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Carbene Catalysis

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 María Pilar García Clemente

Abstract: A series of neutral and cationic Rh^{III}-hydride and Rh^{III}-ethyl complexes bearing a NHC ligand has been synthesized and evaluated as catalyst precursors for H/D exchange of styrene using CD_3OD as a deuterium source. Various ligands have been examined in order to understand how the stereoelectronic properties can modulate the catalytic activity. Most of these complexes proved to be very active and selective in the vinylic H/D exchange, without deuteration at the aromatic positions, displaying very high selectivity toward the β-positions. In particular, the cationic complex $[RhClH(CH_3CN)_3(IPr)]CF_3SO_3$ showed excellent catalytic activity, reaching the maximum attainable degree of β-vinylic deuteration in only 20 min. By modulation of the catalyst structure, we obtained improved α/β selectivity. Thus, the catalyst [RhClH(κ²-O,N-C_9H_6NO)(SIPr)], bearing an 8-quinolinolate ligand and a bulky and strongly electron-donating SIPr as the NHC, showed total selectivity for the β-vinylic positions. This systematic study has shown that increased electron density and steric demand at the metal center can improve both the catalytic activity and selectivity. Complexes bearing ligands with very high steric hindrance, however, proved to be inactive.

Introduction

Deuterium-labeled compounds are nowadays used as essential tools in a wide range of fields, whether it be for fundamental research or practical applications, 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] 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, 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 and challenging task.[2b] Transition-metal-based homogeneous and heterogeneous catalytic systems allow H/D exchange reactions to be performed under mild conditions, preventing substrate decomposition, with high tolerance toward the main functional groups. Moreover, such catalytic systems open the way for greater choice of the deuterium source, such as D_2, D_2O, or organic deuterated solvents, according to the most compatible conditions for the substrate.

Since the pioneering works of Garnett[4] and Shilov[5] in the 1960s, a plethora of transition-metal-based homogeneous catalytic systems for H/D exchange have been developed, including those based on 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 these organometallic catalysts is shown by their ability to deuterate different C–H groups of aliphatic,[2b,6k,m,7b,f,10b,e,i] aromatic,[2b,4a,6k,m,o,s–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 transformations mediated by transition-metal-based catalytic systems proceed according to a C–H activation mechanism (Scheme 1 a).[6,7f,g,k,8b,c,9d,10a–f,h,12,13] The selectivity of the reaction depends on the activation energies of the relevant C–H moieties, which are related to their dissociation energies. Thus, the

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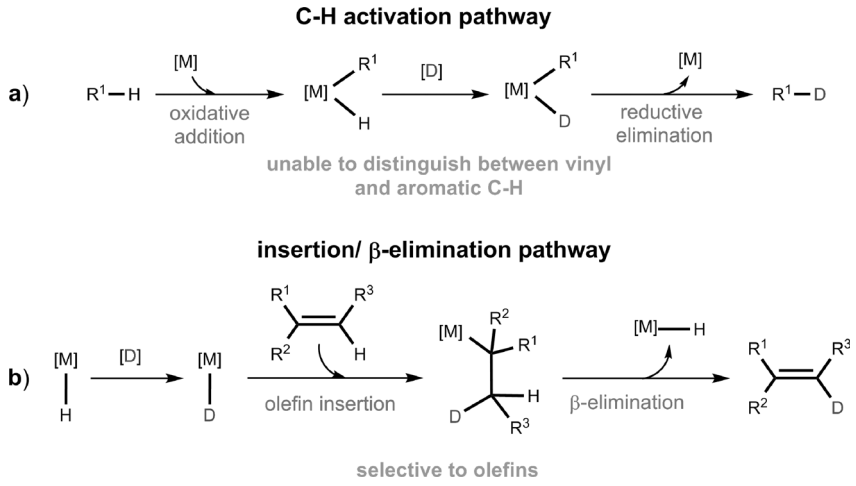


Scheme 1. Possible mechanism for H/D exchange reaction of olefins: C–H activation (top) and insertion/β-elimination pathway (bottom).

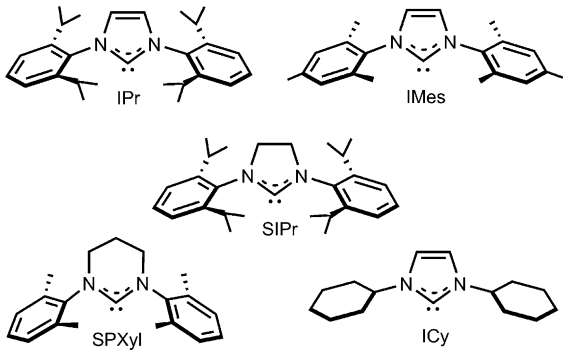
observed reactivity order is generally: C_{sp}–H > C_{sp2}–H > C_{sp3}–H. In particular, in the case of substrates with both aromatic and olefinic groups, for which the C–H bond dissociation energies are comparable, selective activation of the vinylic protons is problematic.[6m,14] An efficient strategy for selective deuterium-labeling of alkenes is to use a metal hydride species that gives rise to an alternative insertion–elimination mechanism, which is not operative for aromatic protons (Scheme 1 b).[4d,6g,7a,e,i,j,11] In addition, a high oxidation state of the metal center may reduce the competitive olefin C–H activation pathway and thereby prevent hydrogenation of the double bond of the target olefin. Moreover, a bulky and strongly electron-donating ancillary ligand should provide additional stability to the hydride-metal species in a high oxidation state, while exerting a significant steric effect in the vicinity of the coordination site, which may dramatically influence the selectivity of the reaction. With this in mind, we envisaged Rh^{III} complexes[7d,i] bearing a N-heterocyclic carbene ligand (NHC)[15] as potential catalysts for facilitating 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 a systematic study of their catalytic activities in the 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]

Results and Discussion

Synthesis of neutral hydride-Rh^{III}-NHC complexes bearing an 8-quinolinolate ligand

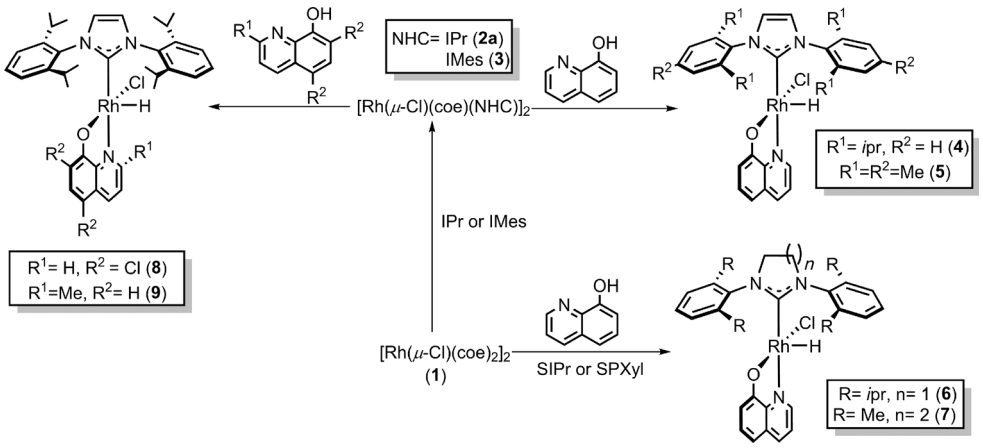
Dinuclear complexes of the type $[Rh(\mu\text{-Cl})(NHC)(\eta^2\text{-olefin})]_2$ are excellent starting materials since they are easy to prepare and very reactive.[16] With the aim of studying the effect of the NHC ligand on the catalytic activity, we prepared several catalytic precursors bearing a range of NHC ligands having different steric demands and electron-donating abilities:[17] 1,3-bis(2,6-diisopropylphenyl)imidazol-2-carbene (IPr), 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-carbene (SIPr), 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-carbene (IMes), 1,3-dicyclohexylimidazol-2-carbene (ICy), and 1,3-bis(2,6-dimethylphenyl)tetrahydropyrimidin-2-carbene (SPXyl), the syntheses of which have been reported in the literature (Scheme 2).[18]

The dinuclear $[Rh(\mu\text{-Cl})(NHC)(\eta^2\text{-coe})]_2$ complexes (coe = cyclooctene) were synthesized as described by James and coworkers.[16b] Thus, reactions of $[Rh(\mu\text{-Cl})(\eta^2\text{-coe})_2]_2$ (**1**) with the



Scheme 2. NHC ligands used in this work.

corresponding free NHC ligands gave the dinuclear complexes $[Rh(\mu\text{-Cl})(IPr)(\eta^2\text{-coe})]_2$ (**2a**) and $[Rh(\mu\text{-Cl})(IMes)(\eta^2\text{-coe})]_2$ (**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 $[RhClH(\kappa^2\text{-O,N-}C_9H_6NO)(NHC)]$ (**4**, IPr; **5**, IMes; Scheme 3). Complexes **4** and **5** were isolated as orange solids in yields of 76[7j] and 79%, respectively. The related mononuclear hydride/8-quinolinolate derivatives bearing carbenes SIPr and SPXyl were synthesized according to a one-pot procedure (Scheme 3). Thus, mixtures of $[Rh(\mu\text{-Cl})(coe)_2]_2$, 8-hydroxyquinoline, and NHC (SIPr or SPXyl) were stirred at room temperature in THF for 2 h to give orange solutions of the complexes $[RhClH(\kappa^2\text{-O,N-}C_9H_6NO)(SIPr)]$ (**6**) and $[RhClH(\kappa^2\text{-O,N-}C_9H_6NO)(SPXyl)]$ (**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 from the reaction mixture revealed the formation of the coordination ion pair $[Rh(\kappa^2\text{-O,N-}C_9H_6NO)(ICy)_3]$-$[RhCl_2(\kappa^2\text{-O,N-}C_9H_6NO)_2]_2$. The formation of this species with three ICy ligands is most probably 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

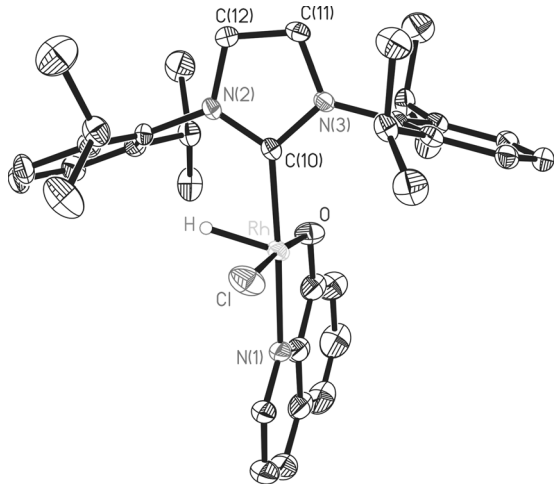


Figure 1. Molecular diagram of **4**. Selected bond lengths [Å] and angles [°]: Rh–Cl 2.2993(7), Rh–O 1.9965(19), Rh–N(1) 2.062(2), Rh–C(10) 1.951(2), Rh–H 1.43(4); Cl-Rh-O 174.70(5), Cl-Rh-C(10) 91.24(7), Cl-Rh-N(1) 95.53(7), Cl-Rh-H 78(2), O-Rh-N(1) 81.45(9), O-Rh-C(10) 92.13(8), O-Rh-H 107(2), N(1)-Rh-C(10)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

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 square base 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 an Rh–C single bond.[15c]

NMR analysis of complexes **5**–**7** showed a pattern of resonances comparable to that of complex **4** (for a summary of the key characteristic NMR data of complexes **4**–**16**, see Table S2 in the Supporting Information). The most noticeable signal in the ^{1}H NMR spectra of complexes **5**, **6**, and **7** at 298 K is a shielded doublet between $\delta = -27.9$ and -28.6 ppm ($J_{Rh,H} = 44$–47 Hz), corresponding to the hydride ligand. Such a high-field-shifted signal with a large Rh-H coupling constant has also been observed in related rhodium hydride complexes, and is a diagnostic of a vacant site *trans* to the hydride ligand.[7j,19] Interestingly, complex **5** showed only one signal for the two imidazole protons of IMes at $\delta = 6.39$ ppm, which, in addition to just three signals at $\delta = 2.47$, 2.44, and 1.90 ppm for the eighteen methyl protons, indicates rapid rotation of the carbene ligand about the Rh–C axis at room temperature. A similar NMR pattern was observed for **6**, compatible with rapid rotation of the SIPr ligand about 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 ($\delta = 2.64$, 2.62, 2.56, and 2.55 ppm). This is in accordance with a reduction in the C(carbene)-N-C(phenyl) angle in the six-membered tetrahydropyrimidine-type carbene, which causes the phenyl substituents to approach the metal center, thereby hampering 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 $\delta = 177.5$ ppm for complex **5**, bearing a carbene with an unsaturated imidazole skeleton, whereas it is shifted to 200.9 and 208.2 ppm for complexes **7** and **6**, respectively, which implies that these saturated carbenes are better electron-donor ligands than the unsaturated carbenes.[20]

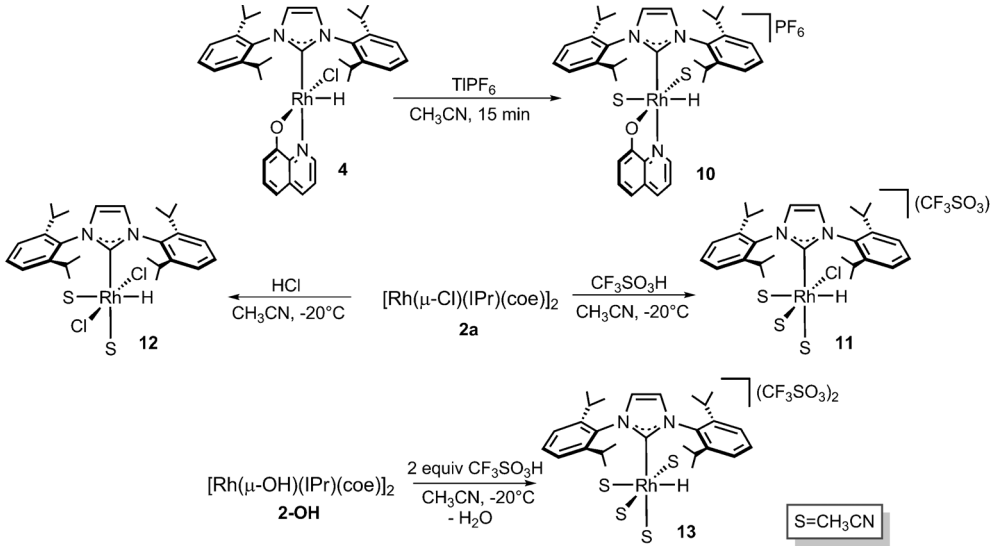
To obtain more information about the influence of the 8-quinolinolate ligand on the catalytic activity, complexes containing an electron-poor analogue, 5,7-dichloro-8-quinolinolate, or the bulkier ligand 2-methyl-8-quinolinolate were prepared. A synthetic route similar to that for **4** was followed for 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, 2-methyl-8-quinolinol and **2a** did not react at room temperature, probably because the methyl group adjacent to the nitrogen atom hinders coordination to the metal. Thus, the reaction was carried out at 80 °C for 2 h 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 their proposed structures. In both cases, the high-field-shifted hydride resonance observed in the ^{1}H NMR spectrum at $\delta = -27.81$ ppm for **8** and at -28.43 ppm for **9** and the large $J_{Rh,H}$ are consistent with those of related unsaturated square-pyramidal complexes described previously. 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

signal of the quaternary carbon atom directly bound to the oxygen atom, which is shifted from $\delta = 170.9$ ppm in **4** to $\delta =$ 164.9 ppm in **8**. In the case of complex **9**, no interaction between the methyl group of the 2-methyl-8-quinolinolate ligand and rhodium is observed.

Synthesis of cationic complexes containing the hydride-Rh-IPr skeleton

Related cationic complexes containing the [RhH(IPr)] moiety were synthesized in order to compare their catalytic properties with those of the neutral complexes **4**–**9**. The 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 that of [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 $\delta = -17.52$ ppm ($J_{Rh,H} = 21.1$ Hz) and a downfield-shifted signal at $\delta = 7.54$ ppm corresponding to the imidazole ring protons. These spectroscopic features provide strongly evidence 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 $^{13}C\{^1H\}$ NMR spectrum displays a broad signal at $\delta = 169.6$ ppm corresponding to the carbene carbon atom. This value is upfield-shifted compared to those of complexes **4** and **4-CH_3CN** ($\delta = 179.0$ and 175.2 ppm, respectively), probably due to the positive charge on the cationic complex **10**.

In order to assess the influence of the 8-quinolinolate ligands on the catalytic activity of complexes of this type, related hydride-Rh^{III}-NHC systems in which the bidentate ligand is replaced by weakly bonded ligands such as acetonitrile were prepared. We synthesized complexes with different numbers of chlorido ligands to obtain compounds with different charges (dicationic, monocationic, and neutral) to better compare this new family of complexes with those described previously. In this case, a different source of hydride to 8-quinolinol was used. One of the simplest species for hydride generation is a strong acid.[7a] We selected two different acids to synthesize complexes with different charges: triflic acid (CF_3SO_3H) and hydrochloric acid. The former was 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 complex [$RhCl_2$H-($CH_3CN)_2$(IPr)] (**12**) by using HCl(aq) (Scheme 4). Attempted 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 equivalents of CF_3SO_3H to a solution of the chlorido-free dimer [Rh(μ-OH)-(IPr)(η^2-coe)]$_2$ (**2-OH**), recently prepared in our laboratories,[21] in acetonitrile at $-20\,^\circ$C, led 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** show the typical pattern for a saturated Rh^{III} complex with an octahedral geometry. In particular, the signal of the hydride ligand appears between $\delta = -15.4$ 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 $\delta = 7.44$ and 7.65 ppm. In the case of **12**, the =CH imidazole protons and the carbon atoms of the IPr ligand are seen to be inequivalent, giving rise to two resonances in both the ^{1}H NMR ($\delta = 7.26$ and 7.25 ppm) and $^{13}C\{^1H\}$ NMR spectra ($\delta = 126.7$ and 125.5 ppm). This spectroscopic evidence points to a "frozen" structure possessing a mirror plane that contains the imidazole plane, with a *trans* disposition of the two chlorido ligands, and rules out a dinuclear structure (Scheme 4). Similarly to the behavior observed for **10**, all acetonitrile ligands exchange with the CD_3CN solvent. The charges of the complexes seem to strongly influence the chemical shifts of the IPr resonances, especially those of the carbene carbon atoms. Specifically, increasing charge gives rise to a progressive shielding of this resonance: $\delta =$ 167.0 ppm for the neutral complex **12**, 161.2 ppm for the cationic species **11**, and 153.8 ppm for the dicationic **13**. The



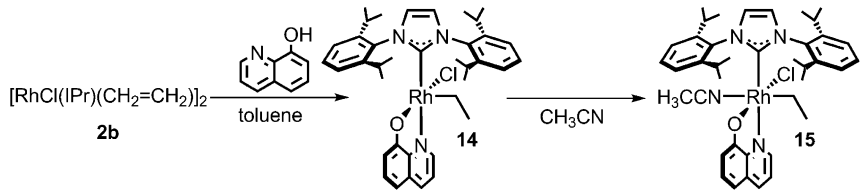
Scheme 4. Synthesis of complexes [RhH(κ^2-O,N-C_9H_6NO)(IPr)($CH_3CN)_2$]PF_6 (**10**), [RhClH($CH_3CN)_3$(IPr)]CF_3SO_3 (**11**), [$RhCl_2$H($CH_3CN)_2$(IPr)] (**12**), and [RhClH($CH_3CN)_4$(IPr)]($CF_3SO_3)_2$ (**13**).

latter proved to be the lowest chemical shift among all of the prepared complexes of the 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 our quest to find an alternative starting complex for the synthesis of Rh^{III} derivatives, we studied the reactivity of the ethylene dimer **2b**. Interestingly, treatment of **2b** with 8-hydroxyquinoline or CF_3SO_3H resulted in the formation of Rh-ethyl compounds as a consequence of insertion of the coordinated ethylene into the Rh–H bond of the 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 described Rh–H complexes, probably because of the large size of this olefin.

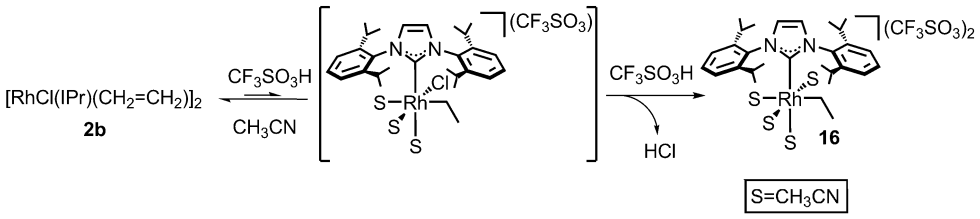
Reaction of [Rh(μ-Cl)(IPr)(η^2-CH_2=CH_2)]$_2$ (**2b**) with 8-hydroxyquinoline in toluene gave an orange solution of the unsaturated complex [RhCl(CH_2CH_3)(κ^2-O,N-C_9H_6NO)(IPr)] (**14**), which was isolated as an orange solid in 86% yield. Similarly to what was observed for complex **4**, coordination of an acetonitrile molecule at the vacant site resulted in the formation of an 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 $\delta = 6.71$ ppm. As already stated, this upfield-shifted signal is indicative of a pentacoordinated structure. This consideration, together with the strong *trans* influence of the ethyl group, leads us to propose a square-pyramidal geometry for complex **14**, with the ethyl group in the apical position. As expected, the methylene protons of the ethyl ligand are diastereotopic, thus showing two doublet of doublet quadruplets with $J_{Rh,H} = 3.2$ Hz. In the $^{13}C\{^1H\}$ NMR spectrum, the signal of the carbene carbon atom appears as a doublet at $\delta =$ 174.5 ppm with $J_{Rh,C} = 51.8$ Hz, similar to the value observed for complex **4**. The ethyl ligand gives rise to a doublet at $\delta =$ 21.0 ppm with $J_{Rh,C} = 28.4$ Hz (> CH_2) and a singlet at 20.6 ppm (CH_3). The saturated complex **15** does not show remarkable differences in its NMR spectra compared to the unsaturated analogue **14**, apart from a deshielding of the proton signal of the imidazole at $\delta = 7.32$ ppm, which is diagnostic of an octahedral saturated Rh^{III}-IPr complex. It is important to remark that, even in this case, the coordination of CH_3CN does not prevent free rotation of the carbene about the Rh–C bond at room temperature. In addition, coordination of an acetonitrile ligand *trans* to the ethyl ligand does not significantly influence the chemical shift of the > CH_2 resonance in the $^{13}C\{^1H\}$ NMR spectrum ($\delta = 20.0$ 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)]$^+$ in analogy to **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 equivalent 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 did not result in 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**.

Single crystals of **16** suitable for X-ray analysis were obtained by slow diffusion of diethyl ether layered on a saturated solution of **16** in CH_2Cl_2. The complex shows a slightly distorted octahedral geometry around the metal center, with the IPr and ethyl ligands in a mutually *cis* disposition (Figure 2). The Rh-C(11) distance of 2.026(7) Å is typical of an Rh–C single bond.[15c] A similar distance is 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 similar distances to the Rh center, Rh–N(1) 1.994(7) Å and Rh–N(3) 1.998(6) Å. However, the acetonitrile ligand *trans* to the ethyl ligand

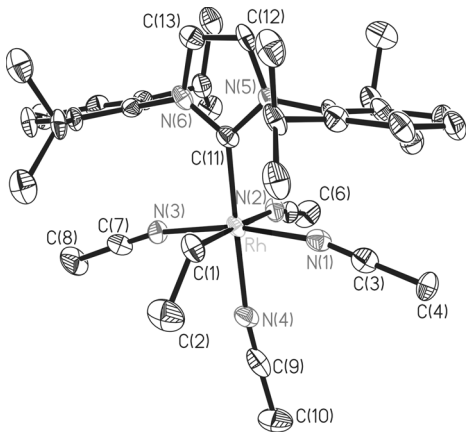


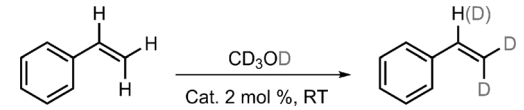
Figure 2. Molecular diagram of the cation of **16**. Selected bond lengths [Å] and angles [°]: Rh–C(1) 2.065(7), Rh–N(1) 1.994(7), Rh–N(2) 2.197(7), Rh–N(3) 1.998(6), Rh–N(4) 2.092(7), Rh–C(11) 2.026(7); C(1)-Rh-N(1) 88.7(3), C(1)-Rh-N(2) 177.1(3), C(1)-Rh-N(3) 90.1(3), C(1)-Rh-N(4) 93.7(3), C(1)-Rh-C(11) 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).

shows 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 ligand *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°, with 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)°. This deviation most probably results from the high steric demand of the carbene ligand in combination with the weakness of the rhodium–acetonitrile bonds. In fact, the acetonitrile ligand disposed *trans* to the IPr ligand is also deformed, but only by 8° (Rh-N(4)-C(9) 172.0(7)°).

The ^{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 the carbene, leads to only one ^{1}H NMR signal for the four isopropyl protons and two signals for the eight methyl groups. As expected for a saturated hydride-Rh^{III}-NHC complex, the signal of the imidazole protons appears downfield-shifted ($\delta = 7.46$ ppm) with respect to the analogous unsaturated complex. The $>CH_2$ protons of the ethyl ligands give rise to a single resonance at $\delta =$ 2.76 ppm, which is in agreement with the C_s symmetry of the complex. Only one signal corresponding to free acetonitrile is observed due to fast exchange with the CD_3CN solvent. The $^{13}C\{^{1}H\}$ NMR spectrum displays a doublet at $\delta = 150.3$ ppm, with $J_{Rh,C} = 52.2$ Hz, corresponding to the carbene carbon atom, which is the most shielded of such centers within all of the complexes described in this work, probably due to the dicationic nature of the complex. The signal of the methylene carbon atom bonded to rhodium appears at $\delta = 18.4$ ppm, similarly to those of **14** and **15**, but the $J_{Rh,C}$ of 17.6 Hz is significantly lower.

Catalytic activity studies

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



Scheme 7. Selective H/D exchange reaction.

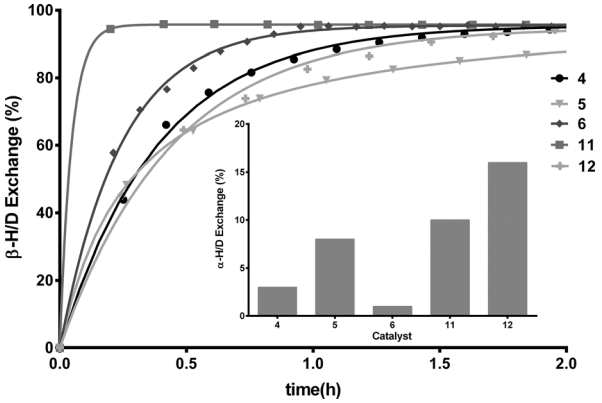


Figure 3. H/D exchange in styrene catalyzed by **4**, **5**, **6**, **11**, and **12**.

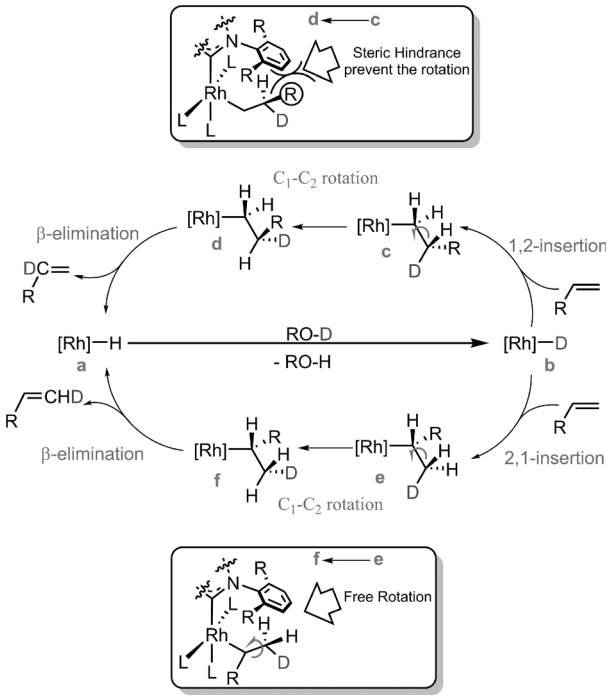
Table 1. Styrene H/D exchange promoted by different catalysts.[a]

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

The catalytic performances of the complexes varied greatly, with modification of the ancillary ligands having the expected dramatic effect thereon. In particular, the results obtained for **6** and **11** stand out among all of the reported data. The cationic acetonitrile-solvated Rh hydride complex $[RhClH(CH_3CN)_3(IPr)]^+$ (**11**) displayed excellent activity in the deuteration of the β-vinyl positions of styrene ($TOF_{1/2}=3110\ h^{-1}$), giving 92% deuterium incorporation in less than 20 min (entry 8). This complex proved to be the most active catalyst among all of those synthesized, giving a tenfold faster reaction rate than the previously reported complex $[RhClH(\kappa^2\text{-}O,N\text{-}C_9H_6NO)(IPr)]$ (**4**) (entry 1). In addition, it is worthy of note that the value of 92% β-deuteration attained with **11** is very close to the maximum theoretical level of β-deuteration attainable under the reaction conditions (92.5%), thus representing a deuteration efficiency of >99%.[23] However, this exceptional increase in catalytic activity was accompanied by a loss of selectivity, as 10% deuteration at the α-vinyl position was also observed. Although the activity of a catalyst is highly important, for practical applications the selectivity is fundamental. In this respect, complex $[RhClH(\kappa^2\text{-}O,N\text{-}C_9H_6NO)(SIPr)]$ (**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 ($TOF_{1/2}=306\ h^{-1}$), outstandingly high selectivity in the deuteration at the β-vinyl positions (also in this case >99% of the maximum theoretical β-deuteration) was achieved, with deuterium incorporation at the α-vinyl position only at trace levels. As regards the other synthesized complexes, good results in terms of catalytic performance were obtained for **5**, **8**, **12**, **14**, and **15** (entries 2, 5, 9, 11, and 12, respectively), with $TOF_{1/2}$ values between 90 and 179 h^{-1}, and good selectivity towards deuteration at the β-vinyl positions of the 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, and 13, respectively).

In order to analyze these results in more detail, taking into account the different natures of the catalyst precursors, it was deemed 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 an Rh^{III}-D species (**b**) (Scheme 8).[24] Then, after coordination of the olefin to complex **b** to give an intermediate species with the ligands in a *cis* disposition,[25] the orientation of the η^2-coordinated olefin determines the insertion pathway. A 1,2-insertion into the Rh–D bond gives rise to the linear product **c**, whereas a 2,1-insertion provides the branched product **e**. At this point, rotation about the C_1-C_2 alkyl axis is essential for effective H/D exchange (**c**→**d**; **e**→**f**).[26] Subsequent β-H elimination from **d** leads to α-deuteration, whereas that from **f** yields the β-deuterated olefin. The critical step determining the selectivity is thus the rotation about the C_1-C_2 alkyl axis. In the case of **c**, the steric hindrance imposed by the ligands in the complex restricts this rotation (and the formation of **d**) due to repulsion between the R group of the alkyl ligand and the substituents of the NHC. As a result, although a deuterium atom



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

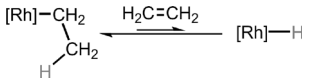
can enter the benzyl position, the hydrogen atom cannot easily leave. On the contrary, in the case of complex **e**, the terminal methyl group can easily rotate to form complex **f**, from which the β-deuterated olefin is obtained after β-H elimination.

The NHC ligand has a strong influence on the catalytic performance. Substituting IPr by IMes in complex **5** (entry 2) leads to decreases in both activity and selectivity. This is probably due to the lower electron-donating ability and bulkiness of IMes with respect to IPr.[15b,20] Complex **6**, bearing the ligand SIPr, proved to be the most selective of the studied catalysts and the most active among those bearing the 8-quinolinolate ligand (entry 3). SIPr, the saturated analogue of IPr, is slightly more electron-donating and bulky,[15b] which may account for the observed improvement in catalytic performance. In view of the trend that an increase in steric hindrance imposed by the NHC ligand improves the selectivity, we envisaged that the introduction of a bulky tetrahydropyrimidine-based NHC ligand (SPXyl) in complex **7** could improve the catalytic outcome. Somewhat surprisingly, however, complex **7** proved to be 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 a deuterium labeling catalyst. The high steric hindrance of the SPXyl ligand most probably prevents 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. Modification of the bidentate O,N ligand led to a complex with lower electronic density (complex **8**) and to another complex with greater steric hindrance close to the metal center (com-

plex **9**). Catalyst **8** bears two chloro substituents on the quinolinolate skeleton, which decrease the electron density at the metal center and thereby reduce the catalytic activity (entry 5), yielding results comparable to those obtained with complex **5** (entry 2). The case of complex **9**, bearing a 2-methyl-8-quinolinolate ligand, is slightly different. Catalyst **9** showed no catalytic activity at room temperature, and only moderate activity and selectivity at 80 °C (entry 6). In this case, contrary to **7**, the hydride ligand in **9** was smoothly exchanged with CD_3OD. Thus, the steric hindrance imposed by the quinolinolate ligand apparently hampers olefin coordination.

The charge on each complex also influences its 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 the 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**) proved to be the most active catalyst precursor among all of those synthesized (entry 8). This result suggests that the presence of a chlorido ligand is essential for the activity of the catalyst. The role of the chlorido ligand is most probably to stabilize the key Rh^{III} catalytic species. In fact, it was observed that complex **10** decomposed rapidly under the reaction conditions, leading to an unidentified mixture of complexes incapable of catalyzing the H/D exchange of styrene. This chlorido effect can also be appreciated in the case of the complexes lacking an 8-quinolinolate ligand and bearing more labile acetonitrile ligands. The excellent catalytic activity of **11** could also be related to the presence of labile acetonitrile ligands, which facilitates the olefin coordination and insertion processes. However, this effect also leads to a loss of selectivity (10% α-deuteration). The presence of two chlorido ligands in the neutral complex [$RhCl_2$H($CH_3CN)_2$(IPr)] (**12**) resulted in a decrease in 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 insertion–elimination mechanism operative for H/D exchange in olefins requires the participation of active hydride species. On this basis, ethyl complexes **14**–**16** should be inactive. However, complex [RhCl(CH_2CH_3)(κ^2-O,N-C_9H_6NO)(IPr)] (**14**) was found to be only slightly less active than its hydride counterpart **4** (entry 11). This can be explained by assuming that such a species could be in equilibrium with a hydride-olefin species (Scheme 9).[22]



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

As expected, the catalytic performance of the acetonitrile complex **15** (entry 12) was identical to that of **14**, since dissociation of the labile acetonitrile ligand produces the same active species. Moreover, the dicationic catalyst precursor [Rh(CH_2CH_3)(IPr)($CH_3CN)_4$]($CF_3SO_3)_2$ (**16**), which does not contain a chlorido ligand, proved 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 has 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 a deuterium source. Most of these complexes proved to be very active and selective in the vinylic H/D exchange of styrene, without concomitant deuteration of the aromatic ring. Moreover, they were able to catalyze deuteration at the vinylic β-positions with very high selectivity.

It has been observed that the NHC ligand plays an important role in the catalytic activity and selectivity. In fact, among the series [RhClH(κ^2-O,N-C_9H_6NO)(NHC)], taking the IPr complex as a reference, the complex bearing the most electron-donating carbene, SIPr, proved to be the most active catalyst, showing outstanding selectivity for the β-vinylic positions, whereas the introduction of a less electron-donating and less bulky carbene such as IMes decreased the catalytic activity and selectivity. On the other hand, complexes bearing carbenes with good electron-donating properties but with large steric hindrance, such as SPXyl, did not show any catalytic activity. The remaining ligands also played an important role in determining the catalytic properties. In fact, complexes without a chlorido ligand were found to be inactive, and the introduction of an 8-quinolinolate ligand with either an electron-withdrawing substituent or a bulky group near to the Rh reduced or completely suppressed the catalytic activity, respectively. Replacement of the chelating 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 excellent catalytic activity, reaching the maximum attainable degree of β-vinylic deuteration in only 20 min. On the other hand, among the ethyl-Rh^{III}-IPr series, complex [RhCl(CH_2CH_3)(8-quinolinolate)(IPr)] also showed good catalytic activity, which can be rationalized by assuming an equilibrium with a 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, should 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, which 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 or 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). Spectral assignments were achieved by a 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 with a Perkin–Elmer 2400 CHNS/O analyzer.

Catalytic H/D exchange

The appropriate catalyst (0.01 mmol) was dissolved in CD_3OD (0.5 mL) in an NMR tube and then the olefin (0.5 mmol) was added; the reaction course was monitored by ^{1}H NMR spectroscopy. The H/D exchange was quantified on the basis of the decrease in the integral of the olefin resonances compared to those of the internal standard hexamethyldisiloxane (2 μL, 10 μmol). Successful deuteration of the olefin was confirmed by ^{2}H NMR spectroscopy.

Preparation of [RhClH(κ^2-O,N-C_9H_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 the mixture was stirred at room temperature for 45 min. It was then concentrated to a volume of about 1 mL, whereupon *n*-hexane (3 mL) was added to induce the precipitation of an orange solid, which was washed with hexane (3×3 mL) and dried in vacuo. Yield: 252 mg (79%); elemental analysis 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, [D$_8$]toluene, 298 K): δ = 8.92 (d, $J_{H,H}$ = 4.6 Hz, 1H; $H_{2\text{-Quin}}$), 7.17 (d, $J_{H,H}$ = 8.1 Hz, 1H; $H_{4\text{-Quin}}$), 7.14 (dd, $J_{H,H}$ = 7.8, 7.7 Hz, 1H; $H_{6\text{-Quin}}$), 6.68 (br, 4H; $H_{Ph\text{-IMes}}$), 7.04 (d, $J_{H,H}$ = 7.7 Hz, 1H; $H_{7\text{-Quin}}$), 6.39 (s, 2H; =CHN), 6.48 (d, $J_{H,H}$ = 7.8 Hz, 1H; $H_{5\text{-Quin}}$), 6.29 (dd, $J_{H,H}$ = 8.1, 4.6 Hz, 1H; $H_{3\text{-Quin}}$), 2.47, 2.44, and 1.90 (all s, 18H; Me_{IMes}), −28.49 ppm (d, 1H, $J_{Rh,H}$ = 46.0 Hz; H-Rh); ^{13}C{^{1}H}-APT NMR (100.6 MHz, [D$_8$]toluene, 298 K): δ = 177.5 (d, $J_{C,Rh}$ = 49.7 Hz; 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 ppm (all s; Me_{IMes}).

Preparation of [RhClH(κ^2-O,N-C_9H_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 the mixture was stirred at room temperature for 30 min. The resulting orange solution was then concentrated to dryness, the residue was redissolved in toluene (10 mL), and the solution was filtered through a bed of Celite. The filtrate was concentrated to a volume of about 1 mL and then *n*-hexane (3 mL) was added to induce the precipitation of an orange solid, which was washed with hexane (3×3 mL) and dried in vacuo. Yield: 231 mg (73%); elemental analysis 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, $J_{H,H}$ = 4.3 Hz, 1H; $H_{2\text{-Quin}}$), 7.19 (dd, $J_{H,H}$ = 7.7, 7.4 Hz, 1H; $H_{6\text{-Quin}}$), 7.12 (d, $J_{H,H}$ = 8.1 Hz, 1H; $H_{4\text{-Quin}}$), 7.10 (m, 6H; $H_{Ph\text{-SIPr}}$), 7.07 (d, $J_{H,H}$ = 7.4 Hz, 1H; $H_{7\text{-Quin}}$), 6.50 (d, $J_{H,H}$ = 7.7 Hz, 1H; $H_{5\text{-Quin}}$), 6.24 (dd, $J_{H,H}$ = 8.1, 4.3 Hz, 1H; $H_{3\text{-Quin}}$), 3.90 and 3.87 (both sept, $J_{H,H}$ = 6.6 Hz, 4H; C*H*Me$_{SIPr}$), 3.83 (m, 4H; $CH_{2\text{-SIPr}}$), 1.64, 1.62, 1.25, and 1.22 (all d, $J_{H,H}$ = 6.6 Hz, 24H; CH*Me*$_{SIPr}$), −28.61 ppm (d, 1H, $J_{Rh,H}$ = 47.3 Hz; H-Rh); ^{13}C{^{1}H}-APT NMR (75.4 MHz, C_6D_6, 298 K): δ = 208.2 (d, $J_{C,Rh}$ = 44.7 Hz; 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 (all 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*H*Me$_{SIPr}$), 27.1, 27.0, 24.6, and 24.5 ppm (all s; CH*Me*$_{SIPr}$).

Preparation of [RhClH(κ^2-O,N-C_9H_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 was obtained as an orange solid. Yield: 327 mg (68%); elemental analysis 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, [D$_8$]toluene, 298 K): δ = 8.89 (dd, $J_{H,H}$ = 4.8, 1.3 Hz, 1H; $H_{2\text{-Quin}}$), 7.24 (dd, $J_{H,H}$ = 8.3, 1.3 Hz, 1H; $H_{4\text{-Quin}}$), 7.21 (dd, $J_{H,H}$ = 7.9, 7.8 Hz, 1H; $H_{6\text{-Quin}}$), 6.9–6.6 (m, 6H; $H_{Ph\text{-SPXyl}}$), 7.05 (dd, $J_{H,H}$ = 7.8, 1.0 Hz, 1H; $H_{7\text{-Quin}}$), 6.53 (dd, $J_{H,H}$ = 7.9, 1.0 Hz, 1H; $H_{5\text{-Quin}}$), 6.35 (dd, $J_{H,H}$ = 8.3, $J_{H,H}$ = 4.8 Hz, 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 ppm (d, 1H, $J_{Rh,H}$ = 44.4 Hz; H-Rh); ^{13}C{^{1}H}-APT NMR (100.6 MHz, [D$_8$]toluene, 298 K): δ = 200.9 (d, $J_{C,Rh}$ = 44.5 Hz; 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 ppm (all s; Me_{SPXyl}).

Preparation of [RhClH(κ^2-O,N-$C_9H_4NOCl_2$)(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 was isolated as an orange solid. Yield: 272 mg (78%); elemental analysis 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, $J_{H,H}$ = 4.4 Hz, 1H; $H_{2\text{-Quin}}$), 7.65 (s, 1H; $H_{6\text{-Quin}}$), 7.65 (d, $J_{H,H}$ = 8.1 Hz, 1H; $H_{4\text{-Quin}}$), 7.2–7.0 (m, 6H; $H_{Ph\text{-IPr}}$), 6.75 (s, 2H; =CHN), 6.18 (dd, $J_{H,H}$ = 8.1, $J_{H,H}$ = 4.4 Hz, 1H; $H_{3\text{-Quin}}$), 3.42 and 3.40 (both sept, $J_{H,H}$ = 6.8 Hz, 4H; C*H*Me$_{IPr}$), 1.58, 1.56, 1.16, and 1.15 (all d, $J_{H,H}$ = 6.8 Hz, 24H; CH*Me*$_{IPr}$), −27.81 ppm (d, 1H, $J_{Rh,H}$ = 43.6 Hz; H-Rh); ^{13}C{^{1}H}-APT NMR (75.4 MHz, C_6D_6, 298 K): δ = 176.7 (d, $J_{C,Rh}$ = 49.2 Hz; 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; C*H*Me$_{IPr}$), 26.3, 26.2, 23.6, and 23.4 ppm (all s; CH*Me*$_{IPr}$).

Preparation of [RhClH(κ^2-O,N-$C_9H_5NOCH_3$)(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 the mixture was stirred at 80 °C for 2 h. It was then concentrated to a volume of about 1 mL, whereupon *n*-hexane (3 mL) was added to induce the precipitation of an orange solid, which was washed with hexane (3×3 mL) and dried in vacuo. Yield: 229 mg (71%); elemental analysis 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, $J_{H,H}$ = 7.9, 7.8 Hz, 1H; $H_{6\text{-Quin}}$), 7.17 (d, $J_{H,H}$ = 8.4 Hz, 1H; $H_{4\text{-Quin}}$), 7.2–7.0 (m, 6H; $H_{Ph\text{-IPr}}$), 7.08 (dd, $J_{H,H}$ = 7.9, 1.0 Hz, 1H; $H_{7\text{-Quin}}$), 6.75 (s, 2H; =CHN), 6.60 (dd, $J_{H,H}$ = 7.8, 1.0 Hz, 1H; $H_{5\text{-Quin}}$), 6.15 (d, $J_{H,H}$ = 8.4 Hz, 1H; $H_{3\text{-Quin}}$), 3.57 and 3.51 (both br, 4H; C*H*Me$_{IPr}$), 2.78 (s, 1H; $CH_{3\text{-Quin}}$), 1.56, 1.54, 1.15, and 1.14 (all d, $J_{H,H}$ = 6.8 Hz, 24H; CH*Me*$_{IPr}$), −28.43 ppm (d, 1H, $J_{Rh,H}$ = 45.2 Hz; H-Rh); ^{13}C{^{1}H}-APT NMR (75.4 MHz, C_6D_6, 298 K): δ = 175.7 (d, $J_{C,Rh}$ =

51.6 Hz; 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*HMe$_{IPr}$), 27.3 (s; $CH_{3\text{-}Quin}$), 26.9, 26.8, 23.9, and 23.8 ppm (all s; CH*Me*$_{IPr}$).

Preparation of [RhH(κ²-O,N-C_9H_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 the mixture was stirred at room temperature for 15 min. The resulting suspension was then filtered through a Celite bed. The filtrate was concentrated to dryness and the residue was triturated with diethyl ether to give an orange solid, which was washed with diethyl ether (3× 2 mL) and dried in vacuo. Yield: 131 mg (68%); elemental analysis 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, $J_{H,H}$ = 4.7 Hz, 1H; $H_{2\text{-}Quin}$), 8.20 (d, $J_{H,H}$ = 8.4 Hz, 1H; $H_{4\text{-}Quin}$), 7.54 (s, 2H; =CHN), 7.36 (dd, $J_{H,H}$ = 8.4, 4.7 Hz, 1H; $H_{3\text{-}Quin}$), 7.24 (dd, $J_{H,H}$ = 8.1, 8.0 Hz, 1H; $H_{6\text{-}Quin}$), 7.5–7.3 (m, 6H; $H_{Ph\text{-}IPr}$), 6.87 (dd, $J_{H,H}$ = 8.1, 1.0 Hz, 1H; $H_{5\text{-}Quin}$), 6.69 (dd, $J_{H,H}$ = 8.0, 1.0 Hz, 1H; $H_{7\text{-}Quin}$), 2.85 and 2.84 (both sept, $J_{H,H}$ = 6.8 Hz, 4H; *C*HMe$_{IPr}$), 1.30, 1.23, 1.19, and 1.17 (all d, $J_{H,H}$ = 6.8 Hz, 24H; CH*Me*$_{IPr}$), −17.52 ppm (d, 1H, $J_{Rh,H}$ = 21.1 Hz; H-Rh); ^{13}C{^{1}H}-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*HMe$_{IPr}$), 26.1, 26.0, 23.5, and 23.4 ppm (all s; CH*Me*$_{IPr}$); ^{13}P NMR (121.5 MHz, CD_3CN, 298 K): δ = −144.6 ppm (sept, $J_{P,F}$ = 706.6 Hz; 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 the mixture was stirred at low temperature for 15 min. The resulting solution was concentrated to a volume of about 1 mL, whereupon cold (−20 °C) diethyl ether was added to induce the precipitation of a white solid, which was washed with diethyl ether (3×4 mL) and dried in vacuo. Yield: 315 mg (73%); elemental analysis 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, $J_{H,H}$ = 7.8 Hz, 2H; $H_{p\text{-}Ph\text{-}IPr}$), 7.46 (d, $J_{H,H}$ = 7.8 Hz, 4H; $H_{m\text{-}Ph\text{-}IPr}$), 7.44 (s, 2H; =CHN), 2.69 and 2.68 (both sept, $J_{H,H}$ = 6.8 Hz, 4H; *C*HMe$_{IPr}$), 1.30, 1.29, 1.11, and 1.08 (all d, $J_{H,H}$ = 6.8 Hz, 24H; CH*Me*$_{IPr}$), −17.05 ppm (d, $J_{Rh,H}$ = 8.4 Hz, 1H; H-Rh); ^{13}C{^{1}H}-APT NMR (100.6 MHz, CD_3CN, 298 K): δ = 161.2 (d, $J_{C,Rh}$ = 49.1 Hz; 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, $J_{C,F}$ = 321.2 Hz; CF_3), 29.5 and 29.4 (both s; *C*HMe$_{IPr}$), 26.2, 25.9, 23.0, and 22.3 ppm (all s; CH*Me*$_{IPr}$); ^{19}F NMR (376 MHz, CD_3CN, 298 K): δ = −78.2 ppm (s; OTf).

Preparation of [$RhCl_2H(CH_3CN)_2$(IPr)] (12)

The complex was prepared as described for **11** starting from **2a** (300 mg, 0.270 mmol) and 37% aqueous HCl (44 μL, 0.540 mmol). A white solid was obtained. Yield: 223 mg (64%); elemental analysis 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; ^{1}H 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, $J_{H,H}$ = 6.6 Hz, 4H; *C*HMe$_{IPr}$), 1.27, 1.26, 1.05, and 1.02 (all d, $J_{H,H}$ = 6.6 Hz, 24H; CH*Me*$_{IPr}$), −18.63 ppm (d, $J_{Rh,H}$ = 8.5 Hz, 1H; H-Rh); ^{13}C{^{1}H}-APT NMR (100.6 MHz, CD_3CN, 253 K): δ = 167.0 (d, $J_{C,Rh}$ = 49.9 Hz; 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*HMe$_{IPr}$), 25.3, 25.2, 22.4, and 22.3 ppm (all s; CH*Me*$_{IPr}$).

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 the mixture was stirred at low temperature for 15 min. The resulting pale-yellow solution was concentrated to a volume of about 1 mL, whereupon cold (−20 °C) diethyl ether was added to induce the precipitation of a white solid, which was washed with diethyl ether (3×4 mL) and dried in vacuo. Yield: 508 mg (91%); elemental analysis 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, $J_{H,H}$ = 7.5 Hz, 2H; $H_{p\text{-}Ph\text{-}IPr}$), 7.52 (t, $J_{H,H}$ = 7.5 Hz, 4H; $H_{m\text{-}Ph\text{-}IPr}$), 7.65 (s, 2H; =CHN), 2.38 (sept, $J_{H,H}$ = 6.8 Hz, 4H; *C*HMe$_{IPr}$), 1.32 and 1.14 (both d, $J_{H,H}$ = 6.8 Hz, 24H; CH*Me*$_{IPr}$), −15.38 ppm (d, $J_{Rh,H}$ = 7.3 Hz, 1H; H-Rh); ^{13}C{^{1}H}-APT NMR (100.6 MHz, CD_3CN, 298 K): δ = 153.8 (d, $J_{C,Rh}$ = 46.7 Hz; 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, $J_{C,F}$ = 321.0 Hz; CF_3), 29.8 (s; *C*HMe$_{IPr}$), 26.0 and 22.7 ppm (both s; CH*Me*$_{IPr}$); ^{19}F NMR (376 MHz, CD_3CN, 298 K): δ = −79.2 ppm (s; OTf).

Preparation of [RhCl(CH_2CH_3)(κ²-O,N-C_9H_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 was obtained as an orange solid. Yield: 325 mg (86%); elemental analysis 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, $J_{H,H}$ = 4.7 Hz, 1H; $H_{2\text{-}Quin}$), 7.31 (d, $J_{H,H}$ = 8.5 Hz, 1H; $H_{4\text{-}Quin}$), 7.29 (dd, $J_{H,H}$ = 7.9, 7.8 Hz, 1H; $H_{6\text{-}Quin}$), 7.06 (m, 6H; $H_{Ph\text{-}IPr}$), 7.13 (dd, $J_{H,H}$ = 7.8, 1.0 Hz, 1H; $H_{7\text{-}Quin}$), 6.71 (s, 2H; = CHN), 6.61 (dd, $J_{H,H}$ = 7.9, 1.0 Hz, 1H; $H_{5\text{-}Quin}$), 6.39 (dd, $J_{H,H}$ = 8.5, 4.7 Hz, 1H; $H_{3\text{-}Quin}$), 3.62 and 3.09 (both ddq, $J_{H,H}$ = 7.3, 7.1 Hz, $J_{Rh,H}$ = 3.2 Hz, 2H; $CH_{2\text{-}Ethyl}$), 3.50 and 3.49 (both sept, $J_{H,H}$ = 6.6 Hz, 4H; *C*HMe$_{IPr}$), 1.65, 1.41, 1.15, and 1.08 (all d, $J_{H,H}$ = 6.6 Hz, 24H; CH*Me*$_{IPr}$), −0.27 ppm (dvt, $J_{Rh,H}$ = 1.5 Hz, N = 14.6 Hz, 3H; $CH_{3\text{-}Ethyl}$); ^{13}C{^{1}H}-APT NMR (100.6 MHz, C_6D_6, 298 K): δ = 174.5 (d, $J_{C,Rh}$ = 51.8 Hz; 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*HMe$_{IPr}$), 27.1, 26.8, 23.6, and 23.5 (all s; CH*Me*$_{IPr}$), 21.0 (d, $J_{Rh,C}$ = 28.4 Hz; $CH_{2\text{-}Ethyl}$), 20.6 ppm (s; $CH_{3\text{-}Ethyl}$).

Preparation of [RhCl(CH_2CH_3)(κ²-O,N-C_9H_6NO)(IPr)(CH_3CN)] (15)

An orange solution of **14** (100 mg, 0.143 mmol) in toluene/CH_3CN (1:1, v/v; 5 mL) was stirred at room temperature for 30 min. It was then concentrated to dryness and subsequent trituration of the residue with hexane induced the precipitation of an orange solid, which was washed with hexane (3×2 mL) and dried in vacuo. Yield: 84 mg (80%); elemental analysis 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, $J_{H,H}$ = 4.2 Hz, 1H; $H_{2\text{-}Quin}$), 7.76 (d, $J_{H,H}$ = 8.1 Hz, 1H; $H_{4\text{-}Quin}$), 7.32 (s, 2H; =CHN), 7.30 (dd, $J_{H,H}$ = 7.9, 7.8 Hz, 1H; $H_{6\text{-}Quin}$), 7.2–7.1 (m, 6H; $H_{Ph\text{-}IPr}$), 7.04 (d, $J_{H,H}$ =

7.9 Hz, 1H; $H_{7\text{-Quin}}$), 6.90 (dd, $J_{H,H}=8.1$, 4.2 Hz, 1H; $H_{3\text{-Quin}}$), 6.78 (d, $J_{H,H}=7.8$ Hz, 1H; $H_{5\text{-Quin}}$), 3.35 and 2.98 (both m, 2H; $CH_{2\text{-Ethyl}}$), 3.44 (br, 4H; C*H*Me$_{IPr}$), 1.60, 1.34, 1.24, and 1.16 (all d, $J_{H,H}=6.5$ Hz, 24H; CH*Me*$_{IPr}$), 1.43 (s; CH_3CN), −0.44 ppm (dvt, $J_{Rh,H}=1.5$ Hz, $N=$ 14.0 Hz, 3H; $CH_{3\text{-Ethyl}}$); $^{13}C\{^1H\}$-APT NMR (100.6 MHz, C_6D_6/CD_3CN, 4:1, 298 K): $\delta=172.4$ (d, $J_{C,Rh}=50.2$ Hz; 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; C*H*Me$_{IPr}$), 26.4, 26.1, 23.0, and 22.9 (all s; CH*Me*$_{IPr}$), 20.0 (d, $J_{Rh,C}=28.5$ Hz; $CH_{2\text{-Ethyl}}$), 19.9 (s; $CH_{3\text{-Ethyl}}$), 0.28 ppm (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 trifluoromethanesulfonic acid (96 μL, 1.080 mmol) and the mixture was stirred at low temperature for 15 min. The resulting pale-yellow solution was concentrated to a volume of about 1 mL, whereupon cold (−20 °C) diethyl ether was added to induce the precipitation of a white solid, which was washed with diethyl ether (3×4 mL) and dried in vacuo. Yield: 417 mg (79%); elemental analysis 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; ^1H NMR (400 MHz, CD_3CN, 298 K): $\delta=7.56$ (t, $J_{H,H}=7.7$ Hz, 2H; $H_{p\text{-Ph-IPr}}$), 7.46 (t, $J_{H,H}=7.7$ Hz, 4H; $H_{m\text{-Ph-IPr}}$), 7.33 (s, 2H; =CHN), 2.76 (dq, $J_{Rh,H}=2.2$ Hz, $J_{H,H}=7.4$ Hz, 2H; $CH_{2\text{-Ethyl}}$), 2.67 (sept, $J_{H,H}=6.8$ Hz, 4H; C*H*Me$_{IPr}$), 1.40 and 1.13 (both d, $J_{H,H}=6.5$ Hz, 24H; CH*Me*$_{IPr}$), 0.95 ppm (t, $J_{H,H}=7.4$ Hz, 3H; $CH_{3\text{-Ethyl}}$); $^{13}C\{^1H\}$-APT NMR (100.6 MHz, CD_3CN, 298 K): $\delta=150.3$ (d, $J_{C,Rh}=52.2$ Hz; Rh-C_{IPr}), 147.2 (both s; $C_{q\text{-IPr}}$), 137.3 (s; C_qN), 133.1 (s; $C_{p\text{-Ph-IPr}}$), 129.0 (s; =CHN), 125.6 (s; $C_{m\text{-Ph-IPr}}$), 122.1 (q, $J_{C,F}=321.2$ Hz; 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 ppm (d, $J_{Rh,C}=17.6$ Hz; $CH_{2\text{-Ethyl}}$); ^{19}F NMR (376 MHz, CD_3CN, 298 K): $\delta=$ −78.2 ppm (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**) or a Bruker APEX II (complex **4**) area detector diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda=0.71073$ Å) and narrow ω rotations (0.3°). Intensities were integrated and corrected for absorption effects with the SMART,[28] SAINT+,[29] and SABABS[30] programs, as included in the APEX 2 package. The structures were solved by direct methods with SHELXS-97,[31] and refined by full-matrix least-squares techniques against F^2 with SHELXL-97.[32] Hydrogen atoms in both structures were included in calculated positions and refined with positional and displacement riding parameters. Particular details concerning the presence of solvent molecules or static disorder are listed below.

Crystal data for complex 4

$C_{36}H_{43}ClN_3ORh\cdot C_7H_8$; $M_r=764.23$; 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; $\beta=94.5440(10)°$; $Z=4$; $V=3743.3(5)$ Å^3; $\rho_{calcd}=1.356$ g cm^{-3}; $\mu=0.565$ mm^{-1}, min. and max. transmission factors: 0.912 and 0.930; $2\theta_{max}=61.26°$; 26635 reflections collected, 9828 unique [$R_{int}=0.0501$]; numbers of data/restraints/parameters: 9828/1/455; final GoF: 0.984, $R_1=0.0395$ [6576 reflections, $I>2\sigma(I)$], $\omega R_2=0.0906$ for all data; largest difference peak: 0.611 e Å^3. A toluene solvent molecule is included in the crystal structure.

Crystal data for complex 16

$C_{39}H_{53}F_6N_6O_6RhS_2\cdot CH_2Cl_2$; $M_r=1067.83$; colorless block; 0.162×0.070×0.057 mm^3; triclinic; $P\bar{1}$; $a=12.134(7)$, $b=12.587(7)$, $c=16.471(9)$ Å; $\alpha=87.112(10)$, $\beta=78.900(9)$, $\gamma=83.677(10)°$; $Z=2$; $V=2452(2)$ Å^3; $\rho_{calcd}=1.446$ g cm^{-3}; $\mu=0.614$ mm^{-1}, min. and max. transmission factors: 0.907 and 0.956; $2\theta_{max}=50.00°$; 24575 reflections collected, 8587 unique [$R_{int}=0.1047$]; numbers of data/restraints/parameters: 8587/0/577; final GoF: 1.074, $R_1=0.0851$ [5841 reflections, $I>2\sigma(I)$], $\omega R_2=0.1863$ for all data; largest difference peak: 1.162 e Å^3. The fluorine atoms of the triflate anions showed high thermal parameters; static disorder was included for one of these anions. A dichloromethane solvent 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 of the relevant highest residual density peaks were found close to the metal atom, with no chemical sense.

CCDC-989941 (**4**) and 989942 (**16**) 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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Keywords: alkenes · deuteration · H/D exchange · *N*-heterocyclic carbenes · rhodium

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[23] a) Assuming that only the vinyl β-protons of styrene and the OD of the CD_3OD can exchange, under the reaction conditions 13.3 mmol of H + D and 12.3 mmol of D are present. For this reason, the maximum grade of β-vinylic deuteration is 92.5% (see the Supplementary Information for further details). b) By increasing the CD_3OD/substrate ratio in the reaction medium, it is possible to increase the degree of deuteration. We confirmed this hypothesis by deuterating styrene (0.5 mmol) using **4** (0.01 mmol, 2%) and CD_3OD (3 mL). Under these conditions, the theoretical maximum deuteration at the vinylic β-position was 98.6%. Experimentally, a value of 98% (3% deuteration at the α-position) was obtained, corresponding to a value higher than 99% with respect to the theoretical value.

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FULL PAPER

Carbene Catalysis

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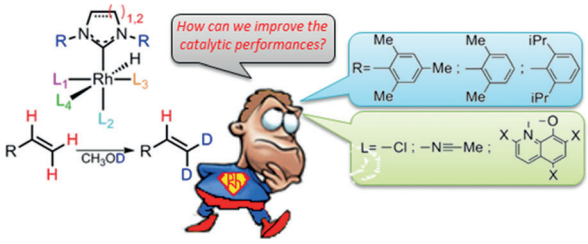
■■ – ■■

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



A series of H-Rh^{III}-NHC complexes with different ancillary ligands has been synthesized and evaluated as catalyst precursors in H/D exchange of α-olefins (see figure). An adequate balance between steric hindrance and electron donation provides a catalytic system with outstanding activity and total selectivity for deuteration at β-vinyl positions.