460 mg, 1.9 mmol) yielded the imidazolium salt **2g** as a white powder (506 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.74 (m, 1 H, NC*H*N), 8.07 (s, 1 H, C*H*Ph$_2$), 7.39–7.28 (m, 11 H, 10 CH_{Ph} + CH_{imid}), 7.09 (m, 1 H, CH_{imid}), 4.30 (dd, ^2J = 8.9, ^3J = 10.2 Hz, 1 H, C$H_{2\,oxa}$), 4.15 (dd, ^2J = 8.9, ^3J = 7.9 Hz, 1 H, C$H_{2\,oxa}$), 3.88 (dd, ^3J = 10.2, ^3J = 7.9 Hz, 1 H, CH_{oxa}), 2.03 (s, 3 H, C(CH_3)$_2$), 2.01 (s, 3 H, C(CH_3)$_2$), 0.82 (s, 9 H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 165.6 (N*C*O), 137.9 (N$_2$*C*), 137.0, 136.9 (*C*$_{Ph}$), 129.3, 129.2, 129.1, 128.6 (*C*H$_{Ph}$), 120.6, 120.0 (*C*H$_{imid}$), 75.6 (*C*H$_{oxa}$), 70.5 (*C*H$_{2\,oxa}$), 66.1 (*C*HNp$_2$), 61.2 (*C*(CH$_3$)$_2$), 33.7 (*C*(CH$_3$)$_3$), 26.4 (C(*C*H$_3$)$_2$), 25.6 (C(*C*H$_3$)$_3$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{26}H_{32}N_3O$ ([M – Br]$^+$) 402.254, found 402.249 (100). FT-IR (KBr): $\tilde{\nu}$ = 1670 (s, $\nu_{C=N}$) cm^{-1}.

3-(Dinaphth-1-ylmethyl)-1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}imidazole-2-ylidene: The imidazolium salt **2e** (100 mg, 0.17 mmol) was suspended in thf (10 mL) and cooled to –78 °C. A suspension of KN[Si(CH$_3$)$_3$]$_2$ (36 mg, 0.18 mmol) in thf (5 mL) was added dropwise to **2e** at –78 °C and the reaction mixture subsequently stirred for 30 min. The resulting yellow mixture was gradually warmed to room temperature and then evaporated under reduced pressure to give a yellow solid. The product was extracted with warm pentane (4 × 15 mL). The solvent was removed at reduced pressure to give the reaction product as a yellow solid (45 mg, 52%). ^{1}H NMR (600 MHz, C_6D_6): δ = 8.83 (s, 1 H, C*H*Np$_2$), 8.36 (d, ^3J = 8.8 Hz, 1 H, CH_{Np}), 8.33 (d, ^3J = 8.8 Hz, 1 H, CH_{Np}), 7.69 (m, 2 H, CH_{Np}), 7.65 (m, 2 H, CH_{Np}), 7.29–7.22 (m, 4 H, CH_{Np}), 7.19–7.13 (m, 4 H, CH_{Np}), 7.00 (d, ^3J = 1.7 Hz, 1 H, CH_{imid}), 6.71 (d, ^3J = 1.7 Hz, 1 H, CH_{imid}), 3.90 (dd, ^2J = 7.8, ^3J = 9.4 Hz, 1 H, C$H_{2\,oxa}$), 3.78 (dd, ^3J = 9.4, ^3J = 7.8, ^3J = 6.1 Hz, 1 H, CH_{oxa}), 3.69 (dd, ^2J = 7.8, ^3J = 7.8 Hz, 1 H, C$H_{2\,oxa}$), 2.15 (s, 6 H, C(CH_3)$_2$), 1.61 (m, 1 H, C*H*(CH$_3$)$_2$), 0.95 (d, ^3J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 0.83 (d, ^3J = 6.7 Hz, 3 H, CH(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ = 217.3 (N$_2$*C*), 169.2 (N*C*O), 138.0, 137.9, 134.4, 131.9, 131.9 (*C*$_{Np}$), 129.0, 128.8, 127.0, 126.8, 126.7, 126.1, 125.5, 124.9 (*C*H$_{Np}$), 119.1, 117.3 (*C*H$_{imid}$), 72.4 (*C*H$_{oxa}$), 70.6 (*C*H$_{2\,oxa}$), 63.4 (*C*HNp$_2$), 58.8 (*C*(CH$_3$)$_2$), 33.7 (*C*H(CH$_3$)$_3$), 28.3, 28.2 (C(*C*H$_3$)$_2$), 18.7, 18.5 (CH(*C*H$_3$)$_2$) ppm. MS (ESI): *m*/*z* (%) = 488.5 (100) [M + H]$^+$.

1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-(dinaphth-1-ylmethyl)imidazole-2-ylidene: Same procedure as the one described above. Reacting imidazolium salt **2f** (100 mg, 0.17 mmol) with KN[Si(CH$_3$)$_3$]$_2$ (36 mg, 0.18 mmol) in thf at –78 °C gives the reaction product as a yellow solid (65 mg, 75%). ^{1}H NMR (600 MHz, C_6D_6): δ = 8.71 (s, 1 H, C*H*Np$_2$), 8.25 (d, ^3J = 8.5 Hz, 1 H, CH_{Np}), 8.21 (d, ^3J = 8.5 Hz, 1 H, CH_{Np}), 7.61–7.53 (m, 4 H, CH_{Np}), 7.18–7.11 (m, 4 H, CH_{Np}), 7.08–7.02 (m, 4 H, CH_{Np}), 6.89 (d, ^3J = 1.5 Hz, 1 H, CH_{imid}), 6.59 (d, ^3J = 1.5 Hz, 1 H, CH_{imid}), 3.75–3.73 (m, 2 H, C$H_{2\,oxa}$ + CH_{oxa}), 3.64 (dd, ^2J = 7.8, ^3J = 10.5 Hz, 1 H, C$H_{2\,oxa}$), 2.03 (s, 6 H, C(CH_3)$_2$), 0.78 (s, 9 H, C(CH_3)$_3$) ppm. ^{13}C{^{1}H} NMR (150 MHz, C_6D_6): δ = 217.3 (N$_2$*C*), 169.1 (N*C*O), 137.9, 137.8, 134.3, 131.7 (*C*$_{Np}$), 128.8, 128.7, 126.9, 126.8, 126.7, 125.9, 125.4, 124.4 (*C*H$_{Np}$), 119.0, 117.3 (*C*H$_{imid}$), 75.8 (*C*H$_{oxa}$), 68.9 (*C*H$_{2\,oxa}$), 63.3 (*C*HNp$_2$), 58.6 (*C*(CH$_3$)$_2$), 33.6 (*C*(CH$_3$)$_3$), 28.1 (C(*C*H$_3$)$_2$), 25.8 (C(*C*H$_3$)$_3$) ppm. MS (FAB): *m*/*z* (%) = 502.5 (100) [M + H]$^+$.

Bromo{1-{1-[(4*S*)-*tert*-butyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-(dinaphth-1-ylmethyl)imidazol-2-ylidene}(η^4-2,5-norbornadiene)-rhodium(I) (3): A solution of the imidazolium salt **2f** (100 mg, 0.17 mmol) in thf (5 mL) was added to a suspension of KN[Si(CH$_3$)$_3$]$_2$ (36 mg, 0.17 mmol) in thf (5 mL) at –78 °C. The resulting yellow solution was stirred for 30 min and a solution of [Rh(nbd)Cl]$_2$ (40 mg, 0.08 mmol) in thf (3 mL) was added. The mixture was stirred and warmed to ambient temperature and stirred 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 Et_2O/CH_2Cl_2 (5:1, 2 × 5 mL) and hexane (5 mL) to yield **3** as a yellow solid (114 mg, 86%). Suitable crystals for an X-ray diffraction study were grown from vapor diffusion of hexane into a solution of **3** in CH_2Cl_2. ^{1}H NMR (600 MHz, CD_2Cl_2, 263 K): δ = 8.36 (d, ^3J = 6.3 Hz, 1 H, CH_{Np}), 8.11 (s, 1 H, C*H*Np$_2$), 8.01 (d, ^3J = 6.1 Hz, 1 H, CH_{Np}), 7.96–7.95 (m, 2 H, CH_{Np}), 7.91 (d, ^3J = 8.0 Hz, 1 H, CH_{Np}), 7.65–7.64 (m, 2 H, CH_{Np}), 7.53 (dd, ^3J = 7.6, ^3J = 7.6 Hz, 1 H, CH_{Np}), 7.49 (dd, ^3J = 7.4, ^3J = 7.4 Hz,

1 H, CH_{Np}), 7.48 (dd, ^3J = 6.6, ^3J = 6.6 Hz, 1 H, CH_{Np}), 7.42 (m, 1 H, CH_{imid}), 7.34 (dd, ^3J = 7.3, ^3J = 7.3 Hz, 1 H, CH_{Np}), 7.25 (dd, ^3J = 7.5, ^3J = 7.5 Hz, 1 H, CH_{Np}), 6.85 (d, ^3J = 7.0 Hz, 1 H, CH_{Np}), 6.74 (d, ^3J = 6.9 Hz, 1 H, CH_{Np}), 6.62 (m, 1 H, CH_{imid}), 5.20 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 4.84 (dd, ^2J = 9.6, ^3J = 9.6 Hz, 1 H, C$H_{2\,oxa}$), 4.62 (m, 2 H, C$H_{2/3/5/6\text{-}nbd}$ + C$H_{2\,oxa}$), 3.69–3.67 (m, 2 H, CH_{oxa} + C$H_{1/4\text{-}nbd}$), 3.57 (m, 1 H, C$H_{1/4\text{-}nbd}$), 3.49 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 3.45 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 2.76 (s, 3 H, C(CH_3)$_2$), 2.00 (s, 3 H, C(CH_3)$_2$), 1.87 (d, ^2J = 8.3 Hz, 1 H, C$H_{2\,nbd}$), 1.39 (s, 9 H, C(CH_3)$_3$), 0.93 (d, ^2J = 8.3 Hz, 1 H, C$H_{2\,nbd}$) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 263 K): δ = 177.4 (d, $^1J(^{103}Rh^{13}C)$ = 56.1 Hz, N_2C), 170.2 (N*C*O), 135.4, 133.9, 133.4, 133.3, 130.5 (*C*$_{Np}$), 130.0 (*C*H$_{Np}$), 129.2 (*C*$_{Np}$), 129.2, 128.9, 128.3, 127.3, 126.8, 126.2, 126.0, 125.1, 125.0, 123.7, 123.3, 122.0 (*C*H$_{Np}$), 120.3, 118.7 (*C*H$_{imid}$), 82.1 (d, $^1J(^{103}Rh^{13}C)$ = 2.4 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 73.8 (d, $^1J(^{103}Rh^{13}C)$ = 3.0 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 73.1 (*C*H$_{oxa}$), 71.8 (*C*H$_{2\,oxa}$), 65.0 (*C*H$_{2\,nbd}$), 62.1 (*C*HNp$_2$), 60.5 (*C*(CH$_3$)$_2$), 60.2 (d, $^1J(^{103}Rh^{13}C)$ = 9.5 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 57.0 (d, $^1J(^{103}Rh^{13}C)$ = 9.8 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 52.7, 50.9 (*C*H$_{1/4\text{-}nbd}$), 35.5 (C(*C*H$_3$)$_2$), 33.2 (*C*(CH$_3$)$_3$), 24.8 (C(*C*H$_3$)$_3$), 23.5 (C(*C*H$_3$)$_2$) ppm. ^{15}N NMR (60 MHz, CD_2Cl_2, 263 K): δ = 198.4, 197.5 (N_{imid}), 180.3 (N_{oxa}) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{41}H_{43}N_3ORh$ ([M – Br]$^+$) 696.246, found 696.246 (100); calcd. for $C_{34}H_{35}N_3ORh$ ([M – C_7H_8 – Br]$^+$) 604.183, found 604.183 (75). FT-IR (KBr): $\tilde{\nu}$ = 1664 (s, $\nu_{C=N}$) cm^{-1}.

{1-{1-[(4*S*)-*tert*-Butyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}-3-(dinaphth-1-ylmethyl)imidazol-2-ylidene}(η^4-2,5-norbornadiene)rhodium(I) Hexafluorophosphate (4): To a solution of **3** (80 mg, 0.10 mmol) in CH_2Cl_2 (5 mL) were added KPF_6 (29 mg, 0.15 mmol) and water (5 mL). The orange-red solution was stirred for 30 min at room temperature. The organic layer was decanted and the aqueous phase was extracted with additional CH_2Cl_2 (2 × 10 mL). The organic layers were combined, dried under Na_2SO_4 and the volatiles were removed in vacuo. The resulting solid was washed with Et_2O (5 mL) and hexane (5 mL) to yield **4** as a yellow solid (78 mg, 90%). Suitable crystals for an X-ray diffraction study were obtained by slow diffusion of pentane into a solution of **4** in $CDCl_3$. ^{1}H NMR (600 MHz, CD_2Cl_2, 263 K): δ = 8.31 (d, ^3J = 7.2 Hz, 1 H, CH_{Np}), 8.06 (s, 1 H, C*H*Np$_2$), 8.00 (d, ^3J = 7.2 Hz, 1 H, CH_{Np}), 7.94–7.92 (m, 2 H, CH_{Np}), 7.89 (d, ^3J = 8.1 Hz, 1 H, CH_{Np}), 7.63–7.60 (m, 2 H, CH_{Np}), 7.50 (dd, ^3J = 7.5, ^3J = 7.5 Hz, 1 H, CH_{Np}), 7.46 (dd, ^3J = 7.5, ^3J = 7.5 Hz, 1 H, CH_{Np}), 7.43 (d, ^3J = 8.6 Hz, 1 H, CH_{Np}), 7.31 (dd, ^3J = 7.5, ^3J = 7.5 Hz, 1 H, CH_{Np}), 7.22 (dd, ^3J = 7.6, ^3J = 7.6 Hz, 1 H, CH_{Np}), 7.14 (m, 1 H, CH_{imid}), 6.82 (d, ^3J = 7.2 Hz, 1 H, CH_{Np}), 6.86 (d, ^3J = 7.0 Hz, 1 H, CH_{Np}), 6.58 (m, 1 H, CH_{imid}), 4.86 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 4.59 (dd, ^2J = 9.8, ^3J = 4.3 Hz, 1 H, C$H_{2\,oxa}$), 4.57 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 4.53 (dd, ^2J = 9.8, ^3J = 9.5 Hz, 1 H, C$H_{2\,oxa}$), 3.64 (m, 1 H, C$H_{1/4\text{-}nbd}$), 3.57 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 3.54 (dd, ^3J = 9.5, ^3J = 4.3 Hz, CH_{oxa}), 3.50 (m, 1 H, C$H_{2/3/5/6\text{-}nbd}$), 3.43 (m, 1 H, C$H_{1/4\text{-}nbd}$), 2.71 (s, 3 H, C(CH_3)$_2$), 1.92 (s, 3 H, C(CH_3)$_2$), 1.17 (d, ^2J = 8.5 Hz, 1 H, C$H_{2\,nbd}$), 1.10 (s, 9 H, C(CH_3)$_3$), 0.92 (d, ^2J = 8.5 Hz, 1 H, C$H_{2\,nbd}$) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 263 K): δ = 177.6 (d, $^1J(^{103}Rh^{13}C)$ = 56.5 Hz, N_2C), 170.7 (N*C*O), 135.6, 134.3, 133.8, 133.5, 130.8 (*C*$_{Np}$), 130.4 (*C*H$_{Np}$), 129.6 (*C*$_{Np}$), 129.6, 129.3, 128.7, 127.7, 127.2, 126.6, 126.3, 125.5, 125.4, 124.1, 123.6, 122.2 (*C*H$_{Np}$), 120.7, 118.4 (*C*H$_{imid}$), 81.8 (d, $^1J(^{103}Rh^{13}C)$ = 5.5 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 74.2 (d, $^1J(^{103}Rh^{13}C)$ = 3.1 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 73.4 (*C*H$_{oxa}$), 71.9 (*C*H$_{2\,oxa}$), 65.4 (*C*H$_{2\,nbd}$), 62.5 (*C*HNp$_2$), 60.9 (d, $^1J(^{103}Rh^{13}C)$ = 10.4 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 60.8 (*C*(CH$_3$)$_2$), 57.6 (d, $^1J(^{103}Rh^{13}C)$ = 9.4 Hz, *C*H$_{2/3/5/6\text{-}nbd}$), 53.2, 51.4 (*C*H$_{1/4\text{-}nbd}$), 35.7 (C(*C*H$_3$)$_2$), 33.7 (*C*(CH$_3$)$_3$), 25.1 (C(*C*H$_3$)$_3$), 23.5 (C(*C*H$_3$)$_2$) ppm. ^{15}N NMR (60 MHz, CD_2Cl_2, 263 K): δ = 198.9, 196.7 (N_{imid}), 189.8 (N_{oxa}) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{41}H_{43}N_3ORh$ ([M – PF_6]$^+$) 696.246, found 696.241 (80); calcd. for $C_{34}H_{35}N_3ORh$ ([M – C_7H_8 – PF_6]$^+$) 604.183, found 604.129 (100). FT-IR (KBr): $\tilde{\nu}$ = 1637 (s, $\nu_{C=N}$) cm^{-1}. $C_{41}H_{43}F_6N_3OPRh$ (841.67): calcd. C 58.51, H 5.15, N 4.99; found C 58.96, H 5.25, N 4.79.

{3-(Diphenylmethyl)-1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}imidazol-2-ylidene}(1,1,3,3-tetramethyl-1,3-divinylsiloxane)platinum(0) (5): To a solution of the imidazolium salt **2d** (468 mg, 1 mmol) and Karstedt's catalyst (2.1–2.4% Pt in xylene, 9.3 g, 1 mmol) in thf (5 mL) was added a solution of KO*t*Bu (178 mg, 1.4 mmol) in thf (5 mL) at –78 °C. The mixture was stirred and warmed to ambient temperature and stirred for 12 h. The orange-red solution was then filtered and the solvents were removed in vacuo. The resulting orange oil was purified by column chromatography (SiO_2, AcOEt/hexane, 35:65) to yield **5** as a white solid (615 mg, 80%). Suitable crystals for an X-ray diffraction study were grown from a saturated solution of **5** in pentane. ^{1}H NMR (600 MHz, CD_2Cl_2, 273 K): δ = 7.37–7.33 (m, 12 H, CH_{Ph}), 7.29 (s, 1 H, C*H*Ph$_2$), 7.28 (d, ^3J = 2.2 Hz, 1 H, CH_{imid}), 7.20 (s, 1 H, C*H*Ph$_2$), 7.19 (m, 1 H, CH_{imid}), 7.08–7.03 (m, 8 H, CH_{Ph}), 6.97 (d, ^3J = 1.1 Hz, 1 H, CH_{imid}), 6.93 (d, ^3J = 1.1 Hz, 1 H, CH_{imid}), 4.36 (dd, ^2J = 8.4, ^3J = 9.5 Hz, 1 H, C$H_{2\,oxa}$), 4.26 (dd, ^2J = 8.5, ^3J = 9.7 Hz, 1 H, C$H_{2\,oxa}$), 4.04 (dd, ^2J = 8.2, ^3J = 8.2 Hz, 1 H, C$H_{2\,oxa}$), 4.00 (dd, ^2J = 8.3, ^3J = 8.2 Hz, 1 H, C$H_{2\,oxa}$), 3.98 (m, 1 H, CH_{oxa}), 3.89 (ddd, ^3J = 9.7, ^3J = 8.3, ^3J = 6.3 Hz, 1 H, CH_{oxa}), 2.25 (d, $^2J(^{195}Pt^1H)$ = 53.2, ^3J = 11.3 Hz, 1 H, CH_2=CHSi), 2.20 (d, $^2J(^{195}Pt^1H)$ = 50.6, ^3J = 11.4 Hz, 1 H, CH_2=CHSi), 1.95 (m, 1 H, CH_2=CHSi), 1.95 (s, 3 H, C(CH_3)$_2$), 1.93 (s, 3 H, C(CH_3)$_2$), 1.89 (m, 1 H, CH_2=CHSi), 1.89 (s, 3 H, C(CH_3)$_2$), 1.86 (s, 3 H, C(CH_3)$_2$), 1.83–1.68 (m, 9 H, 4 CH_2=CHSi + 3 CH$_2$=C*H*Si + 2 C*H*(CH$_3$)$_2$), 1.59 (d, $^2J(^{195}Pt^1H)$ = 52.3, ^3J = 13.5 Hz, 1 H, CH$_2$=C*H*Si), 0.97 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.95 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.89 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.88 (d, ^3J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 0.28 (s, 3 H, SiC$H_{3\,eq}$), 0.27 (s, 3 H, SiC$H_{3\,eq}$), 0.25 (s, 3 H, SiC$H_{3\,eq}$), 0.23 (s, 3 H, SiC$H_{3\,eq}$), –0.28 (s, 3 H, SiC$H_{3\,ax}$), –0.30 (s, 3 H, SiC$H_{3\,ax}$), –0.47 (s, 3 H, SiC$H_{3\,ax}$), –0.51 (s, 3 H, SiC$H_{3\,ax}$) ppm. ^{13}C{^{1}H} NMR (150 MHz, CD_2Cl_2, 273 K): δ = 184.9 (s, $^1J(^{195}Pt^{13}C)$ = 1375.7 Hz, N_2C), 184.1 (s, $^1J(^{195}Pt^{13}C)$ = 1384.3 Hz, N_2C), 167.9, 167.5 (N*C*O), 140.0, 139.8, 139.7 (*C*$_{Ph}$), 128.6, 128.5, 128.4, 128.3, 127.8, 127.7 (*C*H$_{Ph}$), 121.2 (s, $^3J(^{195}Pt^{13}C)$ = 43.3 Hz, *C*H$_{imid}$), 121.0 (s, $^3J(^{195}Pt^{13}C)$ = 44.7 Hz, *C*H$_{imid}$), 119.0 (s, $^3J(^{195}Pt^{13}C)$ = 31.4 Hz, *C*H$_{imid}$), 118.8 (s, $^3J(^{195}Pt^{13}C)$ = 33.3 Hz, *C*H$_{imid}$), 72.2, 72.2 (*C*H$_{oxa}$), 70.8, 70.7 (*C*H$_{2\,oxa}$), 67.5 (s, $^3J(^{195}Pt^{13}C)$ = 48.4 Hz, *C*HPh$_2$), 67.4 (s, $^3J(^{195}Pt^{13}C)$ = 47.2 Hz, *C*HPh$_2$), 60.3, 59.9 (*C*(CH$_3$)$_2$), 43.7 (s, $^1J(^{195}Pt^{13}C)$ = 163.4 Hz, *C*H$_2$=CHSi), 43.0 (s, $^1J(^{195}Pt^{13}C)$ = 166.4 Hz, *C*H$_2$=CHSi), 42.3 (s, $^1J(^{195}Pt^{13}C)$ = 162.8 Hz, *C*H$_2$=CHSi), 42.1 (s, $^1J(^{195}Pt^{13}C)$ = 164.5 Hz, *C*H$_2$=CHSi), 33.8 (s, $^1J(^{195}Pt^{13}C)$ = 122.2 Hz, CH$_2$=*C*HSi), 33.6 (s, $^1J(^{195}Pt^{13}C)$ = 119.8 Hz, CH$_2$=*C*HSi), 33.5 (s, $^1J(^{195}Pt^{13}C)$ = 121.4 Hz, CH$_2$=*C*HSi), 33.4 (s, $^1J(^{195}Pt^{13}C)$ = 121.0 Hz, CH$_2$=*C*HSi), 32.6 (*C*H(CH$_3$)$_2$), 27.6, 27.4, 27.2 (C(*C*H$_3$)$_2$), 18.6, 17.8 (CH(*C*H$_3$)$_2$), 1.2 (Si*C*H$_{3\,eq}$), –2.1, –2.2, –2.9 (Si*C*H$_{3\,ax}$) ppm. ^{15}N NMR (60 MHz, CD_2Cl_2, 273 K): δ = 259.5, 253.9 (N_{oxa}), 253.8, 252.8, 252.8, 251.8 (N_{imid}) ppm. MS (EI+): *m*/*z* (%) = 769.2 (50) [M + H]$^+$, 582.2 (85) [M – $C_8H_{18}OSi_2$ + H]$^+$. FT-IR (KBr): $\tilde{\nu}$ = 1663 (s, $\nu_{C=N}$) cm^{-1}. $C_{33}H_{47}N_3O_2PtSi_2$ (768.99): calcd. C 51.54, H 6.16, N 5.46; found C 51.72, H 6.22, N 5.45.

Dibromo{3-(diphenylmethyl)-1-{1-[(4*S*)-isopropyl-4,5-dihydrooxazol-2-yl]-1-methylethyl}imidazol-2-ylidene}platinum(II) (6): $CsBr_3$ (93 mg, 0.25 mmol) was added to a solution of **5** (190 mg, 0.25 mmol) in toluene (15 mL) and the mixture was allowed to re-

act for 20 min at 60 °C. The formation of a white precipitate was observed and the solvent was evaporated. The resulting solid was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3) to yield **6** as a white solid (104 mg, 56%). Suitable crystals for X-ray diffraction were obtained by vapor diffusion of hexane ito a solution of **6** in CH_2Cl_2 at 0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.57 (s, 1 H, C*H*Ph$_2$), 7.39 (m, 1 H, C*H*$_{Ph}$), 7.38 (m, 1 H, C*H*$_{Ph}$), 7.34–7.29 (m, 6 H, C*H*$_{Ph}$), 7.22 (m, 1 H, C*H*$_{Ph}$), 7.20 (m, 1 H, C*H*$_{Ph}$), 7.04 (d, ^3J = 2.2 Hz, 1 H, C*H*$_{imid}$), 6.86 (d, ^3J = 2.2 Hz, 1 H, C*H*$_{imid}$), 5.20 (m, 1 H, C*H*$_{oxa}$), 4.52 (dd, ^2J = 9.2, ^3J = 10.2 Hz, 1 H, C*H*$_{2\,oxa}$), 4.35 (dd, ^2J = 9.2, ^3J = 5.9 Hz, 1 H, C*H*$_{2\,oxa}$), 2.61 (s, 3 H, C(C*H*$_3$)$_2$), 1.91 (m, 1 H, C*H*(CH$_3$)$_2$), 1.88 (s, 3 H, C(C*H*$_3$)$_2$), 0.57 (d, ^3J = 7.0 Hz, 3 H, CH(C*H*$_3$)$_2$), 0.07 (d, ^3J = 6.7 Hz, 3 H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ = 168.7 (N*C*O), 144.2 (N$_2$*C*), 139.2, 138.3 (*C*$_{Ph}$), 129.6, 128.9, 128.7, 128.5, 128.2, 128.0 (*C*H$_{Ph}$), 120.7, 116.5 (*C*H$_{imid}$), 72.2 (*C*H$_{2\,oxa}$), 68.7 (*C*H$_{oxa}$), 66.5 (*C*HPh$_2$), 60.5 (*C*(CH$_3$)$_2$), 29.9 (C(*C*H$_3$)$_2$), 29.7 (*C*H(CH$_3$)$_2$), 23.6 (C(*C*H$_3$)$_2$), 17.4, 14.7 (CH-(*C*H$_3$)$_2$) ppm. ^{15}N NMR (60 MHz, $CDCl_3$): δ = 199.3, 193.4 (*N*$_{imid}$), 189.0 (*N*$_{oxa}$) ppm. HR-MS (FAB+) *m*/*z* (%): calcd. for $C_{25}H_{29}BrN_3OPt$ ([M – Br]$^+$) 662.114, found 662.117 (40); calcd. for $C_{25}H_{28}N_3OPt$ ([M – 2Br – H]$^+$) 581.188, found 581.165 (100). FT-IR (KBr): $\tilde{\nu}$ = 1641 (s, $\nu_{C=N}$) cm^{-1}.

Dichloro{3-(dinaphth-1-ylmethyl)-1-{1-[(4*S*)-isopropyl-4,5-dihydro-oxazol-2-yl]-1-methylethyl}imidazol-2-ylidene}platinum(II) (7): The imidazolium salt **2e** (300 mg, 0.52 mmol) was dissolved in CH_2Cl_2 (10 mL) and silver oxide (86 mg, 0.37 mmol) was added under exclusion of light. After stirring for five days at room temperature, a solution of [$PtCl_2$(1,5-cod)] (195 mg, 0.52 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was allowed to react for one day at room temperature. The solution was then filtered through celite and the solvent was evaporated. The resulting yellow solid was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH, 97:3) to yield **7** as a white solid (210 mg, 54%). Suitable crystals for X-ray diffraction were obtained by vapor diffusion of hexane into a solution of **7** in CH_2Cl_2 at 0 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.83 (s, 1 H, C*H*Np$_2$), 8.86 (d, ^3J = 8.1 Hz, 1 H, C*H*$_{Np}$), 8.00 (d, ^3J = 8.0 Hz, 1 H, C*H*$_{Np}$), 7.85 (m, 2 H, C*H*$_{Np}$), 7.80 (m, 2 H, C*H*$_{Np}$), 7.59 (m, 1 H, C*H*$_{Np}$), 7.52 (dd, ^3J = 7.1, ^3J = 7.1 Hz, 1 H, C*H*$_{Np}$), 7.44 (dd, ^3J = 7.2, ^3J = 7.2 Hz, 1 H, C*H*$_{Np}$), 7.32 (dd, ^3J = 7.8, ^3J = 7.5 Hz, 1 H, C*H*$_{Np}$), 7.30 (dd, ^3J = 8.1, ^3J = 7.5 Hz, 1 H, C*H*$_{Np}$), 7.17 (dd, ^3J = 7.7, ^3J = 7.7 Hz, 1 H, C*H*$_{Np}$), 6.94 (d, ^3J = 2.1 Hz, 1 H, C*H*$_{imid}$), 6.76 (d, ^3J = 7.2 Hz, 1 H, C*H*$_{Np}$), 6.53 (d, ^3J = 2.1 Hz, 1 H, C*H*$_{imid}$), 6.48 (d, ^3J = 6.1 Hz, 1 H, C*H*$_{Np}$), 5.10 (m, 1 H, C*H*$_{oxa}$), 4.53 (dd, ^2J = 9.7, ^3J = 9.7 Hz, 1 H, C*H*$_{2\,oxa}$), 4.42 (dd, ^2J = 9.2, ^3J = 5.8 Hz, 1 H, C*H*$_{2\,oxa}$), 2.53 (s, 3 H, C(C*H*$_3$)$_2$), 1.91 (m, 1 H, C*H*(CH$_3$)$_2$), 1.88 (s, 3 H, C(C*H*$_3$)$_2$), 0.68 (d, ^3J = 6.9 Hz, 3 H, CH(C*H*$_3$)$_2$), 0.42 (d, ^3J = 6.5 Hz, 3 H, CH(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 168.9 (N*C*O), 141.6 (N$_2$*C*), 137.0, 134.5, 134.0, 133.8, 131.7, 130.9 (*C*$_{Np}$), 129.6, 128.5, 128.4, 128.3, 128.1, 127.4, 127.0, 126.3, 126.2, 125.3, 124.8, 124.6, 124.5, 123.8 (*C*H$_{Np}$), 121.6, 115.7 (*C*H$_{imid}$), 71.9 (*C*H$_{2\,oxa}$), 67.8 (*C*H$_{oxa}$), 61.4 (*C*HNp$_2$), 60.1 (*C*(CH$_3$)$_2$), 30.5 (C(*C*H$_3$)$_2$), 29.5 (*C*H(CH$_3$)$_2$), 23.5 (C(*C*H$_3$)$_2$), 17.6, 15.4 (CH-(*C*H$_3$)$_2$) ppm. MS (FAB+): *m*/*z* (%) = 717.1 (40) [M – Cl]$^+$, 681.1

Table 1. Details of the crystal structure determinations of **2e**, **3**, **4**, **5**, **6** and **7**.

	2e	**3**	**4**	**5**	**6**	**7**
Formula	$[C_{33}H_{34}N_3O][Br]$	$C_{41}H_{43}BrN_3ORh$	$[C_{41}H_{43}N_3ORh][PF_6]$	$C_{33}H_{47}N_3O_2PtSi_2$	$C_{25}H_{29}Br_2N_3OPt$	$C_{33}H_{33}Cl_2N_3OPt$
Crystal system	triclinic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
Space group	*P*1	*P*1	$P2_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a [Å]	9.5637(9)	11.1212(13)	10.0434(7)	12.8775(11)	7.6433(4)	8.0091(4)
b [Å]	9.9034(10)	12.0126(14)	19.8604(14)	15.6965(14)	17.0957(9)	14.6503(8)
c [Å]	15.1840(15)	14.2028(16)	10.8516(8)	17.4003(15)	18.8429(9)	29.5201(16)
α [°]	82.572(2)	65.563(2)				
β [°]	89.163(2)	83.671(2)	104.6900(10)	104.910(2)		
γ [°]	88.962(2)	78.971(2)				
V [Å^3]	1425.7(2)	1694.5(3)	2093.8(3)	3398.7(5)	2462.2(2)	3463.8(3)
Z	2	2	2	4	4	4
M_r	568.54	776.60	961.03	769.01	742.42	753.61
d_c [Mg m^{-3}]	1.324	1.522	1.524	1.503	2.003	1.445
F(000)	592	796	980	1552	1424	1488
μ(Mo-K_α) [mm^{-1}]	1.472	1.721	0.702	4.231	8.967	4.232
Transmission factors						
max., min.	0.7457, 0.6261	0.9189, 0.8467	0.7445, 0.5995	0.7457, 0.6149	0.7464, 0.5075	0.8163, 0.3633
Data collection temp. [K]	150(2)	100(2)	100(2)	200(2)	100(2)	298(2)
θ range [°]	2.1 to 25.0	1.6 to 32.2	1.9 to 32.2	1.2 to 28.3	1.6 to 31.5	1.34 to 25.0
Index ranges (indep. sets)	–11 ... 11,	–16 ... 16,	–15 ... 14,	–17 ... 16,	–11 ... 11,	–9 ... 9,
h,*k*,*l*	–11 ... 11,	–17 ... 17,	–29 ... 29,	–20 ... 20,	0 ... 25,	0 ... 17,
	–18 ... 18	–20 ... 21	0 ... 15	0 ... 23	0 ... 27	0 ... 35
Refl. measured	23903	42316	52083	35584	60855	20849
Refl. unique [R_{int}]	9930 [0.0590]	20702 [0.0723]	13724 [0.0383]	16717 [0.0446]	8101 [0.0606]	6120 [0.0547]
Refl. obsd. [$I \geq 2\sigma(I)$]	8079	12708	13391	11660	7274	4547
Parameters refined	693	858	531	756	293	365
R indices [$F>4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0431, 0.0874	0.0572, 0.1353	0.0232, 0.0580	0.0422, 0.0782	0.0261, 0.0467	0.0396, 0.0919
R indices (all data) $R(F)$, $wR(F^2)$	0.0618, 0.0950	0.1140, 0.1637	0.0242, 0.0587	0.0755, 0.0876	0.0337, 0.0489	0.0563, 0.0984
GooF on F^2	1.001	0.851	1.068	1.007	1.081	0.944
Absol. structure parameter	0.009(6)	0.035(5)	–0.012(9)	0.034(12)	–0.017(5)	–0.018(11)
Largest residual peaks [e·Å^{-3}]	0.473, –0.302	1.475, –1.535	0.889, –0.322	1.260, –0.556	1.546, –0.807	1.305, –1.612

(80) $[M - 2Cl - H]^+$. FT-IR (KBr): $\tilde{\nu}$ = 1655 (s, $\nu_{C=N}$) cm^{-1}. $C_{33}H_{33}Cl_2N_3OPt$ (753.62): calcd. C 52.59, H 4.41, N 5.58; found C 52.80, H 4.75, N 5.36.

X-ray Crystal Structure Determinations: Crystal data and details of the structure determinations are listed in Table 1. Intensity data were collected with Bruker AXS Smart 1000 and Apex CCD diffractometers (Mo-K_α, graphite monochromator, λ = 0.71073 Å). Data were corrected for air and detector absorption, Lorentz and polarization effects;[38] absorption by the crystal was treated with a semiempirical multiscan method.[39,40] The structures were solved by the heavy atom method combined with structure expansion by direct methods applied to difference structure factors[41] (compounds **2e**, **3**, **6** and **7**), by conventional direct methods[42,43] (complex **4**) or by direct methods with dual-space recycling ("Shake-and-Bake")[44] (complex **5**). Refinement was carried out with full-matrix least-squares methods based on F^2 against all unique reflections.[43,45] All non-hydrogen atoms were given anisotropic displacement parameters. Hydrogen atoms were generally placed in calculated positions and refined with a riding model. When justified by the quality of the data the positions of some hydrogen atoms (those on the carbon atoms involved in coordination to the metal) were taken from difference Fourier syntheses and refined.

Due to severe disorder and fractional occupancy, electron density attributed to solvent of crystallization (hexane) was removed from the structure (and the corresponding F_{obs}) of **7** with the BYPASS/SQUEEZE procedure,[46] as implemented in PLATON.[47]

CCDC-701546 (for **2e**), -701550 (for **3**), -701551 (for **4**), -701547 (for **5**), -701549 (for **6**) and -701548 (for **7**) 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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