Catalytic C−H Activation of Hydrocarbons by Rhodium(I) and Iridium(I) Complexes with Hemilabile Quinolyl-Cp Ligands†

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The rhodium(I) and iridium(I) complexes **3a**−**6a** contain the hemilabile Cp-quinoline chelate ligands **1** and **2**, respectively, where the hard nitrogen donor does not displace the good acceptor ligand ethylene. After irradiation with visible light, intensely colored complexes are obtained, where the N-donor coordinates to the metal centers. Depending on the metal atom and on the substitution pattern at the Cp rings, the mono-ethene complex with N-metal coordination can be observed spectroscopically (e.g., **3b**) or C−H addition products are probable intermediates. The iridium complex **6a** is able to activate the aliphatic C−H bond in cyclohexane. With the rhodium complex **5a** as the precatalyst, catalytic H/D exchange reactions have been performed with olefinic substrates. With linear α-olefins a fast double-bond isomerization dominates. The hemilabile ligands stabilize the catalytically active metal complexes without suppressing their activity significantly.

Introduction

The selective activation of C−H bonds of saturated or unsaturated hydrocarbons can be realized by coordinatively unsaturated transition metal complexes. A further important step following the C−H activation is the selective transformation of the hydrocarbon into functionalized molecules.[1] The formation of a free coordination site in a transition metal complex can be accomplished by the photochemically induced dissociation of a ligand. Some cyclopentadienyl rhodium and iridium complexes of the type Cp^RML_n (Cp^R = substituted cyclopentadienyl; M = Rh^I, Ir^I) are well studied examples that are able to activate C−H bonds.[2] After dissociation of a neutral two-electron ligand (L) the resulting 16 valence electron species were characterized using matrix isolation techniques.[3] In solution such unsaturated species often undergo side reactions, which can lead to a decomposition of the active complex.[4,5] Stabilization of the unsaturated species by external ligands often leads to complexes that are no longer able to activate C−H bonds. Therefore, stabilizing ligands must balance the complex reactivity in such a way that the activation of substrates is still possible. This is even more important in catalytic transformations where a stabilizing ligand must coordinate and decoordinate several times. To allow for a sufficient concentration and proximity of the additional donor ligands, so-called hemilabile chelate ligands are ideal.[6] This concept has been applied to Cp ligands where neutral Werner-type donors with N, P, O, or S atoms are attached to the five-membered ring by a suitable spacer (e.g., a C_2 or C_3 chain).[7] We have incorporated the C_2 spacer as well as an sp^2 nitrogen atom into a rigid heterocycle by using quinolyl-functionalized Cp ligands such as **1** or **2**.[8,9] These ligands have a predefined geometry so that the nitrogen donor atom is in a suitable position for the coordination to the metal center. However, the N atom in **1** or **2** is a typical donor ligand with poor acceptor properties and will therefore not bind strongly to electron-rich metals in low oxidation states such as Rh^I

† Dedicated to Professor Gottfried Huttner.

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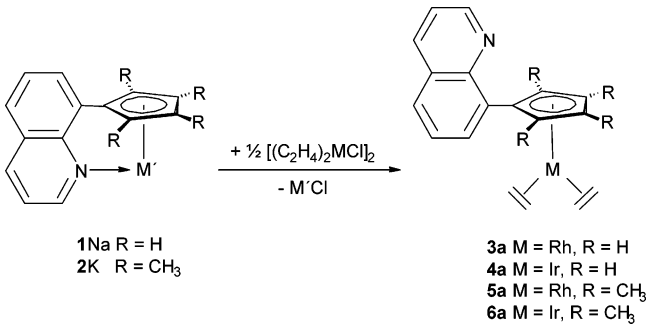
Scheme 1. Preparation of the Rhodium and Iridium Complexes 3a−6a



1Na R = H
2K R = CH_3

3a M = Rh, R = H
4a M = Ir, R = H
5a M = Rh, R = CH_3
6a M = Ir, R = CH_3

or Ir^I. As a consequence, it has a hemilabile character and should not completely decrease the reactivity of unsaturated complexes with these metals. As the stabilizing ligand will always remain in close proximity, a stabilization of the low-coordinate species will always be possible. This prevents decomposition pathways of the active system, which is necessary in catalytic transformations.

Results and Discussion

The reaction of $[(C_2H_4)_2MCl]_2$ (M = Rh, Ir) with [η^5-(8-quinolyl)cyclopentadienyl]sodium (**1**Na) and [2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]potassium (**2**K), respectively, yields the rhodium and iridium bis-ethene complexes **3a**−**6a** after column chromatography in high purity and good yields (Scheme 1).

The ^{1}H NMR spectra of the four complexes **3a**−**6a** show that two molecules of ethene are coordinated to the metal centers. Therefore, the nitrogen atom of the quinolyl moiety does not bind to the metal atom in these complexes. The proton NMR spectra of the rhodium complexes show two broad featureless signals for the ethene hydrogen atoms at room temperature. The ethene units in the iridium complexes exhibit the two well-resolved multiplets of an AA′BB′ spin system. Similar multiplicity patterns were found in other ethene rhodium and iridium complexes of cyclopentadienyl ligands.[10,11]

The embedment of the donor function into the rigid aromatic system in the ligand **1** or **2** leads to a good crystallization behavior of their metal complexes, regardless of whether the donor group coordinates. Crystals of **3a**−**6a** could be obtained from solutions in toluene (**3a**, **4a**, **6a**) or dichloromethane (**5a**) at −28 °C. The X-ray analyses affirm the conclusions of the NMR spectra. The complexes **3a** and **4a** with the ligand **1** crystallize in the monoclinic space group $P2_1/n$ with two independent but very similar molecules in the asymmetric unit (Figure 1). Their tetramethyl-substituted analogues **5a** and **6a** crystallize in the triclinic space group $P\bar{1}$ (Figure 2).

The distances of the metal atoms to the carbon atoms of the five-membered rings lie between 2.2 and 2.3 Å for all four complexes. The ethene ligands are somewhat closer, with metal carbon distances of 2.1−2.15 Å. In

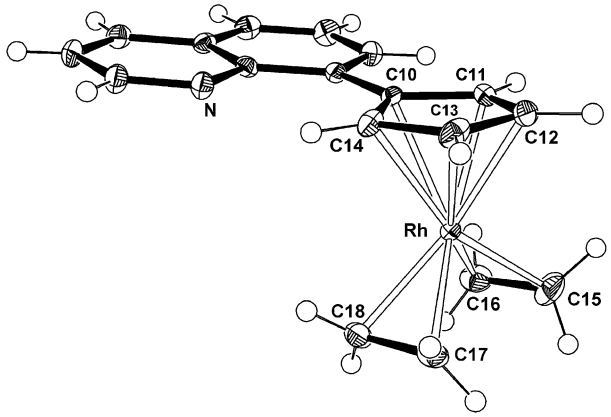


Figure 1. Solid-state molecular structure of **3a** (only one molecule of the asymmetric unit is shown). The structure of the Ir complex **4a** is very similar (see Supporting Information).

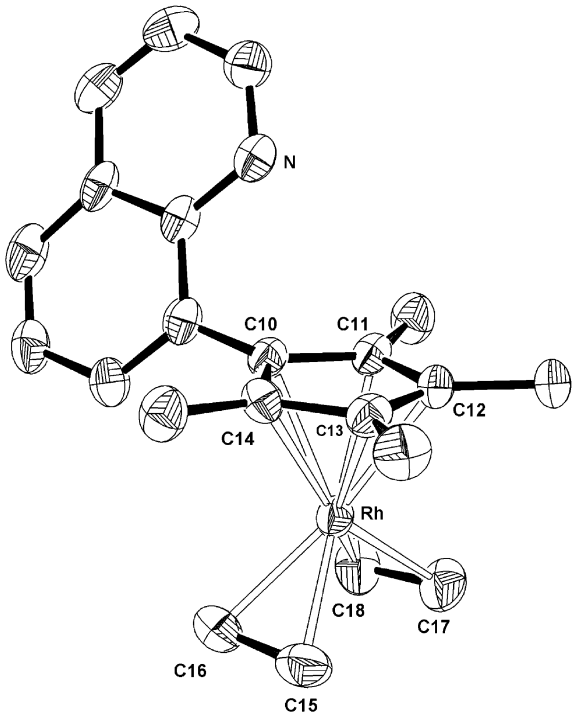


Figure 2. Solid-state molecular structure of **5a** (H atoms omitted for clarity). The structure of the Ir complex **6a** is very similar (see Supporting Information).

the complexes with the ligand **1** the angles between the cyclopentadienyl and the quinoline planes are approximately 170°. This nearly coplanar orientation is not possible in the methyl-substituted derivatives **5a** and **6a**. In these compounds the best planes of the two cycles form angles of 63°.

Photochemical induced removal of a ligand such as CO or ethene is a known method to generate reactive species. We irradiated the complexes **3a**−**6a** with visible light in solvents such as benzene or cyclohexane. Depending on the substitution pattern and on the nature of the metal atom, the reactivity of the complexes after their activation with visible light differs and the nature of the solvent is also very important. The irradiation of the related carbonyl complex **2**$Rh(CO)_2$ in chloroform or dichloromethane leads to an oxidation of the central metal and the formation of the Rh(III)

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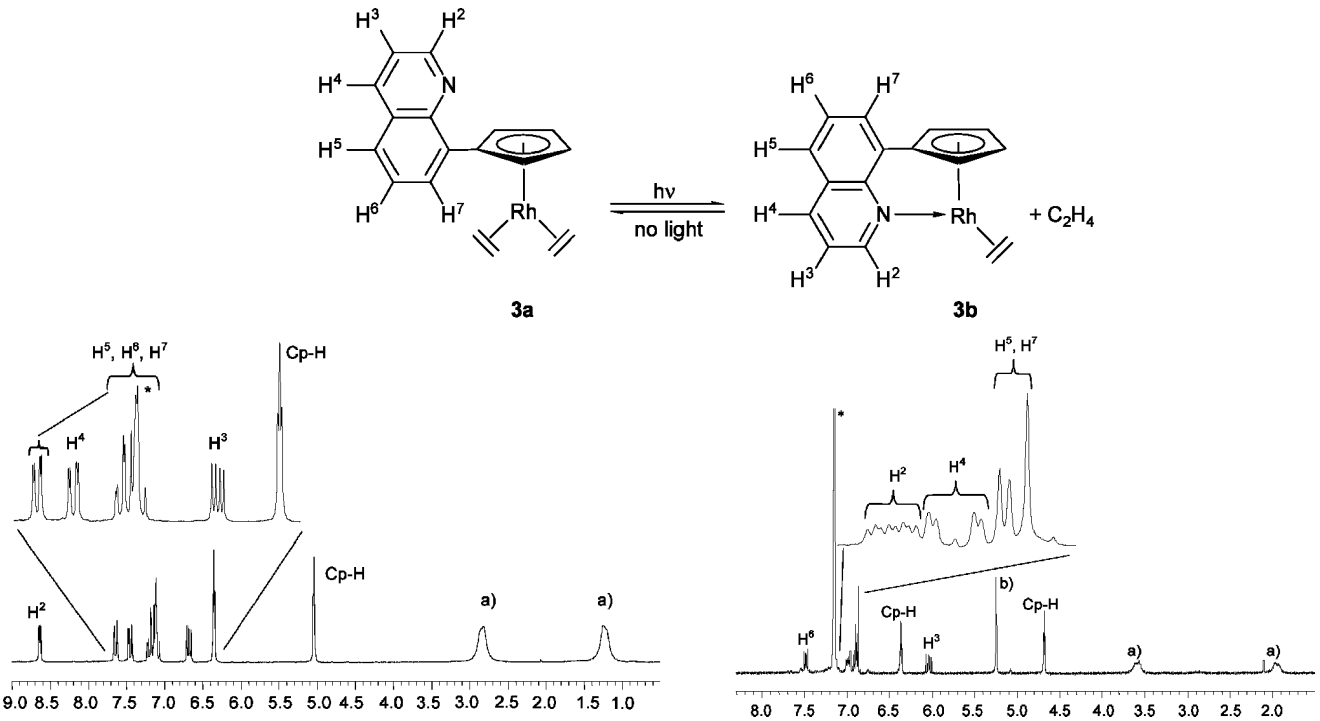

Figure 3. Photochemical transformation of **3a** into **3b** and ^{1}H NMR spectra of **3a** and **3b** in C_6D_6. *Signal due to C_6D_5H; (a) coordinated C_2H_4; (b) noncoordinated C_2H_4.

chloro complex **2**$RhCl_2$.[12] In contrast, the irradiation of the rhodium complex **3a** in deuterated benzene or cyclohexane leads to an intensely colored new compound (**3b**), which in the absence of light reacts slowly back to **3a**. The color of the solution changes from pale yellow to dark blue [**3b** in toluene: $\lambda_{max} = 612$ nm ($\epsilon = 688$ L·mol^{-1}·cm^{-1})]. This band is an indicator for a coordination of the nitrogen atom to the metal center in **3b** caused by metal-quinolyl charge-transfer absorptions. A similar behavior has been described by us for related manganese and rhenium carbonyl complexes.[13] The ^{1}H NMR spectrum of **3b** shows a complete set of new signals compared to **3a**. Between $\delta = 1.86-2.03$ and 3.49−3.67 the two broad resonances of only one ethene ligand are found. The liberated ethene is detected as a singlet at 5.24 ppm. The protons of the cyclopentadienyl ring could be detected as two multiplets between 4.65−4.70 and 6.33−6.38 ppm, respectively. The signals in the aromatic region differ significantly from those in the bis-ethene complex **3a**. The signal of the H^2 atom, which is close to the nitrogen atom, is shifted from 8.67 ppm in **3a** to 6.99 ppm in **3b**. Its coupling pattern proves the nitrogen−rhodium interaction present in **3b** due to its splitting into a doublet of doublets of doublets with coupling constants of $^3J(H^2,H^3) = 5.1$ Hz, $^4J(H^2,H^4) = 1.4$ Hz, and $^3J(H,Rh) = 2.5$ Hz (Figure 3).

The mono-ethene complex **3b** reacts slowly in the dark with the liberated ethene to give the bis-ethene complex **3a**. However, removal of the ethene atmosphere leads to a slow decomposition of the blue mono-ethene compound **3b**. This decomposition reaction was also observed after prolonged irradiation of a solution of **3a** in benzene with visible light for several days. This observation is in agreement with the reactivity of CpRh-$(C_2H_4)_2$, which is described to be photostable under an atmosphere of ethene but decomposes to a red-brown, uncharacterized product by photolysis in a vacuum or in an atmosphere of argon.[4]

The complex $CpIr(CO)(C_2H_4)$ reacts photochemically with deuterated benzene or deuterated cyclohexane to the complexes $CpIr(CO)(C_2H_3)H$ and CpIr(CO)(R)H (R = C_6D_5; C_6D_{11}). The formation of $CpIr(CO)(C_6D_5)H$ instead of the expected deuterido complex CpIr(CO)-$(C_6D_5)D$ formed by direct C−D bond activation of one molecule of d_6-benzene indicates a fast H/D exchange, which leads to the exclusive formation of the hydrido complex.[14]

However, the irradiation of **4a** in C_6D_{12} does not lead to an activation of the C−D bond, and therefore no H/D exchange occurs. The color of the solution turns from yellow to blue, and after 6 h a new set of signals is observed in the proton NMR spectrum, similar to the spectrum of the mono-ethene complex **3b**. Between $\delta = 1.04-1.16$ and 2.94−3.04 two multiplets with the intensity of one ethene ligand are found. The liberated ethene is detected as a singlet at 5.37 ppm. The protons of the cyclopentadienyl ring could be detected as two pseudotriplets at 4.83 and 5.09 ppm, respectively. The signals of the quinolyl ring are found at 6.69, 7.23, 7.44, and between 7.71 and 7.78 ppm. The intense blue color and the changes of the chemical shifts in the proton NMR spectrum, which have the same tendencies as found for the system **3a**/**3b**, indicate that the newly formed compound is the mono-ethene complex **4b**, similar to **3b**.

By performing the photochemical reaction in C_6D_6 the color of the solution turns from yellow to red. After 3.5

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h of irradiation the signals in the ^{1}H NMR spectrum disappeared nearly completely, which shows the high reactivity of **4a** toward aromatic and olefinic C−H bond activation, leading to a fast H/D exchange reaction. The different colors that appear after the irradiation of **4a** in C_6D_{12} and C_6D_6, respectively, indicate the presence of different reaction products in these two cases, but neither NMR investigation in deuterated and nondeuterated aromatic solvents nor mass spectrometric measurements gave further indications of the composition of the red irradiation product of **4a**.

The irradiation of the rhodium complex **5a** in deuterated benzene leads to a change in color from yellow to deep green. The absorption maximum in the visible region lies at $\lambda_{max} = 701$ nm ($\epsilon = 4535$ L·mol^{-1}·cm^{-1}) in toluene and at $\lambda_{max} = 719$ nm ($\epsilon = 4129$ L·mol^{-1}·cm^{-1}) in cyclohexane. The solvatochromic effect is again an indication of a coordination of the quinolyl moiety leading to intramolecular MLCT bonds.[13] In the ^{1}H NMR spectrum a new set of signals can be detected. However, a complete conversion into the new green compound **5b** is possible only in diluted solutions. This is due to an intense absorption band of **5b** with an absorption maximum appearing in toluene at $\lambda_{max} = 356$ nm ($\epsilon = 7491$ L·mol^{-1}·cm^{-1}) and in cyclohexane at $\lambda_{max} = 366$ nm ($\epsilon = 7794$ L·mol^{-1}·cm^{-1}). This so-called inner filter effect inhibits a quantitative formation of **5b** in concentrated solutions of **5a** [**5a** in toluene: $\lambda_{max} = 391$ nm ($\epsilon = 2268$ L·mol^{-1}·cm^{-1}); **5a** in cyclohexane: $\lambda_{max} = 394$ nm ($\epsilon = 2285$ L·mol^{-1}·cm^{-1})].

In the absence of light and under an atmosphere of ethene the color of the green solution turns to yellow. The proton NMR spectrum shows some remarkable differences compared with the spectrum before the irradiation. The resonances of the ethene ligands are much less intense, and some signals of the quinolyl moiety are found to have a different coupling pattern and lower intensity especially in the ring containing the heteroatom. The investigation by mass spectrometry shows that these changes in the NMR spectrum result from an exchange of the hydrogen atoms by deuterium atoms occurring in the quinolyl moiety and in the ethene ligands. The base peak that comes from the fragment $[\mathbf{2}Rh]^+$ shows a broad isotopic distribution with a maximum at $m/z = 354$ and not at $m/z = 351$ as before the irradiation (see Supporting Information).

Such reactions with a H/D exchange of the solvent C_6D_6 and a coordinated olefin ligand are also known after thermal activation in the cases of $(C_5H_5)Rh(C_2H_4)_2$ and $(C_5Me_5)Rh(C_2H_4)_2$. Whereas with $(C_5H_5)Rh(C_2H_4)_2$ some decomposition of the complex was found after 20 h at 100 °C, $(C_5Me_5)Rh(C_2H_4)_2$ was found to remain stable even when the temperature is raised to 140 °C.[2c,5] When a solution of **5a** in benzene is heated under reflux for 3 h, the proton NMR spectrum shows some changes in the signal intensities and coupling patterns but not in the chemical shifts. The intensity of the ethene signals drops from 4 to approximate 2 for each signal. Further heating for 6 h does not lead to a complete H/D exchange in the olefinic ligands. The analysis of the resonances of the quinolyl protons indicates a deuterium incorporation into the H^2 (70%) and H^3 (30%) position.

The photolysis of $(C_5H_5)Rh(C_2H_4)_2$ carried out in a vacuum or under argon leads to the formation of a red-brown precipitate of unknown composition.[4,15] This shows the importance of the quinolyl moiety in **5a**, which can coordinate to the rhodium center after the elimination of one molecule of ethene and thus stabilizes the resulting unsaturated mono-ethene species.

The mechanism of the H/D exchange was investigated by several working groups.[2c,5,16,17] On this basis we can predict the following mechanism for the H/D exchange reaction (Scheme 2).

The first step is the dissociation of an ethene ligand. The unsaturated mono-ethene complex is then stabilized by an intramolecular coordination of the quinolyl nitrogen atom. The Rh^I−N bond in **5b** is weak so that a C−D bond of the solvent can add oxidatively (compound **A** or **B**) followed by the insertion of the olefin ligand into the Rh−D bond. The reductive elimination of a hydrogen atom from the ethyl rhodium species **C** followed by the reductive elimination of a molecule of benzene regenerates the mono-ethene complex **5b**. Several such cycles cause complete deuterium incorporation into the ethene molecules. In addition, a second complex can add oxidatively via a C−H bond so that D-incorporation occurs also in the ligand. In the case of the mono-ethene complex **3b** we proved the coordination of the quinolyl moiety to the rhodium center by NMR investigation. At present we cannot prove whether the N-coordination is also present in compound **C**.

The irradiation of **5a** in deuterated cyclohexane leads also to the formation of the green compound **5b**, but an H/D exchange does not occur. In an atmosphere of ethene **5b** reacts back to unchanged **5a**. This process is completely reversible without any decomposition of the complex. In the ^{1}H NMR spectrum recorded directly after irradiation in C_6D_{12} apart from the signals of **5a** additional signals of the green product are detected. These are two singlets of the four methyl groups at $\delta = 1.57$ and 2.15 and two less intense multiplets at $\delta = 1.19-1.21$ and 1.54−1.57, respectively. The integral ratios show that only one ethene ligand is coordinated. Therefore, the green compound **5b** is a mono-ethene complex probably stabilized by intramolecular coordination of the quinolyl nitrogen atom as in **3b**. The signals of the quinolyl protons between 6.67 and 8.82 ppm of **5b** and **5a** partly overlap. Therefore, a full assignment of these resonances is not possible.

Irradiation of the iridium complex **6a** in deuterated benzene leads to a rapid change in color from pale yellow to red, but no significant changes could be detected in the proton NMR spectrum within 15 min of irradiation. After 2 days of photochemical induced reaction nearly all signals in the ^{1}H NMR spectrum had disappeared; even the two singlets of the methyl groups of the cyclopentadienyl ring could be detected only in low intensity. The mass spectrum proves the existence of a multiple deuterated product that results in a very broad isotopic pattern. A similar but somewhat lower reactiv-

(15) A decomposition reaction was also observed by photolysis of a solution of $(C_5Me_5)Rh(C_2H_4)_2$ in C_6D_6.

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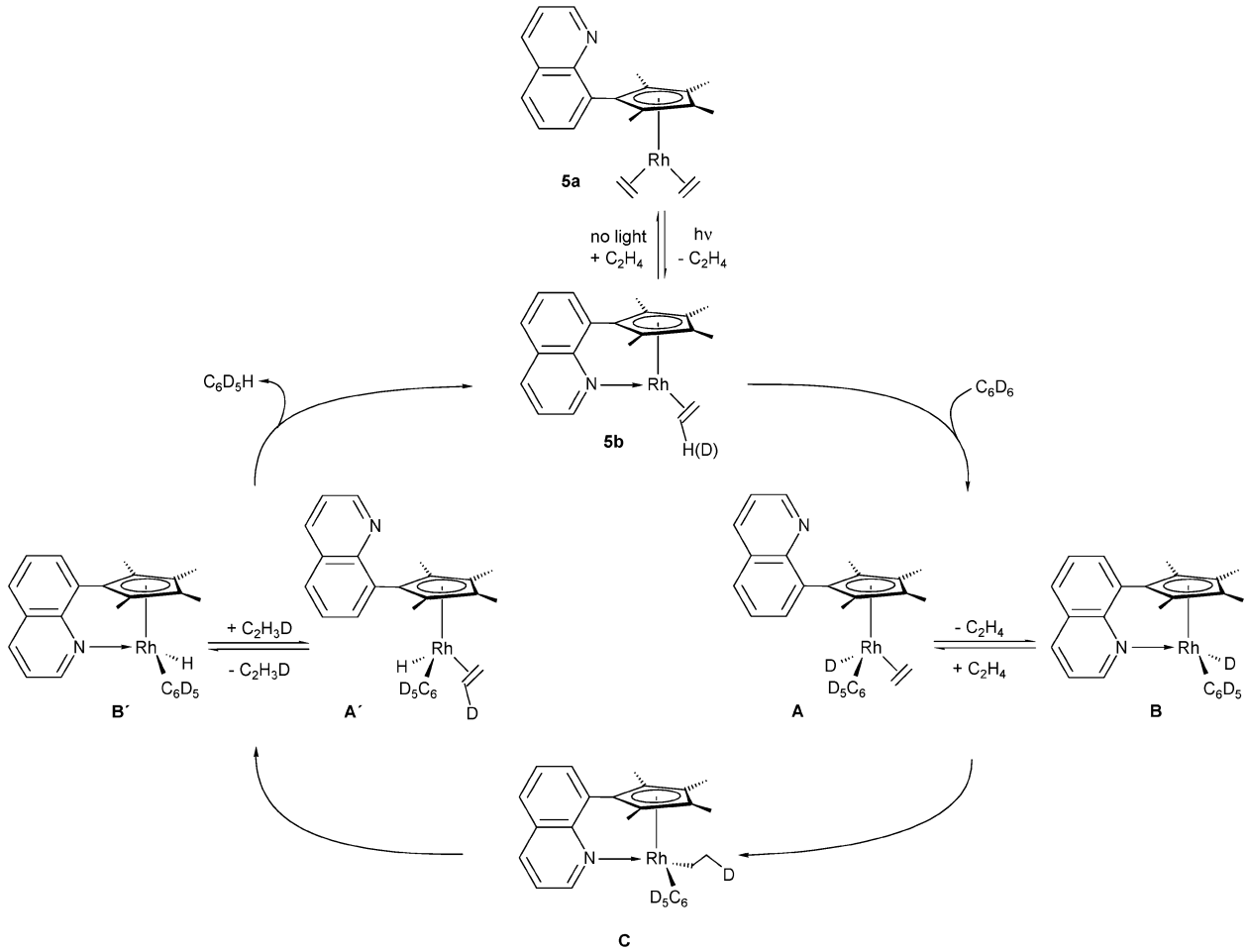
Scheme 2. Proposed Catalytic Cycle for H/D Exchange in Ethene Ligands with Complexes 5a/5b[a]



[a] The formulas **A** and **B** (**A′** and **B′**, respectively) represent possible equilibria with noncoordinated (**A** and **A′**) or coordinated quinolyl ligand during the catalytic cycle.

ity of **6a** is found when the irradiation is performed in C_6D_{12}. After 2 days of irradiation the signal intensity in the ^1H NMR spectrum is significantly reduced but still more intense than in the case of C_6D_6 as the solvent. This shows that the iridium complex **6a** is more reactive toward the activation of C−H bonds than its rhodium analogue **5a**. It even allows the activation of the low-reactive aliphatic C−H bonds of cyclohexane.

The rhodium complex **5a** can activate selectively only aromatic and olefinic C−H bonds during its irradiation with visible light. Its ethene ligands are completely deuterated after some hours of irradiation when the reaction is performed in C_6D_6. Therefore, we tried to use **5a** as a deuteration catalyst for olefinic substrates.

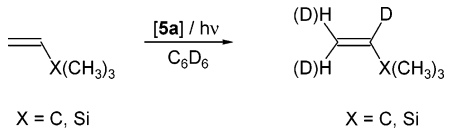
Due to the fact that a complete deuteration of the olefin ligands occurs, the irradiation of a benzene solution of **5a** was performed in an atmosphere of ethene (1 bar ethene pressure) in order to synthesize deuterated ethene. However, in an atmosphere of ethene the deuteration reaction is suppressed. The solution remains yellow and no changes are observed in the ^1H NMR spectrum after several days of irradiation. The excess of ethene inhibits the formation of **5b**, and therefore no free coordination site is generated, which is necessary for the activation of C−H bonds and for H/D exchange reactions.

Substituted olefins usually coordinate more weakly than ethene. Therefore, the rhodium complex **5a** was irradiated in the presence of 1-hexene. However, a fast isomerization of the double bond occurred in this case. This can be explained by the formation of allylic rhodium hydride complexes followed by the reductive elimination of the isomerized hexene. A GC-MS analysis of the reaction mixture shows 2- and 3-hexene in a ratio of 75% to 25%, respectively, beside traces of 1-hexene. The isotopic patterns in the obtained mass spectra of the 2- and 3-hexene show that only a very few H/D exchanges occurred. Therefore, the isomerization reaction is much faster than the H/D exchange reaction. Furthermore, 1,2-substituted olefins are sterically too hindered to act as substrates for an oxidative addition to the rhodium metal center.

For a successful exchange of a hydrogen atom with a deuterium atom, olefins are needed that do not bear hydrogen atoms in the allylic position because of the fast formation of allylic complexes. The irradiation of a degassed benzene solution of 2,2-dimethylbutene and vinyltrimethylsilane, respectively, containing a catalytic amount of **5a** leads to a H/D exchange of the hydrogen atoms (Scheme 3).

In the case of 2,2-dimethylbutene the resonance of the α-hydrogen atom integrates to 45% of its original intensity after one week of irradiation, whereas the *β*-hydrogen atoms still show 95% of its initial integrated intensity. After approximate two weeks of further irradiation only 28% of the original intensity of the

Scheme 3. H/D Exchange in Vinyltrimethylsilane and 2,2-Dimethylbutene Catalyzed by 5a



signal of the α-hydrogen atom is left. The intensity of the resonances of the *β*-hydrogen atoms still amounts to 93%. Beside the resonances of the nondeuterated 2,2-dimethylbutene in the ^{13}C NMR spectrum the signal of the α-C atom in the deuterated compound is somewhat shifted and split into a triplet due to the coupling with the deuterium atom. Due to the low deuterium incorporation into the *β*-position, no such coupling could be detected in this case.

Vinyltrimethylsilane was found to be more reactive than 2,2-dimethylbutene. A total of 50% of deuterium was determined in the α-position after 3 days of irradiation, whereas the *β*-hydrogen atoms still show 92−95% of the initial integrated intensity. After approximately two weeks the intensity of the resonance of the α-hydrogen atom decreased to only 24%. After this period a significant loss in intensity was also found for the signals of the *β*-hydrogen atoms (between 36% and 41%). The preferential α-hydrogen exchange has been observed in related systems, and it is also a support for the general catalytic cycle described in Scheme 2 with olefin insertion into a metal hydride bond.[17]

Conclusion

It has been known for a long time that rhodium(I) and iridium(I) complexes with a cyclopentadienyl spectator ligand and one or two neutral and labile ligands can be activated thermally or photochemically. The resulting complexes are highly reactive, and some of them allow for the activation of C−H bonds. By using the hemilabile, quinoline-functionalized Cp ligands **1** and **2** we were able to stabilize the reactive intermediates without suppressing their reactivity too much. After irradiation of the rhodium complexes **3a** and **5a** the mono-ethene complexes **3b** and **5b**, respectively, were identified by ^1H NMR. Irradiation of the corresponding Ir complexes **4a** and **6a** leads to more reactive complexes. The presence of the oxidative addition products is probable in these cases. The iridium complex **6a** is able to activate the aliphatic C−H bond in cyclohexane. A high concentration of coordinating ligands such as ethene suppresses the reactivity of the complexes. Linear α-olefins are quickly isomerized into internal olefins. If no H atom is present in the *β*-position relative to the double bond of the olefin, a catalytic H/D exchange reaction occurs in the presence of photochemically activated complex **5a**. In this reaction the α-position is the more reactive one, and in the case of 2,2-dimethylbutene the H/D exchange is nearly stereospecific.

Experimental Section

General Procedures. All experiments were carried out under an atmosphere of dry argon. Solvents were dried by using standard procedures and distilled prior to use. [η^5-(8-Quinolyl)cyclopentadienyl]sodium (**1**Na),[8] 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadiene (**2**H),[9a] di-*μ*-chlorotetrakis(ethene)-dirhodium(I),[18] and di-*μ*-chlorotetrakis(ethene)diiridium(I)[19] were prepared according to the literature procedures. All other reagents were used as purchased. NMR: Bruker DRX 200 (200.13 MHz for ^1H, 50.32 MHz for ^{13}C). The ^1H NMR spectra were calibrated using signals of residual protons from the solvent referenced to $SiMe_4$. The ^{13}C spectral chemical shifts are reported relative to the ^{13}C solvent signals. MS: JEOL JMS-700 and VG ZAB-2F.

Table 1. Selected Bond Lengths (Å) for 3a−6a

	3a (M = Rh)	**4a** (M = Ir)	**5a** (M = Rh)	**6a** (M = Ir)
M−C10	2.288(2)	2.270(5)	2.249(5)	2.228(4)
	2.291(3)	2.275(5)		
M−C11	2.201(3)	2.200(5)	2.225(6)	2.221(5)
	2.196(3)	2.186(6)		
M−C12	2.251(3)	2.244(6)	2.272(5)	2.269(4)
	2.249(3)	2.230(6)		
M−C13	2.252(3)	2.256(6)	2.277(5)	2.295(5)
	2.240(3)	2.242(6)		
M−C14	2.244(3)	2.242(5)	2.216(6)	2.214(5)
	2.240(3)	2.258(5)		
M−C15	2.123(3)	2.116(6)	2.127(7)	2.117(6)
	2.129(3)	2.112(6)		
M−C16	2.115(3)	2.097(6)	2.135(6)	2.118(5)
	2.124(3)	2.113(6)		
M−C17	2.130(3)	2.125(6)	2.123(6)	2.117(5)
	2.126(3)	2.117(6)		
M−C18	2.127(3)	2.118(5)	2.125(7)	2.110(5)
	2.133(3)	2.121(5)		
C15−C16	1.409(5)	1.428(11)	1.401(9)	1.428(9)
	1.409(5)	1.425(9)		
C17−C18	1.413(4)	1.433(8)	1.404(9)	1.421(8)
	1.404(4)	1.432(8)		
Cp−M[b]	1.890	1.883	1.887	1.880
	1.892	1.882		

[a] For **3a** and **4a** the values for both independent molecules in the unit cell are given. [b] Shortest distance between the plane defined by the Cp ring and the metal atom.

Bis(η^2-ethene)[η^5-(8-quinolyl)cyclopentadienyl]rhodium(I) (3a). A total of 530 mg (2.46 mmol) of [η^5-(8-quinolyl)-cyclopentadienyl]sodium (**1**Na) dissolved in 25 mL of thf was added dropwise to a solution of 479 mg (1.23 mmol) of di-*μ*-chlorotetrakis(ethene)dirhodium(I) in 25 mL of toluene. The resulting mixture was stirred overnight. The solvents were evaporated. Column chromatography on Al_2O_3/5% H_2O using toluene as eluent yielded 578 mg (1.65 mmol, 67%) of **3a** as a yellow solid. ^1H NMR ($CDCl_3$): *δ* 1.16 (br, 4H, ethene-CH_2); 2.66 (br, 4H, ethene-CH_2); 5.31 (pt, 2H, Cp-CH); 6.34 (pt, 2H, Cp-CH); 7.36 (dd, $^3J(H^3,H^2) = 4.1$ Hz, $^3J(H^3,H^4) = 8.2$ Hz, 1H, H^3); 7.48 (dd, $^3J(H,H) = 8.0$ Hz, $^3J(H,H) = 7.3$ Hz, 1H, H^6); 7.65 (dd, $^3J(H,H) = 8.1$ Hz, $^4J(H,H) = 1.5$ Hz, 1H, H^5 or H^7); 7.80 (dd, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 1.4$ Hz, 1H, H^5 or H^7); 8.11 (dd, $^3J(H,^4H^3) = 8.3$ Hz, $^4J(H,^4H^2) = 2.0$ Hz, 1H, H^4); 8.92 (dd, $^3J(H^2,H^3) = 4.1$ Hz, $^4J(H^2,H^4) = 1.9$ Hz, 1H, H^2). ^{13}C NMR ($CDCl_3$): *δ* 39.3 (d, $^1J(Rh,C) = 13.3$ Hz, ethene-CH_2); 86.9 (d, $^1J(Rh,C) = 4.4$ Hz, Cp-CH); 89.4 (d, $^1J(Rh,C) = 3.9$ Hz, Cp-CH); 104.5 (d, $^1J(Rh,C) = 3.9$ Hz, quart. Cp-C); 120.9, 126.2, 126.7, 128.1, 136.3, 149.4 (quinoline-CH); 128.9, 132.5, 145.9 (quart. $C_{quinoline}$). MS (EI): *m/z* (%) 351 (1) [M^+]; 323 (16) [$M^+ - C_2H_4$]; 295 (100) [$M^+ - 2\,C_2H_4$]. Anal. Calcd for $C_{18}H_{18}NRh$ (351.25): C 61.55, H 5.17, N 3.99. Found: C 61.28, H 5.19, N 3.97.

Bis(η^2-ethene)[η^5-(8-quinolyl)cyclopentadienyl]iridium(I) (4a). A total of 228 mg (1.06 mmol) of [η^5-(8-quinolyl)-cyclopentadienyl]natrium(I) (**1**Na) dissolved in 20 mL of thf was added dropwise to a solution of 300 mg (0.53 mmol) of di-*μ*-chlorotetrakis(ethene)diiridium(I) in 20 mL of toluene cooled at −78 °C. The resulting mixture was warmed to room

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Table 2. Crystal Data and Experimental Details

	3a	4a	5a	6a
empirical formula	$C_{18}H_{18}NRh$	$C_{18}H_{18}IrN$	$C_{22}H_{26}NRh$	$C_{22}H_{26}IrN$
fw	351.24	440.53	407.35	496.64
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
unit cell dimens				
a, Å	14.5264(8)	14.5137(8)	7.310(5)	7.2888(1)
b, Å	6.9596(4)	6.9902(4)	11.092(6)	11.0309(2)
c, Å	27.986(2)	27.8759(15)	12.134(7)	12.0453(2)
α, deg	90	90	81.36(4)	81.382(1)
β, deg	93.454(1)	93.593(1)	78.19(5)	78.660(1)
γ, deg	90	90	72.32(5)	72.152(1)
volume, Å^3	2824.2(3)	2822.6(3)	913.4(10)	899.69(3)
Z	8	8	2	2
density(calc), g/cm^3	1.652	2.073	1.481	1.833
F(000)	1424	1680	420	484
cryst size, mm^3	0.38 × 0.27 × 0.16	0.36 × 0.10 × 0.07	0.10 × 0.17 × 0.35	0.51 × 0.44 × 0.10
θ range for data collection, deg	1.62 to 32.02	1.54 to 32.04	1.72 to 25.06	1.73 to 28.29
index ranges	$-21 \le h \le 21$, $0 \le k \le 10$, $0 \le l \le 41$	$-18 \le h \le 21$, $-10 \le k \le 10$, $-38 \le l \le 41$	$-8 \le h \le 8$, $-12 \le k \le 13$, $0 \le l \le 14$	$-9 \le h \le 9$, $-14 \le k \le 14$, $-16 \le l \le 15$
no. of reflns collected	47 841	24 556	3226	11 993
no. of indep reflns	9719 [R(int) = 0.0284]	9540 [R(int) = 0.0304]	3226 [R(int) = 0.0000]	4392 [R(int) = 0.0446]
no. of data/restraints/params	9719/0/505	9540/0/426	3226/0/278	4392/0/316
goodness-of-fit on F^2	1.341	1.156	1.063	1.115
final R indices [$I > 2\sigma(I)$]	R1 = 0.0394, wR2 = 0.0857	R1 = 0.0408, wR2 = 0.0825	R1 = 0.0453, wR2 = 0.1014	R1 = 0.0372, wR2 = 0.0989
R indices (all data)	R1 = 0.0409, wR2 = 0.0862	R1 = 0.0471, wR2 = 0.0846	R1 = 0.0728, wR2 = 0.1096	R1 = 0.0379, wR2 = 0.0995
largest diff peak and hole, e Å^{-3}	2.183 and −1.953	4.048 and −3.618	0.571 and −0.504	2.337 and −3.856

temperature overnight. The solvents were evaporated. Column chromatography on Al_2O_3/5% H_2O using toluene as eluent yielded 270 mg (0.61 mmol, 56%) of **4a** as a dark yellow solid. ^{1}H NMR ($CDCl_3$): δ 0.67−0.77 (m, 4H, ethene-CH_2); 2.35−2.45 (m, 4H, ethene-CH_2); 5.32 (pt, 2H, Cp-CH); 6.35 (pt, 2H, Cp-CH); 7.35 (dd, ^3J(H^3,H^2) = 4.1 Hz, ^3J(H^3,H^4) = 8.2 Hz, 1H, H^3); 7.47 (dd, ^3J(H,H) = 8.0 Hz, ^3J(H,H) = 7.3 Hz, 1H, H^6); 7.67 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.5 Hz, 1H, H^5 or H^7); 7.73 (dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.5 Hz, 1H, H^5 or H^7); 8.10 (dd, ^3J(H,^{4}H^3) = 8.3 Hz, ^4J(H,^{4}H^2) = 1.8 Hz, 1H, H^4); 8.91 (dd, ^3J(H^2,H^3) = 4.1 Hz, ^4J(H^2,H^4) = 1.8 Hz, 1H, H^2). ^{13}C NMR ($CDCl_3$): δ 20.1 (ethene-CH_2); 81.9, 84.6 (Cp-CH); 100.3 (quart. Cp-C); 121.0, 126.2, 127.1, 128.7, 136.2, 149.4 (quinoline-CH); 128.7, 131.5, 145.8 (quart. $C_{quinoline}$). MS (EI): *m/z* (%) 413 (54) [$M^+ - C_2H_4$]; 385 (100) [$M^+ - 2\ C_2H_4$]; 359 (22) [$M^+ - 2\ C_2H_4 - C_2H_2$]; 192.5 (18) [$M^{2+} - 2\ C_2H_4$]. HR-MS (EI): calcd for $C_{16}H_{14}N^{193}Ir$ 413.0756; found 413.0751. Anal. Calcd for $C_{18}H_{18}NIr$ (440.57): C 49.07, H 4.12, N 3.18. Found: C 49.27, H 4.30, N 3.31.

Bis(η^2-ethene)[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(I) (5a). To a suspension of 103 mg (2.6 mmol) of potassium hydride in 25 mL of thf was added 641 mg (2.3 mmol) of 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadiene (**2**H). After stirring for 3 h at room temperature the violet suspension was transferred to a solution of 500 mg (1.3 mmol) of di-μ-chlorotetrakis(ethene)dirhodium(I) in 25 mL of toluene via cannula. The resulting brown solution was stirred overnight. The solvents were evaporated and the residue suspended in toluene. The precipitated inorganic salts were separated by filtration with a reversal frit (G4), and the dark filtrate was chromatographed on Al_2O_3/5% H_2O with toluene as eluent to give 870 mg (2.14 mmol, 83%) of **5a** as a yellow solid. ^{1}H NMR ($CDCl_3$): δ 1.32 (s, 6H, CH_3); 1.36−1.47 (br, 4H, ethene-CH_2); 1.90−1.97 (br, 4H, ethene-CH_2); 1.98 (d, ^3J(Rh,H) = 0.5 Hz, 6H, CH_3); 7.33 (dd, ^3J(H^3,H^2) = 4.2 Hz, ^3J(H^3,H^4) = 8.1 Hz, 1H, H^3); 7.55 (dd, ^3J(H,H) = 7.1 Hz, ^3J(H,H) = 8.1 Hz, 1H, H^6); 7.77 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 1.5 Hz, 1H, H^5 or H^7); 8.15 (dd, ^3J(H,^{4}H^3) = 8.1 Hz, ^4J(H^4,H^2) = 1.7 Hz, 1H, H^4); 8.42 (dd, ^3J(H,H) = 7.1 Hz, ^4J(H,H) = 1.5 Hz, 1H, H^5 or H^7); 8.91 (dd, ^3J(H^2,H^3) = 4.2 Hz, ^4J(H^2,H^4) = 1.7 Hz, 1H, H^2). ^{1}H NMR (C_6D_6): δ 1.32 (s, 6H, CH_3); 1.66−1.72 (br, 4H, ethene-CH_2); 1.77 (d, ^3J(Rh,H) = 0.5 Hz, 6H, CH_3); 2.13−2.19 (br, 4H, ethene-CH_2); 6.73 (dd, ^3J(H^3,H^2) = 4.0 Hz, ^3J(H^3,H^4) = 8.2 Hz, 1H, H^3); 7.37 (dd, ^3J(H,H) = 6.6 Hz, ^3J(H,H) = 8.2 Hz, 1H, H^6); 7.45 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 2.0 Hz, 1H, H^5 or H^7); 7.58 (dd, ^3J(H,^{4}H^3) = 8.3 Hz, ^4J(H^4,H^2) = 1.9 Hz, 1H, H^4); 8.63 (dd, ^3J(H,H) = 6.6 Hz, ^4J(H,H) = 1.9 Hz, 1H, H^5 or H^7); 8.65 (dd, ^3J(H^2,H^3) = 4.0 Hz, ^4J(H^2,H^4) = 1.9 Hz, 1H, H^2). ^{13}C NMR ($CDCl_3$): δ 8.9, 10.2 (CH_3); 44.8 (d, ^1J(Rh,C) = 13.7 Hz, C_2H_4); 97.8 (d, ^1J(Rh,C) = 3.8 Hz, quart. C_{Cp}); 98.3 (d, ^1J(Rh,C) = 3.8 Hz, quart. C_{Cp}); 106.5 (d, ^1J(Rh,C) = 4.6 Hz, quart. C_{Cp}); 120.5 126.2, 127.4, 136.1, 138.0, 149.9 (quinoline-CH); 128.3, 134.0, 147.9 (quart. $C_{quinoline}$). MS (EI): *m/z* (%) 407 (6) [M^+]; 379 (15) [$M^+ - C_2H_4$]; 351 (100) [$M^+ - 2\ C_2H_4$]; 175.5 (9) [$M^{2+} - 2\ C_2H_4$]; 103 (5) [Rh^+]. Anal. Calcd for $C_{22}H_{26}NRh$ (407.37): C 64.87, H 6.43, N 3.44. Found: C 65.21, H 6.38, N 3.33.

Bis(η^2-ethene)[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]iridium(I) (6a). To a suspension of 37 mg (0.92 mmol) of potassium hydride in 25 mL of thf was added 233 mg (0.93 mmol) of 2,3,4,5-tetramethyl-1-(8-quinolyl)-cyclopentadiene (**2**H). After stirring for 3 h at room temperature the violet suspension was added to a solution of 265 mg (0.47 mmol) of di-μ-chlorotetrakis(ethene)diiridium(I) in 25 mL of toluene, which was kept at −78 °C. The resulting mixture was warmed to room temperature overnight. The solvents were evaporated. Column chromatography on Al_2O_3/5% H_2O using toluene as eluent yielded 205 mg (0.41 mmol, 45%) of **6a** as a dark yellow solid. ^{1}H NMR ($CDCl_3$): δ 0.88−0.98 (m, 4H, ethene-CH_2); 1.35 (s, 6H, CH_3); 1.58−1.68 (m, 4H, ethene-CH_2); 2.03 (s, 6H, CH_3); 7.34 (dd, ^3J(H^3,H^2) = 4.2 Hz, ^3J(H^3,H^4) = 8.3 Hz, 1H, H^3); 7.47−7.58 (m, 1H, H^6); 7.79 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.2 Hz, 1H, H^5 or H^7); 8.15 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.6 Hz, 1H, H^4); 8.26 (dd, ^3J(H,^{4}H^3) = 7.1 Hz, ^4J(H,^{4}H^2) = 1.2 Hz, 1H, H^5 or H^7); 8.91 (dd, ^3J(H^2,H^3) = 4.2 Hz, ^4J(H^2,H^4) = 1.6 Hz, 1H, H^2). ^{13}C NMR ($CDCl_3$): δ 8.2, 10.1 (Cp-CH_3); 24.9 (ethene-CH_2); 93.8, 95.0, 100.4 (quart. C_{Cp}); 120.6, 126.5, 127.8, 136.1, 139.4, 150.1 (quinoline-CH); 128.2, 132.9, 147.3 (quart. $C_{quinoline}$). MS (EI): *m/z* (%) 497 (6) [M^+], 469 (63) [$M^+ - C_2H_4$], 441 (100) [$M^+ - 2\ C_2H_4$], 249 (54) [$M^+ - 2\ C_2H_4 - Ir$], 234 (69) [$M^+ - 2\ C_2H_4 - Ir - CH_3$]. Anal.

Calcd for $C_{22}H_{26}NIr$ (496.68): C 53.20, H 5.28, N 2.82. Found: C 53.78, H 5.32, N 2.98.

(η^2-Ethene)[η^5-(8-quinolyl)cyclopentadienyl]rhodium-(I) (3b). A solution of 5 mg (14 μmol) of **3a** in 0.5 mL of C_6D_6 was added to a NMR tube closed by a Teflon valve. The yellow solution was irradiated with the light of a 150 W Hg high-pressure lamp for 8 h, during which the color of the solution turned to blue. The solution was investigated directly by NMR spectroscopy. ^{1}H NMR (C_6D_6): δ 1.86−2.03 (m, 2H, ethene-CH_2); 3.49−3.67 (m, 2H, ethene-CH_2); 4.65−4.70 (m, 2H, Cp-CH); 5.24 (s, free ethene); 6.04 (dd, $^3J(H^3,H^2)$ = 5.1 Hz, $^3J(H^3,H^4)$ = 8.3 Hz, 1H, H^3); 6.33−6.38 (m, 2H, Cp-CH); 6.87 (d, 1H, H^5 or H^7); 6.88 (d, 1H, H^5 or H^7); 6.94 (dd, $^3J(H^4,H^3)$ = 8.3 Hz, $^3J(H,^4H^2)$ = 1.4 Hz, 1H, H^4); 6.99 (ddd, $^3J(H^2,H^3)$ = 5.1 Hz, $^4J(H^2,H^4)$ = 1.4 Hz, ^3J(H,Rh) = 2.5 Hz, 1H, H^2); 7.48 (dd, ^3J(H,H) = 3.4 Hz, ^3J(H,H) = 5.2 Hz, 1H, H^6).

(η^2-Ethene)[η^5-(8-quinolyl)cyclopentadienyl]iridium-(I) (4b). A solution of 5 mg (11 μmol) of **4a** in 0.5 mL of C_6D_{12} was added to a NMR tube closed by a Teflon valve. The yellow solution was irradiated with the light of a 150 W Hg high-pressure lamp for 6 h, during which the color of the solution turned to blue. The solution was investigated directly by NMR spectroscopy. ^{1}H NMR (C_6D_{12}): δ 1.04−1.16 (m, 2H, ethene-CH_2); 2.94−3.04 (m, 2H, ethene-CH_2); 4.83 (pt, 2H, Cp-CH); 5.37 (s, free ethene); 5.95 (pt, 2H, Cp-CH); 6.69 (dd, $^3J(H^3,H^2)$ = 5.5 Hz, $^3J(H^3,H^4)$ = 8.4 Hz, 1H, H^3); 7.23−7.44 (m, 3H, quinoline-CH); 7.71−7.78 (m, 2H, quinoline-CH).

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Supporting Information Available: Molecular structures of **4a** and **6a**; CIF files for **3a**, **4a**, **5a**, and **6a**; ^{1}H NMR and ^{13}C NMR spectra; and UV/vis spectra are available free of charge via the Internet at http://pubs.acs.org.

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