Hydride-Rhodium(III)-N-Heterocyclic Carbene Catalysts for Vinyl-Selective H/D Exchange: A Structure-Activity Study

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Dedicated in memory of Prof. Dr. María Pilar García Clemente

Abstract: A series of neutral and cationic Rh^{III}-hydride and Rh^{III}-ethyl complexes bearing a NHC ligand have been synthesized and evaluated as catalyst precursors for H/D exchange reaction of styrene using CD_3OD as deuterium source. An array of varied ligands has been selected in order to understand how the stereoelectronic properties can modulate the catalytic activity. Most of these complexes resulted to be very active and selective in the vinylic-H/D exchange, without deuteration of the aromatic hydrogens, presenting very high selectivity toward the *β*-positions. In particular the cationic complex $[RhClH(CH_3CN)_3(IPr)]CF_3SO_3$ showed an excellent catalytic activity reaching the maximum attainable degree of *β*-vinylic deuteration in only 20 min. Modulation of catalyst structure results in an improvement of the α/β selectivity. Thus, the $[RhClH(\kappa^2\text{-}O,N\text{-}C_9H_6NO)(SIPr)]$ catalyst, bearing a 8-quinolinolate ligand and an electron-donor and bulky NHC as SIPr, showed total selectivity for the *β*-vinylic positions. This systematic study has shown that an increase in electron density and steric pressure on the metal center produces an improvement of catalytic activity and selectivity. Complexes bearing ligands with a very high steric hindrance resulted to be inactive.

Keywords: H/D-exchange reactions • Rhodium • NHC • olefins • deuteration

Introduction

Deuterium-labeled compounds are nowadays used as central tools in a wide range of fields, whether it be for fundamental research or practical applications, as for example, drug metabolism, structural study of biological macromolecules, reaction mechanisms and kinetics, quantification of environmental pollutants and residual pesticides, synthesis of heavy drugs, production of innovative optical materials or markers in diesel oil.[1] The straightforward H/D-exchange in the target molecule is a more efficient and cost effective preparative method than the classical multistep synthesis from deuterated starting materials.[2] However, the direct substrate deuteration generally requires harsh reaction conditions which constitutes a major drawback.[3] For this reason, the development of new catalysts with high activity and selectivity represents a very important challenging task.[2b] Transition metal based homogeneous and heterogeneous catalytic systems allow to carry out the H/D-exchange reaction under mild conditions, preventing substrate decomposition, with high tolerance toward the main functional groups. Moreover, such catalytic systems open the way for the choice of the deuterium source, such as D_2, D_2O or organic deuterated solvents, in function of the most compatible conditions for the substrate.

After the pioneer works by Garnett,[4] and Shilov[5] in the sixties, we have witnessed the development of a plethora of transition metal based homogeneous catalytic systems for H/D exchange, including iridium,[4c,6] rhodium,[4d,6g,t,7] palladium,[7h,8] platinum,[4a,b,5,7h,8a,c,9] ruthenium,[7i,10] cobalt,[11] and osmium.[7i,10h,12] The versatility of the organometallic catalysts is shown by their ability to deuterate different C-H groups from aliphatic,[2b,6k,m,7b,f,10b,e,i] aromatic,[2b,4a,6k,m,o,6s-u,7b,g,k,9d,10e,h,j,12] and vinylic substrates.[6a,n,7a,d,e,i,10g] However, the control of regio- and stereoselectivity still remains an important challenge, especially for the deuteration of olefins in the presence of aromatic groups.

In this context, a key issue to take into account is that most of the transition metal-based catalytic systems proceed according to a C-H activation mechanism (Scheme 1a).[6,7f,g,k,8b,c,9d,10a-f,10h,12-13] The selectivity of the reaction depends on the activation energy of distinct C-H moieties, which is related to their dissociation energies, thus, the observed reactivity order of reaction is generally: C_{sp}-H>C_{sp2}-H>C_{sp3}-H. Particularly, in the case of substrates with both aromatic and olefinic groups, where the C-H bond dissociation energy is comparable, the selective activation of the vinylic protons is problematic.[14] An efficient strategy for the selective alkene deuterium-labeling consists in the use of metal-hydride species that proceed by an alternative insertion-elimination mechanism, which is not operative for aromatic protons (Scheme 1b).[4d,6g,7a,e,i,j,11] In addition, a high oxidation state of the metal center might reduce the competitive olefin C-H activation pathway and should prevent hydrogenation of the double bond of the target olefin. Moreover, a bulky powerful electron-donor ancillary ligand should provide additional stability to the hydride-metal species in high oxidation state while imparting an adequate steric pressure on the vicinity of the coordination site that can dramatically influence the reaction

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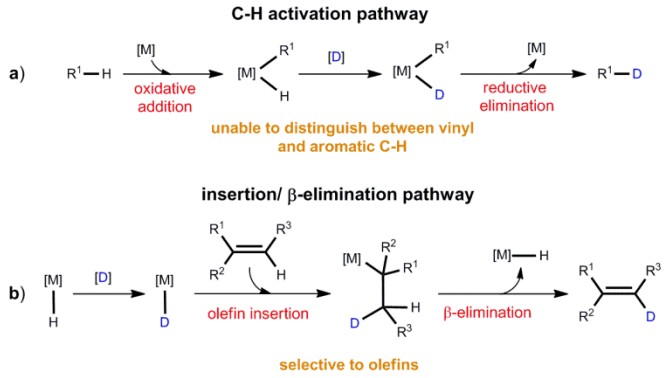
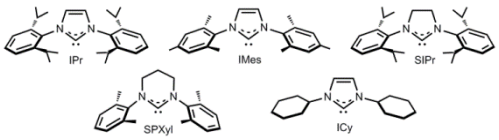
selectivity. With this in mind, we envisage Rh^{III} complexes[7d,i] bearing a N-heterocyclic carbene ligand (NHC)[15] as potential catalysts to carry out the H/D exchange of olefins in an active and selective manner. Thus, in this work we report the synthesis of a set of hydride-Rh^{III}-NHC catalysts and the systematic study of their catalytic activity in deuterium labeling of styrene. The results of this study have allowed us to disclose highly efficient catalysts and to establish a relationship between the structure of the complex and its catalytic activity. A part of this work has been previously communicated.[7j]



Scheme 1. Possible mechanism for H/D exchange reaction of olefins: C-H activation (top) and insertion/β-elimination pathway (bottom).

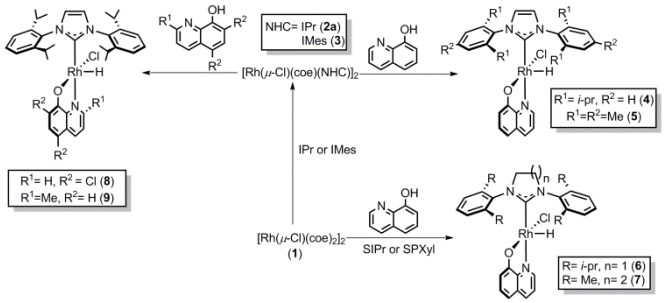
Results and Discussion

Synthesis of neutral hydride-Rh^{III}-NHC complexes bearing a 8-quinolinolate ligand. Dinuclear complexes of the type [Rh(μ-Cl)(NHC)(η^2-olefin)]$_2$ are excellent starting materials since they are easy to prepare and very reactive.[16] With the aim of studying the effect of the NHC ligand on the catalytic activity we have prepared several catalytic precursors bearing a range NHC ligands having different steric hindrance and electron-donor ability:[17] 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-carbene (IPr), 1,3-bis-(2,6-diisopropylphenyl)imidazolidin-2-carbene (SIPr), 2,4,6-(trimethylphenyl)imidazol-2-carbene (IMes), 1,3-dicyclohexylimidazol-2-carbene (ICy) and 2,6-(dimethylphenyl)tetrahydropyrimidin-2-carbene (SPXyl), whose synthesis is reported in literature (Scheme 2).[18]



Scheme 2. NHC ligands used in this work.

The dinuclear [Rh(μ-Cl)(NHC)(η^2-coe)]$_2$ complexes were synthetized as described by James and coworkers.[16b] Thus, reaction of [Rh(μ-Cl)(η^2-coe)$_2$]$_2$ (**1**) with the free NHC ligands gave the dinuclear complexes [Rh(μ-Cl)(IPr)(η^2-coe)]$_2$ (**2a**) and [Rh(μ-Cl)(IMes)(η^2-coe)]$_2$ (**3**). Following the previously reported synthetic scheme,[7j] treatment of the dimers **2a** and **3** with 8-hydroxyquinoline in toluene at room temperature led to the diastereoselective synthesis of the 16-electron complexes [RhClH(κ^2-O,N-C_9H_6NO)(NHC)] (**4**, IPr; **5**, IMes) (Scheme 3). Complexes **4** and **5** were isolated as orange solids in 76%[7j] and 79% yield, respectively. The synthesis of related mononuclear hydride/8-quinolinolate derivatives bearing carbenes SIPr and SPXyl was carried out following a one-pot procedure (Scheme 3). Thus, a mixture of [Rh(μ-Cl)(coe)$_2$]$_2$, 8-hydroxyquinoline and NHC (SIPr or SPXyl) was stirred at room temperature in THF for 2 h to give orange solutions of complexes [RhClH(κ^2-O,N-C_9H_6NO)(SIPr)] (**6**) and [RhClH(κ^2-O,N-C_9H_6NO)(SPXyl)] (**7**), which were isolated as orange solids in good yields. Unfortunately, this synthetic approach did not work well for the ICy ligand. X-ray analysis of a crop of red crystals collected form the reaction mixture revealed the formation of the coordination ion-par [Rh(κ^2-O,N-C_9H_6NO)(ICy)$_3$][RhCl$_2$(κ^2-O,N-C_9H_6NO)$_2$]$_2$. Most probably the formation of this species with three ICy ligands is a consequence of the lesser steric demand of the ICy ligand (Figure S1, Supporting Information).



Scheme 3. Synthesis of neutral hydride-Rh-NHC 8-quinolinolate complexes **1-9.**

An X-ray diffraction structural analysis of complex [RhClH(κ^2-O,N-C_9H_6NO)(IPr)] (**4**) (Figure 1) substantiates the suggested strong *trans* influence of the hydride favoring the formation a square-pyramidal structure with the hydride located in the apical position. The IPr ligand is located *trans* to the N-donor atom of the bidentate 8-quinolinolate ligand (N(1)-Rh-C(10) = 171.92(9)°), with the chlorido ligand *trans* to the O-donor atom (Cl-Rh-O = 174.70(5)°)). The wingtips of the IPr adopt an out-of-plane disposition from the squarebase of the pyramid with the aromatic rings pointing to the vacant site and the hydride ligand. The rhodium-carbene separation (Rh-C(10) = 1.951(2) Å) agrees well with the expected value for a single Rh-C bond..[15c]

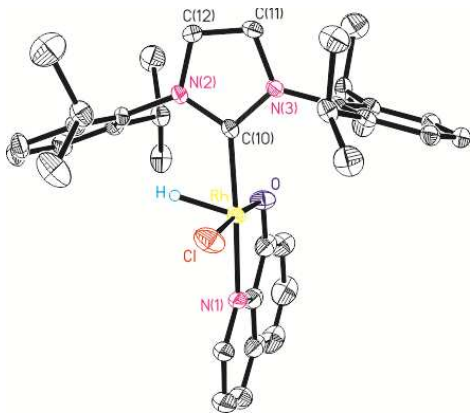
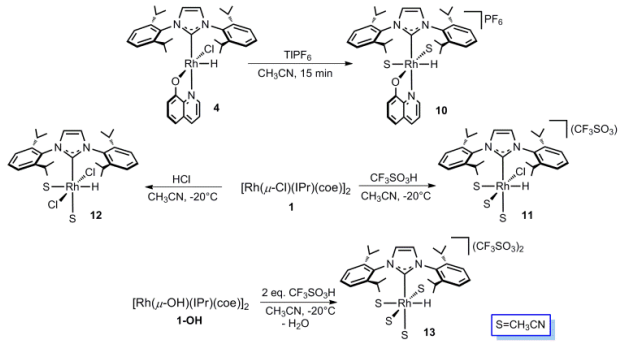


Figure 1. Molecular diagram of **4**. Selected bond lengths (Å) and angles (º): Rh-Cl 2.2993(7), Rh-O 1.9965(19), Rh-N(1) 2.062(2), Rh-C(10) 1.951(2), Rh-H 1.43(4); Cl-Rh-O 174.70(5), Cl-Rh-C(10) 91.24(7), Cl-Rh-N(1) 95.53(7), Cl-Rh-H 78(2), O-Rh-N(1) 81.45(9), O-Rh-C(10) 92.13(8), O-Rh-H 107(2), N(1)-Rh-C(10) 171.92(9), N(1)-Rh-H 109(2), C(10)-Rh-H 68(2).

The NMR analysis of complexes **5**-**7** showed a pattern of resonances comparable to that of complex **4** (for a resume of the most characteristic NMR data of complexes **4**-**16** see table S2 in supporting information). The most noticeable signals of the ^{1}H-NMR spectra of complexes **5**, **6** and **7** at 298 K is a shielded doublet between δ -27.9 and -28.6 ppm (J_{Rh-H} = 44-47 Hz) corresponding to the hydride ligand. This high-field shifted signal and the large Rh-H coupling constant has also been observed in related rhodium-hydride complexes and is a diagnostic for a vacant site *trans* to hydride ligand.[7j, 19] Interestingly, complex **5** showed only one signal for the two imidazole protons of IMes at δ 6.39 ppm, which, in addition to three signals δ 2.47, 2.44, and 1.90 ppm for the eighteen methyl protons, indicates rapid rotation of the carbene ligand around the Rh-C axis at room temperature. A similar NMR-pattern was observed for **6**, which is compatible with the fast rotation of the SIPr ligand around the Rh-C bond. However, the carbene ligand in **7** does not rotate as demonstrated by the presence of four signals for the four methyl groups of the SPXyl ligand (δ 2.64, 2.62, 2.56 and 2.55 ppm). This is in accordance with the reduction of the C(carbene)-N-C(phenyl) angle in the six-membered tetrahydropirimidine-type carbene, which produces the approaching of the phenyl substituents to the metal center hampering the rotation.[18b] A salient feature of the ^{13}C{^{1}H}-APT spectra of **5**-**7** is a deshielded doublet resonance corresponding to the Rh-C_{NHC} carbon atom. This signal appears at δ 177.5 ppm for complexes **5**, bearing a carbene with a unsaturated imidazol skeleton, whereas it is shifted to 200.9 ppm and 208.2 ppm for complex **7** and **6**, respectively, which suggested that these saturated carbenes are better electron donor ligands than the unsatured carbenes.[20]

To get more information about the influence of the 8-quinolinolate ligand on the catalytic activity, complexes containing an electron-poor analog, 5,7-dichloro-8-quinolinolate, or the bulkier ligand 2-methyl-8-quinolinolate were prepared. A synthetic route similar to that for **4** has been used in the synthesis of the 5,7-dichloro-8-quinolinolate complex, [RhClH(κ^2-O,N-$C_9H_4NOCl_2$)(IPr)] (**8**), which was obtained in 78% yield. On the other hand, the 2-methyl-8-quinolinol and **2a** did not react at room temperature, probably because of the presence of the methyl group near of nitrogen that hinders the coordination to the metal. Thus, the reaction was carried out at 80°C for 2 hours to give [RhClH(κ^2-O,N-$C_9H_5NOCH_3$)(IPr)] (**9**) in 72% isolated yield (Scheme 3). The ^{1}H and ^{13}C{^{1}H} NMR spectra of **8** and **9** are in accordance with the proposed structure. In both cases the high-field shifted hydride resonance observed in the ^{1}H-NMR signal at δ -27.81 ppm for **8** and -28.43 ppm for **9**, and the large J_{Rh-H} are consistent with those of related unsaturated square-pyramidal complexes previously described. The different electronic structure of **8** with respect to **4** is reflected in the signals of the quinolinic ring, especially in the ^{13}C NMR of the quaternary carbon atom directly bounded to the oxygen that is shifted from 170.9 ppm in **4** to 164.9 ppm in **8**. In the case of the complex **9** no interaction between the methyl of the 2-methyl-8-quinolinolate ligand and rhodium has been observed.

Synthesis of cationic complexes containing the hydride-Rh-IPr skeleton. Related cationic complexes containing the [RhH(IPr)] moiety have been synthesized in order to compare their catalytic properties with those of neutral complexes **4**-**9**. Complex [RhH(κ^2-O,N-C_9H_6NO)(IPr)($CH_3CN)_2$](PF_6) (**10**) was prepared by removing the chlorido ligand in **4** by treatment with $TlPF_6$ in acetonitrile (Scheme 4). Complex **10** was isolated as an orange solid in 68% yield. The ^{1}H NMR spectrum of **10** in CD_3CN showed the same pattern as [RhClH(κ^2-O,N-C_9H_6NO)(IPr)(CH_3CN)] (**4-CH_3CN**) (the acetonitrile solvate of **4**)[7j] with a hydride signal at δ -17.52 ppm (J_{Rh-H} of 21.1 Hz) and a downfield shifted signal at δ 7.54 ppm corresponding to the imidazole ring protons. These spectroscopic evidences strongly suggest that complex **10** in CH_3CN solution is octahedral with a weakly coordinated acetonitrile ligand *trans* to the hydride ligand. In fact, both acetonitrile molecules exchange with the CD_3CN solvent. The ^{13}C{^{1}H} spectrum displays a broad signal at δ 169.6 ppm corresponding to the carbene carbon atom. This value is upfield-shifted compared to that of complexes **4** or **4-CH_3CN** (179.0 and 175.2 ppm respectively), probably due to the positive charge in the cationic complex **10**.



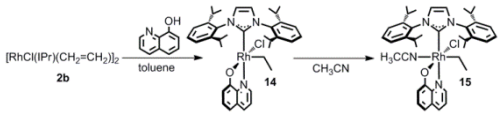
Scheme 4. Synthesis of complexes [RhH(κ^2-O,N-C_9H_6NO)(IPr)($CH_3CN)_2$]PF_6 (**10**), [RhClH($CH_3CN)_3$(IPr)]CF_3SO_3 (**11**), [$RhCl_2$H($CH_3CN)_2$(IPr)] (**12**) and [RhClH($CH_3CN)_4$(IPr)]($CF_3SO_3)_2$ (**13**).

In order to assess the influence of 8-quinolinolate ligands on the catalytic activity of this type complexes, related hydride-Rh^{III}-NHC where the bidentate ligand has been replaced by weakly bonded ligands such as acetonitrile were prepared. We synthesized complexes with a different number of chlorido ligands to obtain compounds with different charge (dicationic, monocationic and neutral) to better compare this new family of complexes with those previously described. In this case another source of hydride different from the 8-quinolinol has been used. One of the simplest species for hydride generation is a strong acid.[7a] We have selected two different acids to synthesize complexes with different charge: triflic acid (CF_3SO_3H) and hydrochloric acid. The former has been chosen for the relatively low coordination ability of the triflate anion, thus producing cationic Rh^{III}-hydride derivatives after reaction with Rh^I complexes. In contrast, reaction with HCl should lead to neutral Cl-Rh^{III}-H complexes due to the simultaneous coordination of a chlorido ligand. Thus, two new complexes were prepared starting from dimer **2a** and the corresponding acid in acetonitrile at low temperature: the cationic complex [RhClH($CH_3CN)_3$(IPr)]CF_3SO_3 (**11**) by addition of CF_3SO_3H, and the neutral [$RhCl_2$H($CH_3CN)_2$(IPr)] (**12**) by using HCl(aq) (Scheme 4). The preparation of a dicationic complex by treatment of complexes **11** or **12** with $AgPF_6$ or $TlPF_6$ was unsuccessful. However, the addition of two equiv of CF_3SO_3H to an acetonitrile solution of the chlorido-free dimer [Rh(μ-OH)(IPr)(η^2-coe)]$_2$ (**2-OH**) at -20°C, prepared recently in our laboratories,[21] lead to the formation of the dicationic complex [RhH($CH_3CN)_4$(IPr)]($CF_3SO_3)_2$ (**13**) in 91% isolated yield. The NMR spectra of **11**-**13** showed the typical pattern for a saturated Rh^{III} complex with an octahedral geometry. In particular, the hydride ligand appears between δ -15.4 and -18.7 ppm with a very small J_{Rh-H} (7-8 Hz). Moreover, the signals of the imidazole protons in **11** and **13** also support this geometry since they are downfield shifted to 7.44 and 7.65 ppm. In the case of **12**, the =CH

imidazole protons and carbons of the IPr ligand were found to be inequivalent and showed two resonances both in the ^{1}H NMR (δ 7.26 and 7.25 ppm) and in the ^{13}C{^{1}H} NMR spectrum (δ 126.7 and 125.5 ppm). This spectroscopic evidence points to a freeze structure bearing a mirror plane which contains the imidazole plane, with a *trans* disposition of both chlorido ligands and discards a dinuclear structure (Scheme 4). Similarly to the behaviour observed for **10**, all acetonitrile ligands exchange with the CD_3CN solvent. The charge of the complexes seems to strongly influence the chemical shift of the IPr resonances, especially in the case of the carbene carbon atom. In fact, the increase in the charge involves a progressive shielding of this resonance: δ 167.0 ppm for the neutral complex **12**, 161.2 ppm for the cationic species **11**, and 153.8 ppm for the dicationic **13**, which resulted to be the lowest chemical shift among all the prepared complexes of type H-Rh^{III}-IPr.

Synthesis of Et-Rh^{III}-IPr complexes. Recently our research group reported the synthesis and characterization of a new Rh^I dinuclear complex [Rh(μ-Cl)(IPr)(η^2-CH_2=CH_2)]$_2$ (**2b**).[16e] In search for an alternative starting complex for the synthesis of Rh^{III} derivatives we have studied the reactivity of the ethylene dimer **2b**. Interestingly, treatment of **2b** with 8-hydroxoquinoline or CF_3SO_3H resulted in the formation of Rh-ethyl compounds as a consequence of the insertion of the coordinated ethylene into the Rh-H bond of intermediate Rh^{III}-hydride species.[7a,22] It is worthy of note that a similar reactivity was observed with styrene, although the insertion products could not be isolated in the solid state.[7j] However, the insertion of cyclooctene has never been observed in any of the Rh-H described complexes, probably because of the large size of this olefin.

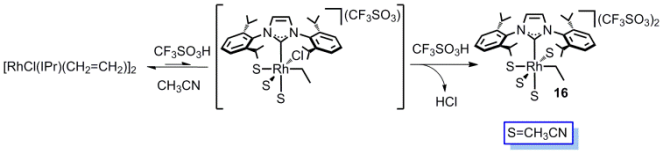
Reaction of [Rh(μ-Cl)(IPr)(η^2-CH_2=CH_2)]$_2$ (**2b**) with 8-hydroxyquinoline in toluene gave an orange solution of the unsaturated complex [RhCl(CH_2CH_3)(κ^2-O,N-C_9H_6NO)(IPr)] (**14**) which was isolated as an orange solid in 86% yield. Similarly to complex **4**, the coordination of an acetonitrile molecule at the vacant site results in the formation of the 18 e$^-$ complex [RhCl(CH_2CH_3)(κ^2-O,N-C_9H_6NO)(IPr)(CH_3CN)] (**15**) (Scheme 5).



Scheme 5. Synthesis of Rh-ethyl species **14** and **15**.

The spectroscopic properties of complex **14** closely resemble those of **4**. The ethyl group does not seem to affect the rotation of the carbene moiety and at room temperature only one signal for the imidazole protons was observed at δ 6.71 ppm. As already stated, this upfield shifted signal points to a pentacoordinated structure. This consideration, together with the strong *trans* influence of the ethyl group, leads us to propose a square-pyramidal geometry tfor complex **14** with the ethyl in the apical position. As it could be expected, the methylene protons of the ethyl ligand are diasterotopic thus showing two doublet of doublet of quadruplets with a J_{Rh-H} of 3.2 Hz. In the ^{13}C{^{1}H} NMR spectrum the carbene carbon atom appears as a doublet at δ 174.5 ppm with a J_{Rh-C} of 51.8 Hz, similar to the value observed for complex **4**. The ethyl ligand was observed as a doublet at δ 21.0 ppm with a J_{Rh-C} of 28.4 Hz (>CH_2) and a singlet at 20.6 ppm (CH_3). The saturate complex **15** do not show remarkable differences in the NMR spectra compared to the unsaturated analog **14** apart from the deshielding of the proton signal of the imidazole at δ 7.32 ppm which is a diagnostic for an octahedral saturate Rh^{III}-IPr complex. It is important to remark that, even in this case, at room temperature, the coordination of CH_3CN does not prevent the free rotation of the carbene around the Rh-C bond. In addition, the coordination of an acetonitrile ligand *trans* to the ethyl ligand does not influence significantly the chemical shift of the >CH_2 resonance in the ^{13}C{^{1}H} NMR spectrum (δ = 20.0 ppm, J_{Rh-C} = 28.5 Hz).

The reaction of [Rh(μ-Cl)(IPr)(η^2-CH_2=CH_2)]$_2$ (**2b**) with CF_3SO_3H in CH_3CN, did not afford the monocationic ethyl complex [RhCl(CH_2CH_3)(CH_3CN)$_3$(IPr)]$^+$ analogous of **11**. In fact, treating **2b** with 1 equiv of acid in CH_3CN gave an equimolar mixture of **2b** and the dicationic product [Rh(CH_2CH_3)(IPr)(CH_3CN)$_4$](CF_3SO_3)$_2$ (**16**). Treatment of this mixture with a second equiv of CF_3SO_3H gave a pale yellow solution of **16** which was isolated as a white solid in 79 % yield (Scheme 6). Surprisingly, treatment of the hydride species **11** with an excess of CF_3SO_3H does not result in the formation of the dicationic complex **13** (analogous to **16**). It is therefore evident that the ethyl ligand provides a special stereoelectronic environment that increases the reactivity of the monocationic species.



Scheme 6. Preparation of the dicationic complex **16**.

Singlecrystals of **16** suitable for X-ray analysis were obtained by slow diffusion of diethylether over a saturated solution of **16** in CH_2Cl_2 (Figure 2). The complex shows a slightly distorted octahedral geometry around the metal center with the IPr and ethyl ligands in *cis* disposition. The Rh-C(11) distance of 2.026(7) Å is typical of a single Rh-C bond.[15c] A similar distance can be observed between the Rh and the ethyl ligand (2.065(7) Å), with the methyl group pointing down from the IPr ligand with a torsion angle C(11)(IPr)-Rh-C1-C2 of 162.2(7)°. The two acetonitrile molecules oriented mutually *trans* exhibit a similar distance to the Rh center, Rh-N(1) 1.994(7)Å and Rh-N(3) 1.998(6)Å. However, the acetonitrile *trans* to the ethyl ligand has a longer Rh-N(2) separation of 2.197(7)Å which is in agreement with the high *trans* influence of the ethyl ligand. The acetonitrile *trans* to the IPr ligand shows an intermediate Rh-N bond distance of 2.092(7) Å. It is remarkable that the acetonitrile ligands *cis* to IPr are bonded in a bent fashion, presenting a deviation of about 14°, and angles of Rh-N(1)-C(3) 165.5(6)°, Rh-N(2)-C(5) 166.3(6)° and Rh-N(3)-C(7) 166.9(7)°. Probably, this deviation results from the high steric pressure exerted by the carbene ligand in combination with the weakness of the rhodium-acetonitrile bonds. In fact, the acetonitrile disposed *trans* to the IPr ligand is also deviated, but by only 7.7° (Rh-N(4)-C(9) 172.0(7)°).

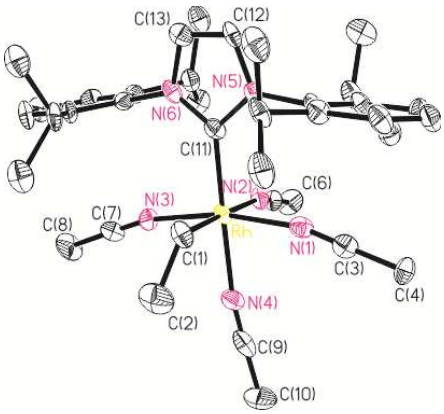
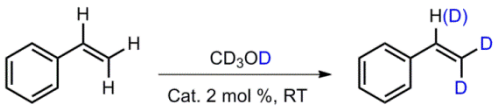


Figure 2. Molecular diagram of the cation of **16**. Selected bond lengths (Å) and angles (º): Rh-C(1) 2.065(7), Rh-N(1) 1.994(7), Rh-N(2) 2.197(7), Rh-N(3) 1.998(6), Rh-N(4) 2.092(7), Rh-C(11) 2.026(7); C(1)-Rh-N(1) 88.7(3), C(1)-Rh-N(2) 177.1(3), C(1)-Rh-N(3) 90.1(3), C(1)-Rh-N(4) 93.7(3), C(1)-Rh-C(11) 86.8(3), N(1)-Rh-N(2) 92.9(3), N(1)-Rh-N(3) 168.0(2), N(1)-Rh-N(4) 82.6(3), N(1)-Rh-C(11) 96.3(3), N(2)-Rh-N(3) 87.9(3), N(2)-Rh-N(4) 84.1(3), N(2)-Rh-C(11) 95.4(3), N(3)-Rh-N(4) 85.6(3), N(3)-Rh-C(11) 95.6(3), N(4)-Rh-C(11) 178.8(3).

^{1}H and ^{13}C{^{1}H} NMR spectra of **16** are in accordance with the proposed structure. In this case the symmetry of the complex, in combination with the rapid rotation of carbene, lead to only one ^{1}H-NMR signal for the four isopropyl protons and two signals for the eight methyl groups. The signal of the imidazole protons, as expected for a saturated hydride-Rh^{III}-NHC- complex, appeared downfield shifted (δ 7.46 ppm) with respect to the analogue unsaturated complex. The >CH_2 protons of the ethyl ligands display a single resonance at δ 2.76 ppm, which is in agreement with the C_s symmetry of the complex. Only one signal corresponding to free acetonitrile was observed due to fast exchange with the CD_3CN solvent. The ^{13}C{^{1}H} NMR spectrum displays a doublet at δ 150.3 ppm, with J_{Rh-C} = 52.2 Hz, corresponding to the carbene carbon atom, which is the most shielded within all complexes described in the work, probably due to the dicationic nature of the complex. The signal of methylene-carbon atom bonded to rhodium appears at δ 18.4 ppm, similarly to that of **14** and **15**, but the J_{Rh-C} of 17.6 Hz was significantly lower.

Catalytic activity studies. The synthesized complexes have been evaluated as catalysts for H/D exchange in olefins using CD_3OD as deuterium source. Styrene was chosen as a model olefin for the evaluation of catalytic activity and selectivity (Scheme 7). The reactions were performed in a NMR tube sealed under argon containing 0.5 mL of CD_3OD with a 2 mol % of catalyst loading at 25°C and was monitored by NMR spectroscopy. Vinylic deuteration was exclusively observed for all the catalysts with a very high selectivity towards *β* position (Figure 3, Table 1).



Scheme 7. Selective H/D exchange reaction

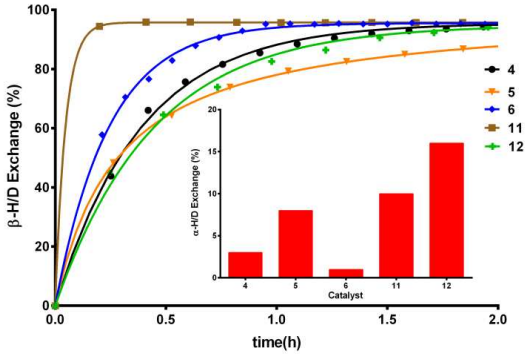


Figure 3. H/D exchange in styrene catalyzed by **4**, **5**, **6**, **11**, and **12**.

Table 1. Styrene H/D exchange promoted by different catalysts.[a]

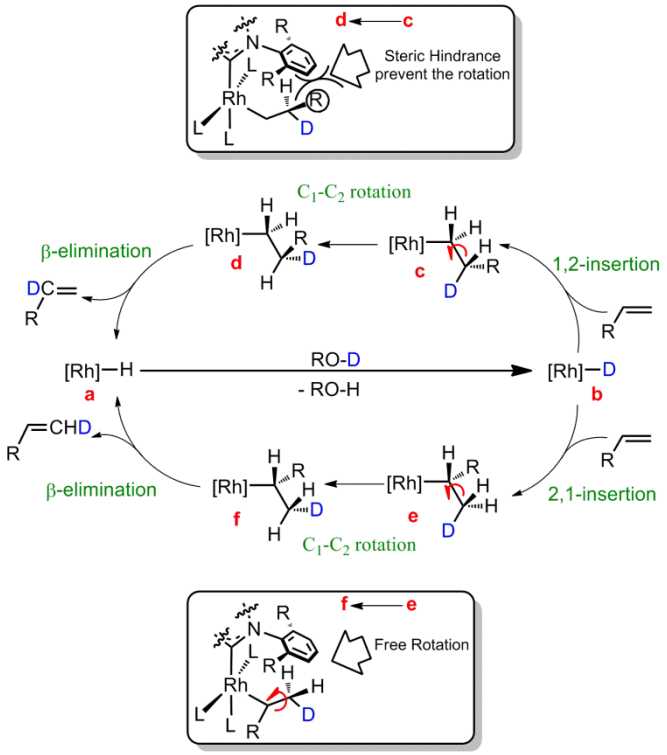
Entry	Catalyst	t[h]	*α*-D[%][b]	*β*-D[%][b]	$TOF_{1/2}$ [h^{-1}][c]
1	**4**	3	3	92	192
2	**5**	5	8	92	178
3	**6**	1	trace	92	306
4	**7**	24[d]	trace	trace	---
5	**8**	6	12	91	90
6	**9**	7[d]	13	86	39
7	**10**	24[d]	2	8	---
8	**11**	0.3	10	92	3110
9	**12**	2.2	16	91	171
10	**13**	24[d]	trace	trace	---
11	**14**	4	6	92	139
12	**15**	4	6	92	139
13	**16**	24[d]	trace	trace	---

[a] Reaction conditions: [Styrene] = 1M in 0.5 mL of CD_3OD with 2 mol % of catalyst at 25°C. [b] % of deuterium incorporation at the determined position (*α* or *β*). [c] H/D exchange at *β*-position, TOF calculated at 50% of conversion. [d] Reaction performed at 80°C.

As can be observed from Table 1, the catalytic performance of the complexes is very different and, as expected, modification of the ancillary ligands have a dramatic effect on the catalytic properties. In particular the results obtained for **6** and **11** stand out among all the reported data. The cationic acetonitrile-solvated Rh-hydride complex $[RhClH(CH_3CN)_3(IPr)]^+$ (**11**) reached excellent values of activity in the deuteration of *β*-vinyl protons of the styrene ($TOF_{1/2}$ = 3110 h^{-1}), with a 92% of deuterium incorporation in less than 20 min (entry 8). This complex resulted to be the most active catalyst among all synthesized, being 10 times faster than the previously reported complex [RhClH(κ^2-O,N-C_9H_6NO)(IPr)] (**4**) (entry 1). In

addition, is worthy of note that the value of 92% of *β*-deuteration attained with **11** approaches to the maximum theoretical value of *β*-deuteration attainable under the reaction conditions (92.5%), thus reaching an deuteration efficiency of >99%.[23] However, this exceptional increase in catalytic activity is accompanied by a loss of selectivity as 10% of deuteration at the α-vinyl position was observed. The activity of a catalyst is highly important but, for practical applications, the selectivity is fundamental. In this respect, complex [RhClH(κ^2-O,N-C_9H_6NO)(SIPr)] (**6**) is certainly the catalyst precursor with the best catalytic performance. In fact, as can be observed from Table 1 (entry 3), in addition to its excellent catalytic activity ($TOF_{1/2}$ = 306 h^{-1}) an outstandingly high selectivity values in the deuteration of the *β*-vinyl hydrogens (also in this case >99% of the maximum theoretical *β*-deuteration value) was achieved with deuterium incorporation at the α-vinyl position only at trace levels. For what concerns the other synthesized complexes, good results in terms of catalytic performance were obtained for complexes **5**, **8**, **12**, **14** and **15** (entries 2, 5, 9, 11 and 12, respectively), with $TOF_{1/2}$ values between 90 to 179 h^{-1}, and good selectivity towards the *β*-vinyl deuterated olefin. On the other hand, complex **9** showed moderate activity at 80°C (entry 6) and complexes **7**, **10**, **13**, and **16** were practically inactive even at 80°C (entries 4, 7, 10, 13, respectively).

In order to analyze these results in more detail taking into account the different nature of catalyst precursors, it seem important to focus on the mechanism by which these catalysts operate. As previously proposed,[7j] the first step of the process is the exchange of the hydride ligand Rh^{III}-H (**a**) by deuterium from the deuterated solvent (CD_3OD) to generate a Rh^{III}-D (**b**) species (Scheme 8).[24] Then, after coordination of the olefin to complex **b** to give an intermediate species with both ligands in *cis* disposition ,[25] the orientation of the η^2-coordinated olefin determines the insertion pathway. A 1,2 insertion on the Rh-D bond give rise to the linear product **c**, whereas a 2,1 insertion provides the branched product **e**. At this point, rotation around the C_1-C_2 alkyl axis is essential in order to an effective H/D exchange (**c** → **d**; **e** → **f**).[26] Subsequent *β*-H elimination in **d** produces *α*-deuteration whereas that in **f** give rise to the *β*-deuterated olefin. The critical step determining the selectivity is the rotation around the C_1-C_2 alkyl axis. In the case of **c**, the steric hindrance imposed by the ligands in the complex, restricts that rotation (and the formation of **d**) due to repulsion between the R group of the alkyl ligand and the substituents of the NHC, thus meaning that although a deuterium atom can enter the benzyl position the hydrogen atom cannot easily leave. On the contrary, in the case of complex **e,** the terminal methyl group can easily rotate to form complex **f,** from which the *β*-deuterated olefin is obtained after *β*-H elimination.



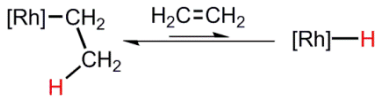
Scheme 8. Mechanism of H/D exchange of olefins mediated by Rh^{III}-H catalyst.

The NHC ligand has a strong influence on the catalytic performance. The substitution of IPr for IMes in complex **5** (entry 2) produces a decrease both of the activity and selectivity. This is probably due to the lower electron-donor ability and bulkiness of IMes with respect to IPr.[15b,20]. Complex **6**, bearing the ligand SIPr, is the more selective throughout the studied catalysts and the most active among those having the 8-quinolinolate ligand (entry 3). SIPr, the saturate analog of the IPr, is slightly more electron-donor and bulky,[15b] which can explain the observed improvement of the catalytic performance. In view of the trend that an increase of steric hindrance imparted by the NHC ligand results in a selectivity improvement, we envisage that the introduction of a bulky tetrahydropyrimidine-based NHC ligand (SPXyl) in complex **7** could improve the catalytic outcome. However, rather surprisingly, complex **7** was completely ineffective (entry 4). It has been found that the hydride ligand of **7** does not undergo H/D exchange in CD_3OD even at 80°C, thus explaining its inactivity as deuterium labeling catalyst. Most likely the high steric hindrance of the SPXyl ligand prevent hydride-CD_3OD interaction. Thus, it becomes evident that bigger is better but without overshooting.

The steric and electronic properties of the 8-quinolinolate ligand also have an impact on the catalytic performance. The modification of the bidentate O-N ligand lead to a complex with a lower electronic density (complex **8**) and to another complex with more steric hindrance close to the metallic center (complex **9**). Catalyst **8** presents two chloro substituents in the quinolinolate skeleton that decrease the electron density on the metal center thus reducing the catalytic activity (entry 5), with results comparable to those obtained for the complex **5** (entry 2). The case for complex **9** bearing a 2-methyl-8-quinolinolate ligand is slightly different. Catalyst **9** showed no catalytic activity at room temperature, reaching only a moderate activity and selectivity at 80°C (entry 6). In this case, contrary to **7**, the hydride ligand in **9** is smoothly deuterated by

CD_3OD. Thus, most probably the steric hindrance imposed by the quinolinolate ligand should difficult olefin coordination.

The charge of the complexes also influences the catalytic performance. In fact, the catalyst precursor [RhH(κ^2-O,N-C_9H_6NO)(IPr)$(CH_3CN)_2$](PF_6) (**10**), the cationic derivative of complex **4** obtained by elimination of chlorido ligand, showed no catalytic activity at all (entry 7). In sharp contrast, the cationic chlorido complex [RhClH$(CH_3CN)_3$(IPr)]CF_3SO_3 (**11**) is the most active catalyst precursor among all synthesized (entry 8). This result suggests that the presence a chlorido ligand is essential for the activity of the catalyst. Most probably the role of chlorido ligand was the stabilization of key Rh^{III} catalytic. In fact, it has been observed that complex **10** decomposed rapidly under the reaction conditions leading to an unidentified mixture of complexes unable to catalyze the H/D exchange of styrene. This chlorido effect can be appreciated also in the case of the complexes lacking a 8-quinolinolate ligand bearing more labile acetonitrile ligands. The excellent catalytic activity of **11** could be also related to the presence of labile acetonitrile ligands that facilitates the olefin coordination and insertion processes. However, this effect also leads to a loss of the selectivity (10% α-deuteration). The presence of two chlorido ligands in the neutral complex [$RhCl_2H(CH_3CN)_2$(IPr)] (**12**), resulted in a decrease of the catalytic activity (entry 9). Finally, the dicationic complex lacking a chloride ligand [$RhH(CH_3CN)_4$(IPr)]$(CF_3SO_3)_2$ (**13**) was totally inactive (entry 10). As shown in Scheme 8, the operative insertion-elimination mechanism for H/D exchange in olefins requires the participation of active hydride species. For this reason, ethyl complexes **14**-**16** should be inactive. However, complex [RhCl(CH_2CH_3)(κ^2-O,N-C_9H_6NO)(IPr)] (**14**) is only slightly less active than the hydride counterpart **4** (entry 11). That fact can be explained assuming that such species could be in equilibrium with hydride-olefin species.[22]



Scheme 9. Equilibrium between Rh-ethyl and Rh-H/ethylene species.

As it could be expected, the catalytic performance of the acetonitrile complex **15** (entry 12) is identical to that of **14**, since the dissociation of the labile acetonitrile ligand produces the same active species. Also, the dicationic catalyst precursor [$Rh(CH_2CH_3)$(IPr)$(CH_3CN)_4$]$(CF_3SO_3)_2$ (**16**), which does not contain a chlorido ligand, resulted to be completely inactive (entry 13).

Conclusions

A series of new hydride-Rh^{III}-NHC and ethyl-Rh^{III}-NHC complexes containing different substituted quinolinolate or acetonitrile donor ligands have been synthesized and fully characterized. Both types of Rh^{III}-NHC complexes have been used as catalysts for the H/D exchange of olefins using CD_3OD as deuterium source. Most of these complexes resulted to be very active and selective in the vinylic-H/D exchange of styrene, without the concomitant deuteration of the aromatic region. Moreover, they were able to deuterate the vinylic-β-positions with very high selectivity.

It has been observed that the NHC ligand play an important role in the catalytic activity and selectivity. In fact, along the series [RhClH(κ^2-O,N-C_9H_6NO)(NHC)], and taking the IPr complex as a reference, the complex bearing a better electron-donor carbene, SIPr, resulted the most active catalyst with outstanding selectivity for the *β*-vinylic positions, while the introduction of a less electron-donor and less bulky carbene such as IMes decreased the catalytic activity and selectivity. On the other hand, complexes bearing carbenes with good electron-donor properties but with large steric hindrance, as the SPXyl, did not show any catalytic activity. The remaining involved ligands also played an important role in the catalytic proprieties. In fact, complexes without chlorido ligand are inactive, and the introduction of a 8-quinolinolate ligand with an electron-withdrawing substituents or a bulky group near to the Rh, reduced or suppressed the catalytic activity, respectively. Replacement of the chelate quinolinolate ligand by weakly bonded acetonitrile ligands increased the catalytic activity but decreased the selectivity of the catalyst. In fact, the cationic complex [RhClH$(CH_3CN)_3$(IPr)]$^+$ showed an excellent catalytic activity reaching the maximum attainable degree of *β*-vinylic deuteration in only 20 min. On the other hand, along the ethyl-Rh^{III}-IPr series, complex [RhCl(CH_2CH_3)(8-quinolinolate)(IPr)] also showed a good catalytic activity which can be rationalized assuming an equilibrium with hydride-olefin species. In conclusion, this work represents an in-depth study for developing improved catalytic systems by ligand modification which along with the understanding of the catalytic mechanism, allow for the design of better performing catalysts.

Experimental Section

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques. Organic solvents were obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies), except for THF that was dried over sodium and distilled under argon prior to use. The starting materials [Rh(*μ*-Cl)(η^2-coe)$_2$]$_2$ (**1**),[27] [Rh(*μ*-Cl)(IPr)(η^2-coe)]$_2$ (**2a**),[16b] [Rh(*μ*-Cl)(IPr)(η^2-CH_2=CH_2)]$_2$ (**2b**),[16e] [Rh(*μ*-OH)(IPr)(η^2-coe)]$_2$ (**2-OH**),[21] [Rh(*μ*-Cl)(IMes)(η^2-coe)]$_2$ (**3**),[16b] [RhClH(κ^2-O,N-C_9H_6NO)(IPr)] (**4**),[7j] IPr,[18a] IMes,[18a] ICy,[18c] SPXyl,[18b] and SIPr,[18d] were prepared following the procedures described in the literature. ^{1}H, ^{31}P{^{1}H}, ^{19}F and ^{13}C{^{1}H} NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300 or a Bruker Avance 500 and 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}) or external H_3PO_4 (^{31}P{^{1}H}) or $CFCl_3$ (^{19}F). Coupling constants, *J*, are given in hertz. Spectral assignments were achieved by combination of ^{1}H-^{1}H COSY, ^{13}C{^{1}H}-APT and ^{1}H-^{13}C HSQC/HMBC experiments. C, H, and N analyses were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Catalytic H/D Exchange. In a NMR tube 0.01mmol of catalyst were dissolved in 0.5 mL of CD_3OD and then the olefin (0.5 mmol) was added and the reaction course monitored by ^{1}H-NMR spectroscopy. The H/D exchange was quantified on the basis of the decrease in the integral value of the olefin resonances compared to those of the internal standardhexamethyldisiloxane (2 μL, 10 μmol). The successful deuteration of the olefin was confirmed by ^{2}H-NMR spectroscopy.

Preparation of [RhClH(κ^2-O,N-C_8H_6NO)(IMes)] (5). A yellow solution of **3** (300 mg, 0.271 mmol) in toluene (10 mL) was treated with 8-hydroxyquinoline (79 mg, 0.542 mmol) and stirred at room temperature for 45 min. The solution was concentrated to ca. 1 mL and then *n*-hexane (3 mL) was added to induce the precipitation of an orange solid which was washed with hexane (3 x 3 mL) and dried in vacuo. Yield: 252 mg (79%). Anal. Calcd. for $C_{30}H_{31}N_3ClORh$: C, 61.28; H, 5.31; N, 7.15. Found: C, 61.54; H, 5.39; N, 7.11. ^{1}H NMR (400 MHz, tol-d_8, 298 K): δ 8.92 (d, $J_{H\text{-}H}$ = 4.6, 1H, $H_{2\text{-}Quin}$), 7.17 (d, $J_{H\text{-}H}$ = 8.1, 1H, $H_{4\text{-}Quin}$), 7.14 (dd, $J_{H\text{-}H}$ = 7.8, 7.7, 1H, $H_{6\text{-}Quin}$), 6.68 (br, 4H, $H_{Ph\text{-}IMes}$), 7.04 (d, $J_{H\text{-}H}$ = 7.7, 1H, $H_{7\text{-}Quin}$), 6.39 (s, 2H, =CHN), 6.48 (d, $J_{H\text{-}H}$ = 7.8, 1H, $H_{5\text{-}Quin}$), 6.29 (dd, $J_{H\text{-}H}$ = 8.1, 4.6, 1H, $H_{3\text{-}Quin}$), 2.47, 2.44, and 1.90 (all s, 18H, Me_{IMes}), -28.49 (d, 1H, $J_{Rh\text{-}H}$ = 46.0, H-Rh). ^{13}C{1H}-APT NMR (100.6 MHz, *tol-d*$_8$, 298 K): δ 177.5 (d, $J_{C\text{-}Rh}$ = 49.7, Rh-C_{IPr}), 171.1 (s, $C_{8\text{-}Quin}$), 146.5 (s, $C_{2\text{-}Quin}$), 145.5 (s, $C_{8a\text{-}Quin}$), 139.6, 137.8, and 137.5 (all s, $C_{q\text{-}IMes}$), 137.6 (s, C_qN), 137.1 (s, $C_{4\text{-}Quin}$), 130.9 (s, $C_{4a\text{-}Quin}$), 129.9 and 129.8 (both s, $CH_{Ph\text{-}IMes}$), 129.5 (s, $C_{6\text{-}Quin}$), 123.4 (s, =CHN), 120.8 (s, $C_{3\text{-}Quin}$), 114.4 (s, $C_{7\text{-}Quin}$), 111.3 (s, $C_{5\text{-}Quin}$), 21.3, 18.9, and 18.8 (all s, Me_{IMes}).

Preparation of [RhClH(κ^2-O,N-C_8H_6NO)(SIPr)] (6). A yellow suspension of **1** (300 mg, 0.418 mmol) in THF (10 mL) was treated with SIPr (327 mg, 0.838 mmol) and 8-hydroxyquinoline (121 mg, 0.836 mmol) and stirred at room temperature for 30 min. The resulting orange solution was evaporated to dryness, dissolved in 10 mL of toluene and filtered through a bed of celite. The filtrate was concentrated to ca. 1 mL and then *n*-hexane (3 mL) was added to induce the precipitation of an orange solid which was washed with hexane (3 x 3 mL) and dried in vacuo. Yield: 231 mg (73%). Anal. Calcd. for $C_{36}H_{45}N_3ClORh$: C, 64.14; H, 6.73; N, 6.23. Found: C, 64.56; H, 6.85; N, 6.15. ^{1}H NMR (300 MHz, C_6D_6, 298 K):δ 8.97 (d, $J_{H\text{-}H}$ = 4.3, 1H, $H_{2\text{-}Quin}$), 7.19 (dd, $J_{H\text{-}H}$ = 7.7, 7.4, 1H, $H_{6\text{-}Quin}$), 7.12 (d, $J_{H\text{-}H}$ = 8.1, 1H, $H_{4\text{-}Quin}$), 7.10 (m, 6H, $H_{Ph\text{-}SIPr}$), 7.07 (d, $J_{H\text{-}H}$ = 7.4, 1H, $H_{7\text{-}Quin}$), 6.50 (d, $J_{H\text{-}H}$ = 7.7, 1H, $H_{5\text{-}Quin}$), 6.24 (dd, $J_{H\text{-}H}$ = 8.1, 4.3, 1H, $H_{3\text{-}Quin}$), 3.90 and 3.87 (both sept, $J_{H\text{-}H}$ = 6.6, 4H, C<u>H</u>Me_{SIPr}), 3.83 (m, 4H, $CH_{2\text{-}SIPr}$), 1.64, 1.62, 1.25, and 1.22 (all d, $J_{H\text{-}H}$ = 6.6, 24H, CH<u>Me</u>$_{SIPr}$), -28.61 (d, 1H, $J_{Rh\text{-}H}$ = 47.3, H-Rh). ^{13}C{1H}-APT NMR (75.4 MHz, C_6D_6, 298 K): δ 208.2 (d, $J_{C\text{-}Rh}$ = 44.7, Rh-C_{SIPr}), 170.9 (s, $C_{8\text{-}Quin}$), 148.9 (s, $C_{q\text{-}SIPr}$), 146.5 (s, $C_{2\text{-}Quin}$), 145.2 (s, $C_{8a\text{-}Quin}$), 137.2 (s, $C_{4\text{-}Quin}$), 136.1 (s, C_qN), 130.8 (s, $C_{4a\text{-}Quin}$), 130.3, 125.2, and 125.1 (s, $CH_{Ph\text{-}SIPr}$), 129.6 (s, $C_{6\text{-}Quin}$), 120.9 (s, $C_{3\text{-}Quin}$), 114.3 (s, $C_{7\text{-}Quin}$), 111.1 (s, $C_{5\text{-}Quin}$), 54.4 (s, $CH_{2\text{-}SIPr}$), 29.5 and 29.4 (both s, C<u>H</u>Me_{SIPr}), 27.1, 27.0, 24.6, and 24.5 (all s, CH<u>Me</u>$_{SIPr}$).

Preparation of [RhClH(κ^2-O,N-C_8H_6NO)(SPXyl)] (7). The complex was prepared as described for **6** starting from **1** (300 mg, 0.418 mmol), SPXyl (245 mg, 0.836 mmol), and 8-hydroxyquinoline (121 mg, 0.836 mmol), and obtained as an orange solid. Yield: 327 mg (68%). Anal. Calcd. for $C_{29}H_{31}N_3ClORh$: C, 60.48; H, 5.43; N, 7.30. Found: C, 60.86; H, 5.53; N, 6.95. ^{1}H NMR (500 MHz, tol-d_8, 298 K):δ 8.89 (dd, $J_{H\text{-}H}$ = 4.8, 1.3, 1H, $H_{2\text{-}Quin}$), 7.24 (dd, $J_{H\text{-}H}$ = 8.3, 1.3, 1H, $H_{4\text{-}Quin}$), 7.21 (dd, $J_{H\text{-}H}$ = 7.9, 7.8, 1H, $H_{6\text{-}Quin}$), 6.9-6.6 (m, 6H, $H_{Ph\text{-}SPXyl}$), 7.05 (dd, $J_{H\text{-}H}$ = 7.8, 1.0, 1H, $H_{7\text{-}Quin}$), 6.53 (dd, $J_{H\text{-}H}$ = 7.9, 1.0, 1H, $H_{5\text{-}Quin}$), 6.35 (dd, $J_{H\text{-}H}$ = 8.3, $J_{H\text{-}H}$ = 4.8, 1H, $H_{3\text{-}Quin}$), 3.0-2.9 (m, 4H, CH_2N_{SPXyl}), 2.64, 2.62, 2.55, and 2.56 (all s, 12H, $Me_{6\text{-}Xyl}$), 1.76 and 1.65 (both m, 2H, $CH_{2\text{-}SPXyl}$), -27.94 (d, 1H, $J_{Rh\text{-}H}$ = 44.4, H-Rh). ^{13}C{1H}-APT NMR (100.6 MHz, tol-d_8, 298 K): δ 200.9 (d, $J_{C\text{-}Rh}$= 44.5, Rh-C_{SPXyl}), 170.6 (s, $C_{8\text{-}Quin}$), 147.2 and 139.0 (both s, C_qN), 146.2 (s, $C_{2\text{-}Quin}$), 145.1 (s, $C_{8a\text{-}Quin}$), 137.0 (s, $C_{4\text{-}Quin}$), 139.6, 139.4, 137.5, and 137.2 (all s, $C_{q\text{-}SPXyl}$), 129.8, 129.5, 129.3. 129.2, 128.9, and 128.5 (s, $CH_{Ph\text{-}SPXyl}$), 130.9 (s, $C_{4a\text{-}Quin}$), 129.5 (s, $C_{6\text{-}Quin}$), 120.8 (s, $C_{3\text{-}Quin}$), 113.9 (s, $C_{7\text{-}Quin}$), 110.7 (s, $C_{5\text{-}Quin}$), 47.3 and 46.7 (both s, CH_2N_{SPXyl}), 21.9 (s, $CH_{2\text{-}SPXyl}$), 19.8, 19.6, 18.8, and 18.7 (all s, Me_{SPXyl})

Preparation of [RhClH(κ^2-O,N-$C_8H_4NOCl_2$)(IPr)] (8). The complex was prepared as described for **5** starting from **2a** (300 mg, 0.235 mmol) and 5,7-dichloro-8-hydroxyquinoline (100 mg, 0.470 mmol), and isolated as an orange solid. Yield: 272 mg (78%). Anal. Calcd. for $C_{36}H_{41}N_3Cl_3ORh$: C, 58.35; H, 5.58; N, 5.67. Found: C, 58.74; H, 5.40; N, 5.59. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 8.85 (d, $J_{H\text{-}H}$ = 4.4, 1H, $H_{2\text{-}Quin}$), 7.65 (s, 1H, $H_{6\text{-}Quin}$), 7.65 (d, $J_{H\text{-}H}$ = 8.1, 1H, $H_{4\text{-}Quin}$), 7.2-7.0 (m, 6H, $H_{Ph\text{-}IPr}$), 6.75 (s, 2H, =CHN), 6.18 (dd, $J_{H\text{-}H}$ = 8.1, $J_{H\text{-}H}$ = 4.4, 1H, $H_{3\text{-}Quin}$), 3.42 and 3.40 (both sept, $J_{H\text{-}H}$ = 6.8, 4H, C<u>H</u>Me_{IPr}), 1.58, 1.56, 1.16, and 1.15 (all d, $J_{H\text{-}H}$ = 6.8, 24H, CH<u>Me</u>$_{IPr}$), -27.81 (d, 1H, $J_{Rh\text{-}H}$ = 43.6, H-Rh). ^{13}C{1H}-APT NMR (75.4 MHz, C_6D_6, 298 K): δ 176.7 (d, $J_{C\text{-}Rh}$= 49.2, Rh-C_{IPr}), 164.9 (s, $C_{8\text{-}Quin}$), 147.6 and 147.5 (both s, $C_{q\text{-}IPr}$), 147.4 (s, $C_{2\text{-}Quin}$), 145.5 (s, $C_{8a\text{-}Quin}$), 137.9 (s, C_qN), 133.9 (s, $C_{4\text{-}Quin}$), 130.8, 125.7, and 124.5 (s, $CH_{Ph\text{-}IPr}$), 129.6 (s, $C_{6\text{-}Quin}$), 125.1 (s, =CHN), 121.2 (s, $C_{3\text{-}Quin}$), 117.6 (s, $C_{7\text{-}Quin}$), 112.9 (s, $C_{5\text{-}Quin}$), 126.6 (s, $C_{4a\text{-}Quin}$), 29.0 and 28.9 (both s, CH<u>Me</u>$_{IPr}$), 26.3, 26.2, 23.6, and 23.4 (all s, C<u>H</u>Me_{IPr}).

Preparation of [RhClH(κ^2-O,N-$C_8H_5NOCH_3$)(IPr)] (9). A yellow solution of **2a** (300 mg, 0.235 mmol) in toluene (10 mL) was treated with 2-methyl-8-hydroxyquinoline (75 mg, 0.470 mmol) and stirred at 80°C for 2 hours. The solution was concentrated to ca. 1 mL and then *n*-hexane (3 mL) was added to induce the precipitation of an orange solid which was washed with hexane (3 x 3 mL) and dried in vacuo. Yield: 229 mg (71%). Anal. Calcd. for $C_{37}H_{45}N_3ClORh$: C, 64.77; H, 6.61; N, 6.12. Found: C, 65.04; H, 6.93; N, 6.12. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.23 (dd, $J_{H\text{-}H}$ = 7.9, 7.8, 1H, $H_{6\text{-}Quin}$), 7.17 (d, $J_{H\text{-}H}$ = 8.4, 1H, $H_{4\text{-}Quin}$), 7.2-7.0 (m, 6H, $H_{Ph\text{-}IPr}$), 7.08 (dd, $J_{H\text{-}H}$ = 7.9, 1.0, 1H, $H_{7\text{-}Quin}$), 6.75 (s, 2H, =CHN), 6.60 (dd, $J_{H\text{-}H}$ = 7.8, 1.0, 1H, $H_{5\text{-}Quin}$), 6.15 (d, $J_{H\text{-}H}$ = 8.4, 1H, $H_{3\text{-}Quin}$), 3.57 and 3.51 (both br, 4H, C<u>H</u>Me_{IPr}), 2.78 (s, 1H, $CH_{3\text{-}Quin}$), 1.56, 1.54, 1.15, and 1.14 (all d, $J_{H\text{-}H}$ = 6.8, 24H, CH<u>Me</u>$_{IPr}$), -28.43 (d, 1H, $J_{Rh\text{-}H}$ = 45.2, H-Rh). ^{13}C{1H}-APT NMR (75.4 MHz, C_6D_6, 298 K): δ 175.7 (d, $J_{C\text{-}Rh}$ = 51.6, Rh-C_{IPr}), 170.5 (s, $C_{8\text{-}Quin}$), 162.3 (s, $C_{2\text{-}Quin}$), 148.1 and 148.0 (both s, $C_{q\text{-}IPr}$), 144.4 (s, $C_{8a\text{-}Quin}$), 137.5 (s, $C_{4\text{-}Quin}$), 137.2 (s, C_qN), 131.0, 124.8, and 124.7 (s, $CH_{Ph\text{-}IPr}$), 129.1 (s, $C_{4a\text{-}Quin}$), 128.3 (s, $C_{6\text{-}Quin}$), 125.1 (s, =CHN), 124.4 (s, $C_{3\text{-}Quin}$), 115.1 (s, $C_{7\text{-}Quin}$), 111.4 (s, $C_{5\text{-}Quin}$), 29.4 and 29.3 (both s, C<u>H</u>Me_{IPr}), 27.3 (s, $CH_{3\text{-}Quin}$), 26.9, 26.8, 23.9, and 23.8 (all s, CH<u>Me</u>$_{IPr}$).

Preparation of [RhH(κ^2-O,N-C_8H_6NO)(IPr)(CH_3CN)$_2$]PF_6 (10). An orange solution of **4** (150 mg, 0.223 mmol) in CH_3CN (5 mL) was treated with $TlPF_6$ (78 mg, 0.223 mmol) and stirred at room temperature for 15 min. The suspension was filtered through a celite bed. Then, the solvent was evaporated to dryness and the residue stirred with diethyl ether to give an orange solid which was washed with diethyl ether (3 x 2 mL) and dried in vacuo. Yield: 131 mg (68%). Anal. Calcd. for $C_{40}H_{49}N_5ORhPF_6$: C, 55.62; H, 5.72; N, 8.11. Found: C, 55.86; H, 5.88; N, 8.05.^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 8.40 (d, $J_{H\text{-}H}$ = 4.7, 1H, $H_{2\text{-}Quin}$), 8.20 (d, $J_{H\text{-}H}$ = 8.4, 1H, $H_{4\text{-}Quin}$), 7.54 (s, 2H, =CHN), 7.36 (dd, $J_{H\text{-}H}$ = 8.4, 4.7, 1H, $H_{3\text{-}Quin}$), 7.24 (dd, $J_{H\text{-}H}$ = 8.1, 8.0, 1H, $H_{6\text{-}Quin}$), 7.5-7.3 (m, 6H, $H_{Ph\text{-}IPr}$), 6.87 (dd, $J_{H\text{-}H}$ = 8.1, 1.0, 1H, $H_{5\text{-}Quin}$), 6.69 (dd, $J_{H\text{-}H}$ = 8.0, 1.0, 1H, $H_{7\text{-}Quin}$), 2.85 and 2.84 (both sept, $J_{H\text{-}H}$ = 6.8, 4H, C<u>H</u>Me_{IPr}), 1.30, 1.23, 1.19, and 1.17 (all d, $J_{H\text{-}H}$ = 6.8, 24H, CH<u>Me</u>$_{IPr}$), -17.52 (d, 1H, $J_{Rh\text{-}H}$ = 21.1, H-Rh). ^{13}C{1H}-APT NMR (100.6 MHz, CD_3CN, 298 K): δ 171.3 (s, $C_{8\text{-}Quin}$), 169.6 (br, Rh-C_{IPr}), 148.1 and 148.0 (both s, $C_{q\text{-}IPr}$), 146.8 (s, $C_{2\text{-}Quin}$), 144.4 (s, $C_{8a\text{-}Quin}$), 138.8 (s, $C_{4\text{-}Quin}$), 138.3 (s, C_qN), 131.7, 125.5, and 125.4 (s, $CH_{Ph\text{-}IPr}$), 131.4(s, $C_{4a\text{-}Quin}$), 130.7 (s, $C_{6\text{-}Quin}$), 127.4 (s, =CHN), 125.0 (s, $C_{3\text{-}Quin}$), 115.3 (s, $C_{7\text{-}Quin}$), 112.0 (s, $C_{5\text{-}Quin}$), 29.7 and 29.6 (both s, C<u>H</u>Me_{IPr}), 26.1, 26.0, 23.5, and 23.4 (all s, CH<u>Me</u>$_{IPr}$). ^{13}P NMR (121.5 MHz, CD_3CN, 298 K): δ -144.6 (sept, $J_{P\text{-}F}$ = 706.6, PF_6)

Preparation of [RhClH(CH_3CN)$_3$(IPr)]OTf (11). A yellow suspension of **2a** (300 mg, 0.270 mmol) in CH_3CN (10 mL) at 253 K was treated with HOTf (48 µL, 0.540 mmol) and stirred at low temperature for 15 min. The resulting solution was concentrated to ca. 1 mL and then, the addition of cold diethyl ether (253 K) induced the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 315 mg (73%). Anal. Calcd. for $C_{34}H_{46}N_5F_3ClO_3SRh$: C, 51.03; H, 5.79; N, 8.75; S, 4.00. Found: C, 51.30; H, 6.04; N, 8.43; S, 4.12. ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 7.59 (t, $J_{H\text{-}H}$ = 7.8, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.46 (d, $J_{H\text{-}H}$ = 7.8, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 7.44 (s, 2H, =CHN), 2.69 and 2.68 (both sept, $J_{H\text{-}H}$ = 6.8, 4H, C<u>H</u>Me_{IPr}), 1.30, 1.29, 1.11, and 1.08 (all d, $J_{H\text{-}H}$ = 6.8, 24H, CH<u>Me</u>$_{IPr}$), -17.05 (d, $J_{Rh\text{-}H}$ = 8.4, 1H, H-Rh). ^{13}C{1H}-APT NMR (100.6 MHz, CD_3CN, 298 K): δ 161.2 (d, $J_{C\text{-}Rh}$ = 49.1, Rh-C_{IPr}), 147.2 (both s, $C_{q\text{-}IPr}$), 137.4 (s, C_qN), 131.7 (s, $C_{p\text{-}Ph\text{-}IPr}$), 127.5 (s, =CHN), 125.0 (s, $C_{m\text{-}Ph\text{-}IPr}$), 122.1 (q, $J_{C\text{-}F}$ = 321.2, CF_3), 29.5 and 29.4 (both s, C<u>H</u>Me_{IPr}), 26.2 25.9, 23.0, and 22.3 (all s, CH<u>Me</u>$_{IPr}$). ^{19}F NMR (376 MHz, CD_3CN, 298 K): δ -78.2 (s, OTf).

Preparation of [RhCl$_2$H(CH_3CN)$_2$(IPr)] (12). The complex was prepared as described for **11** starting from **2a** (300 mg, 0.270 mmol) and HCl 37% (water solution) (44 µL, 0.540 mmol). A white solid was obtained. Yield: 223 mg (64%). Anal. Calcd. for $C_{31}H_{43}N_4Cl_2Rh$: C, 57.68; H, 6.71; N, 8.68. Found: C, 58.06; H, 6.88; N, 8.61. 1H NMR (400 MHz, CD_3CN, 253 K): δ 7.52 (m, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.39 (m, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 7.26 and 7.25 (br, 2H, =CHN), 3.14 and 2.85 (both sept, $J_{H\text{-}H}$ = 6.6, 4H, C<u>H</u>Me_{IPr}), 1.27, 1.26, 1.05, and 1.02 (all d, $J_{H\text{-}H}$ = 6.6, 24H, CH<u>Me</u>$_{IPr}$), -18.63 (d, $J_{Rh\text{-}H}$ = 8.5, 1H, H-Rh). ^{13}C{1H}-APT NMR (100.6 MHz, CD_3CN, 253 K): δ 167.0 (d, $J_{C\text{-}Rh}$ = 49.9, Rh-C_{IPr}), 147.6 and 147.3 (both s, $C_{q\text{-}IPr}$), 138.1 and 137.0 (both s, C_qN), 130.4 and 129.7 (both s, $C_{p\text{-}Ph\text{-}IPr}$), 126.7 and 125.5 (both s, =CHN), 123.7 and 125.5 (both s, $C_{m\text{-}Ph\text{-}IPr}$), 28.3 and 28.2 (both s, C<u>H</u>Me_{IPr}), 25.3, 25.2, 22.4, and 22.3 (all s, CH<u>Me</u>$_{IPr}$).

Preparation of [RhH(CH_3CN)$_4$(IPr)](OTf)$_2$ (13). A yellow suspension of **2-OH** (300 mg, 0.242 mmol) in CH_3CN (10 mL) at -20°C was treated with HOTf (175 µL, 1.455 mmol) and stirred at low temperature for 15 min. The resulting pale yellow solution was concentrated to ca. 1 mL and then, the addition of cold diethyl ether (-20°C) induced the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 508 mg (91%). Anal. Calcd. for $C_{37}H_{49}N_6F_6O_6S_2Rh$: C, 46.54; H, 5.17; N, 8.80; S, 6.72 Found: C, 46.19; H, 4.98; N, 8.72; S, 6.92.^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 7.68 (t, $J_{H\text{-}H}$ = 7.5, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.52 (t, $J_{H\text{-}H}$ = 7.5, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 7.65 (s, 2H, =CHN), 2.38 (sept, $J_{H\text{-}H}$ = 6.8, 4H, C<u>H</u>Me_{IPr}), 1.32 and 1.14 (both d, $J_{H\text{-}H}$ = 6.8, 24H, CH<u>Me</u>$_{IPr}$), -15.38 (d, $J_{Rh\text{-}H}$ = 7.3, 1H, H-Rh). ^{13}C{1H}-APT NMR (100.6 MHz, CD_3CN, 298 K): δ 153.8 (d, $J_{C\text{-}Rh}$ = 46.7, Rh-C_{IPr}), 147.1 (s, C_q), 136.4 (s, C_qN), 132.7 (s, $C_{p\text{-}Ph\text{-}IPr}$), 128.9 (s, =CHN), 125.6 (s, $C_{m\text{-}Ph\text{-}IPr}$), 122.0 (q, $J_{C\text{-}F}$ = 321.0, CF_3), 29.8 (s, C<u>H</u>Me_{IPr}), 26.0 and 22.7 (both s, CH<u>Me</u>$_{IPr}$). ^{19}F NMR (376 MHz, CD_3CN, 298 K): δ -79.2 (s, OTf).

Preparation of [RhCl(CH_2CH_3)(κ^2-O,N-C_8H_6NO)(IPr)] (14). The complex was prepared as described for **5** starting from **2b** (300 mg, 0.270 mmol) and 8-hydroxyquinoline (78 mg, 0.540 mmol), and obtained as an orange solid. Yield: 325 mg (86%). Anal. Calcd. for $C_{38}H_{47}N_3ClORh$: C, 65.19; H, 6.77; N, 6.00. Found: C, 65.56; H, 6.32; N, 6.24. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ 9.17 (d, $J_{H\text{-}H}$ = 4.7, 1H, $H_{2\text{-}Quin}$), 7.31 (d, $J_{H\text{-}H}$ = 8.5, 1H, $H_{4\text{-}Quin}$), 7.29 (dd, $J_{H\text{-}H}$ = 7.9, 7.8, 1H, $H_{6\text{-}Quin}$), 7.06 (m, 6H, $H_{Ph\text{-}IPr}$), 7.13 (dd, $J_{H\text{-}H}$ = 7.8, 1.0, 1H, $H_{7\text{-}Quin}$), 6.71 (s, 2H, =CHN), 6.61 (dd, $J_{H\text{-}H}$ = 7.9, 1.0 1H, $H_{5\text{-}Quin}$), 6.39 (dd, $J_{H\text{-}H}$ = 8.5, 4.7, 1H, $H_{3\text{-}Quin}$), 3.62 and 3.09 (both ddq, $J_{H\text{-}H}$ = 7.3, 7.1, $J_{Rh\text{-}H}$ = 3.2, 2H, $CH_{2\text{-}Ethyl}$), 3.50 and 3.49 (both sept, $J_{H\text{-}H}$ = 6.6, 4H, C<u>H</u>Me_{IPr}), 1.65, 1.41, 1.15, and 1.08 (all d, $J_{H\text{-}H}$ = 6.6, 24H, CH<u>Me</u>$_{IPr}$), -0.27 (dvt, $J_{Rh\text{-}H}$ = 1.5, N = 14.6, 3H, $CH_{3\text{-}Ethyl}$). ^{13}C{1H}-APT NMR (100.6 MHz, C_6D_6, 298 K): δ 174.5 (d, $J_{C\text{-}Rh}$ = 51.8, Rh-C_{IPr}), 171.5 (s, $C_{8\text{-}Quin}$), 147.8 and 147.5 (both s, $C_{q\text{-}IPr}$), 146.6 (s, $C_{2\text{-}Quin}$), 145.2 (s, $C_{8a\text{-}Quin}$), 137.1 (s, $C_{4\text{-}Quin}$), 136.2 (s, C_qN), 131.0 (s, $C_{4a\text{-}Quin}$), 130.9, 124.5, and 124.2 (all s, $CH_{Ph\text{-}IPr}$), 129.9 (s, $C_{6\text{-}Quin}$), 125.7 (s, =CHN), 120.1 (s, $C_{3\text{-}Quin}$), 115.1 (s, $C_{7\text{-}Quin}$), 110.8 (s, $C_{5\text{-}Quin}$), 29.5 and 29.4 (both s, C<u>H</u>Me_{IPr}), 27.1, 26.8, 23.6, and 23.5 (all s, CH<u>Me</u>$_{IPr}$), 21.0 (d, $J_{Rh\text{-}C}$ = 28.4, $CH_{2\text{-}Ethyl}$), 20.6 (s, $CH_{3\text{-}Ethyl}$).

Preparation of [RhCl(CH_2CH_3)(κ^2-O,N-C_8H_6NO)(IPr)(CH_3CN)] (15). An orange solution of **14** (100 mg, 0.143 mmol) in a 1:1 toluene/CH_3CN mixture (5 mL) was stirred at room temperature for 30 minutes. The solvent was evaporated to dryness and subsequent addition of hexane induced the precipitation of an orange solid which was washed with hexane (3 x 2 mL) and dried in vacuo. Yield: 84 mg (80%). Anal. Calcd. for $C_{40}H_{50}N_4ClORh$: C, 64.33; H, 6.45; N, 7.25. Found: C, 64.82; H, 6.80; N, 7.56. ^{1}H NMR (400 MHz, C_6D_6/CD_3CN 4:1, 298 K): δ 9.08 (d, $J_{H\text{-}H}$ = 4.2, 1H, $H_{2\text{-}Quin}$), 7.76 (d, $J_{H\text{-}H}$ = 8.1, 1H, $H_{4\text{-}Quin}$), 7.32 (s, 2H, =CHN), 7.30 (dd, $J_{H\text{-}H}$ = 7.9, 7.8, 1H, $H_{6\text{-}Quin}$), 7.2-7.1 (m, 6H, $H_{Ph\text{-}IPr}$), 7.04 (d, $J_{H\text{-}H}$ = 7.9, 1H, $H_{7\text{-}Quin}$), 6.90 (dd, $J_{H\text{-}H}$ = 8.1, 4.2, 1H, $H_{3\text{-}Quin}$), 6.78 (d, $J_{H\text{-}H}$ = 7.8, 1H, $H_{5\text{-}Quin}$), 3.35 and 2.98 (both m, 2H, $CH_{2\text{-}Ethyl}$) 3.44 (br, 4H, C<u>H</u>Me_{IPr}), 1.60, 1.34, 1.24, and 1.16 (all d, $J_{H\text{-}H}$ = 6.5, 24H, CH<u>Me</u>$_{IPr}$), 1.43 (s, CH_3CN), -0.44 (dvt, $J_{Rh\text{-}H}$ = 1.5, N = 14.0, 3H, $CH_{3\text{-}Ethyl}$). ^{13}C{1H}-APT NMR (100.6 MHz, C_6D_6/CD_3CN 4:1, 298 K): δ 172.4 (d, $J_{C\text{-}Rh}$ = 50.2, Rh-C_{IPr}), 170.9 (s, $C_{8\text{-}Quin}$), 147.5 and

147.1 (both s, $C_{q\text{-}IPr}$), 145.9 (s, $C_{2\text{-}Quin}$), 144.6 (s, $C_{8a\text{-}Quin}$), 137.1 (s, $C_{4\text{-}Quin}$), 135.8 (s, C_qN), 130.6 (s, $C_{4a\text{-}Quin}$), 130.5, 124.1, and 123.7 (all s, $CH_{Ph\text{-}IPr}$), 129.6 (s, $C_{6\text{-}Quin}$), 126.0 (s, =CHN), 121.0 (s, $C_{3\text{-}Quin}$), 116.9 (s, CH_3CN), 114.7 (s, C_7-Quin), 110.4 (s, C_5-Quin), 29.1 and 29.1 (both s, $\underline{C}HMe_{IPr}$), 26.4, 26.1, 23.0, and 22.9 (all s, $CH\underline{Me}_{IPr}$), 20.0 (d, $J_{Rh\text{-}C}$ = 28.5, $CH_{2\text{-}Ethyl}$), 19.9 (s, $CH_{3\text{-}Ethyl}$), 0.28 (s, CH_3CN).

Preparation of $[Rh(C_2H_5)(CH_3CN)_3(IPr)](OTf)_2$(16). A yellow suspension of **3** (300 mg, 0.270 mmol) in CH_3CN (10 mL) at -20°C was treated with trifluoromethansulfonic acid (96 μL, 1.080 mmol) and stirred at low temperature for 15 min. The resulting pale yellow solution was concentrated to ca. 1 mL and then, the addition of cold diethyl ether (-20°C) induced the precipitation of a white solid which was washed with diethyl ether (3 x 4 mL) and dried in vacuo. Yield: 417 mg (79%). Anal. Calcd. for $C_{39}H_{53}N_6F_6O_6S_2Rh$: C, 47.66; H, 5.44; N, 8.55; S, 6.52. Found: C, 47.99; H, 5.51; N, 8.60; S, 6.75. ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ 7.56 (t, $J_{H\text{-}H}$ = 7.7, 2H, $H_{p\text{-}Ph\text{-}IPr}$), 7.46 (t, $J_{H\text{-}H}$ = 7.7, 4H, $H_{m\text{-}Ph\text{-}IPr}$), 7.33 (s, 2H, =CHN), 2.76 (dq, $J_{Rh\text{-}H}$ = 2.2, $J_{H\text{-}H}$ = 7.4, 2H, $CH_{2\text{-}Ethyl}$), 2.67 (sept, $J_{H\text{-}H}$ = 6.8, 4H, $C\underline{H}Me_{IPr}$), 1.40 and 1.13 (both d, $J_{H\text{-}H}$ = 6.5, 24H, $CH\underline{Me}_{IPr}$), 0.95 (t, $J_{H\text{-}H}$ = 7.4, 3H, $CH_{3\text{-}Ethyl}$). ^{13}C{1H}-APT NMR (100.6 MHz, CD_3CN, 298 K): δ 150.3 (d, $J_{C\text{-}Rh}$ = 52.2, Rh-C_{IPr}),147.2 (both s, $C_{q\text{-}IPr}$), 137.3 (s, C_qN), 133.1 (s, $C_{p\text{-}Ph\text{-}IPr}$), 129.0 (s, =CHN), 125.6 (s, $C_{m\text{-}Ph\text{-}IPr}$), 122.1 (q, $J_{C\text{-}F}$ = 321.2, CF_3), 29.9 (s, CH_{MeIPr}), 26.0 and 23.0 (both s, CH_{MeIPr}), 19.8 (s, $CH_{3\text{-}Ethyl}$), 18.4 (d, $J_{Rh\text{-}C}$ = 17.6, $CH_{2\text{-}Ethyl}$). ^{19}F NMR (376 MHz, CD_3CN, 298 K): δ -78.2 (s, OTf).

Crystal structure determination for complexes 4 and 16: X-ray diffraction data were collected at 100(2) K on a Bruker SMART APEX CCD (complex **16**) and on a Bruker APEX II (complex **4**) area detector diffractometers with graphite monochromated $Mo_{K\alpha}$ radiation (λ=0.71073 Å) by using narrow ω rotations (0.3º). Intensities were integrated and corrected for absorption effects with SMART,[28] SAINT+,[29] and SABABS[30] programs, included in APEX 2 package. The structures were solved by direct methods with SHELXS-97,[31] and refined by full-matrix least squares on F^2 with SHELXL-97.[32] Hydrogen atoms for both structures were included in calculated positions and refined with positional and displacement riding parameters. Particular details concerning the presence of solvent or static disorder are listed below.

Crystal data for complex 4: $C_{36}H_{43}ClN_3ORh \cdot C_7H_8$; M = 764.23; orange prism; 0.167 × 0.136 × 0.130 mm^3; monoclinic; $P2_1/n$; a = 13.1379(10), b = 13.8002(11), c = 20.7115(16)Å; β = 94.5440(10)º; Z = 4; V = 3743.3(5) Å^3; ρ_{calcd} = 1.356 gcm^{-3}; μ = 0.565 mm^{-1}, min. and max. transmission factors: 0.912 and 0.930; $2\theta_{max}$ = 61.26; 26635 reflections collected, 9828 unique [R_{int} = 0.0501]; number of data/restraints/parameters: 9828/1/455; final GoF: 0.984, R_1 = 0.0395 [6576 reflections, $I>2\sigma(I)$], ω$R2$ = 0.0906 for all data; largest difference peak: 0.611 eÅ^3. A solvent toluene molecule has been included in the crystal structure.

Crystal data for complex 16: $C_{39}H_{53}F_6N_6O_6RhS_2 \cdot CH_2Cl_2$; M = 1067.83; colourless block; 0.162 × 0.070 × 0.057 mm^3; triclinic; P-1; a = 12.134(7), b = 12.587(7), c = 16.471(9)Å; α = 87.112(10), β = 78.900(9), γ= 83.677(10)º; Z = 2; V = 2452(2)Å^3; ρ_{calcd} = 1.446 gcm^{-3}; μ = 0.614 mm^{-1}, min. and max. transmission factors: 0.907 and 0.956; $2\theta_{max}$ = 50.00; 24575 reflections collected, 8587 unique [R_{int} = 0.1047]; number of data/restraints/parameters: 8587/0/577; final GoF: 1.074, R_1 = 0.0851 [5841 reflections, $I>2\sigma(I)$], ω$R2$ = 0.1863 for all data; largest difference peak: 1.162 eÅ^3. Fluorine atoms of the triflate anions showed high thermal parameters; static disorder was included for one of the anions. A solvent dichloromethane molecule was also observed in the crystal structure; both chlorine atoms were also included in a disordered model with complementary occupancy factors (0.674/0.326(19). All the relevant highest residual density peaks have found close to the metal atom, with no chemical sense.
CCDC-989941 (4) and CCDC-989942 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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