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Rhodium(III) and Iridium(III) Complexes with Quinolyl-Functionalized Cp Ligands: Synthesis and Catalytic Hydrogenation Activity

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Bis(ethene) complexes of rhodium(I) and iridium(I) with 8-quinolylcyclopentadienyl ligands (Cp^Q and Cp^{Q*}) were oxidized by a photochemically induced reaction with chlorine-containing solvents or by treatment with iodine. Upon this oxidation, the quinoline ring rotates and the N donor coordinates to the metal centers. Substitution of the halogenido ligands through acetato groups leads to highly soluble derivatives, in which the acetate moiety acts as a monodentate or bidentate ligand. The new Rh complexes were evaluated as catalysts for the hydrogenation of 1-hexene. The coordinatively saturated complexes show hydrogenation activity without the necessity of external bases. The catalytic activity is highest for the cationic complex $[Cp^{Q*}Rh(O_2CCH_3)]^+PF_6^-$ (**6b**), which contains a bidentate acetato ligand.

Introduction

Cyclopentadienyl ligands with an attached neutral heteroatom donor were studied intensely in the past years due to their ability to modify significantly the properties of metal complexes relative to their analogues with conventional cyclopentadienyl ligands.[1] In most cases, the Cp moiety binds strongly to metals and, depending on the electronic and steric demand of the metal center, the donor function may coordinate strongly or weakly. In the latter case, the hemilabile ligand behavior can lead to reversible protection of a reactive, vacant coordination site so that the coordination and transformation of other molecules is possible.[2] We have incorporated a C_2 spacer as well as an sp^2 nitrogen atom into a rigid heterocycle by using quinolyl-functionalized Cp ligands. Their predefined geometry allows the coordination of the nitrogen atom to the cyclopentadienyl-bonded metal center. As expected, hard metal centers in high oxidation states are strongly bound by the N donor, whereas a much weaker or even no coordination is observed for metal atoms in low oxidation states.[3] We showed that coordinatively unsaturated $CpRh^I$ and $CpIr^I$ complexes are stabilized by hemilabile 8-quinolylcyclopentadienyl ligands and that such systems are catalysts for C–H activation.[4] It is well known that CpRh and CpIr complexes with the metal atoms in oxidation state +III are catalytically active in the hydrogenation of α-olefins.[5] Most of such compounds are dimeric and dissociation opens a vacant coordination site that is necessary for their catalytic activity. In this work we evaluated the catalytic hydrogenation activity of several Rh^{III} complexes with 8-quinolylcyclopentadienyl ligands that are coordinatively saturated due to the intramolecular coordination of the 8-quinolyl unit.

Results and Discussion

Recently we reported the synthesis of bis(η^2-ethene) complexes of rhodium(I) and iridium(I) with 8-quinolyl-functionalized Cp ligands (**1a**–**d**, Scheme 1).[4] Dissolved in aromatic or aliphatic solvents, these complexes lose one ethene ligand upon irradiation with visible light. The resulting mono-η^2-ethene complexes are stabilized by coordination of the hemilabile quinoline moiety. This interaction is very weak, leading to high reactivity of the complexes. Derivatives **2b**–**d** react with aliphatic or aromatic solvents and H/H (or H/D) exchange is catalyzed.[4] For this process an oxidative addition of the solvent molecule is most probable. However, we have not been able to isolate or identify such a species.

When the irradiation of complexes **1a**–**d** is performed in the presence of $Si(CH_3)_3Cl$ or in solvents like $CHCl_3$ or CH_2Cl_2, the metal centers are oxidized leading to dichlorido Rh^{III} (Ir^{III}) derivatives **3a**–**d**. The use of I_2 as an oxidation agent leads to the diiodido derivatives **4a**–**d**.[6]

Whereas the interaction of the relatively hard N donor with the electron rich d^8-metal centers in **2a**–**d** is very weak, the N–M bonding is reinforced upon oxidation of the metal atoms, leading to very stable compounds. In contrast to tetramethyl-substituted compounds **3b/d** and **4b/d**, derivatives **3a/c** and **4a/c** are only sparingly soluble in common organic solvents. In the ^1H NMR spectra of the rhodium complexes, the H^2 proton, which is in the neighborhood of the nitrogen atom, is observed with an additional coupling to

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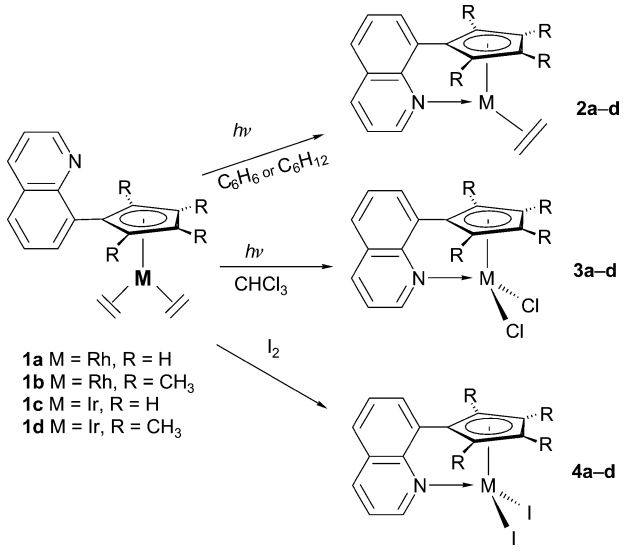


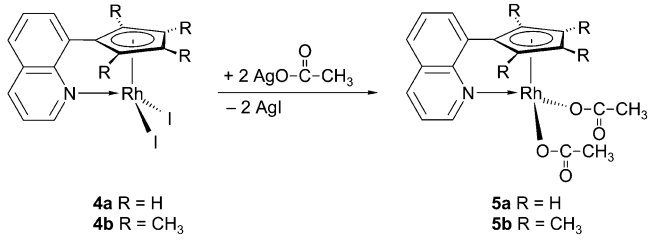
Scheme 1. Preparation of the rhodium(III) and iridium(III) complexes.

the ^{103}Rh center [^3J(Rh,H) = 1.7 Hz]. This coupling proves the N–Rh coordination in solution.

Crystals from **3a** suitable for X-ray analysis were obtained from a solution of **1a** in chloroform that was irradiated with visible light (Figure 1). Due to the low solubility of related iodido complex **4a**, crystallization of this compound was not possible, whereas crystals of tetramethyl derivative **4b** grew easily from a chloroform solution at room temperature.

X-ray analyses established the coordination of the nitrogen atoms to the metal centers. The Rh–N distance does not change significantly from dichlorido to diiodido complexes [**3b**: 2.113(7) Å,[3f] **4b**: 2.111(3) Å] but depends on the substitution at the Cp ring [**3a**: 2.089(1) Å]. This can be explained by the difference in electron density at the metal center caused by the additional methyl groups on the Cp ring. The better donating ability of the tetramethyl Cp ligand leads to a somewhat weaker Rh–N interaction in **3b** relative to that in **3a**. The Rh–C10 distance is significantly shorter than the other Rh–C bonds, showing that the metal atom is not centered below the five-membered ring but slightly shifted towards the heterocycle.

The halogenido ligands in **3b** and **4b** can be substituted by acetate groups upon reaction with silver acetate. This substitution occurs while maintaining the coordination of the nitrogen atom to the metal center. The introduction of the acetato ligands has a great influence on the properties of the metal complexes that is most obvious in the increased solubility of the complexes in organic solvents like chloroform, dichloromethane or toluene. Compounds **5a** and **5b** are even soluble in water (Scheme 2).



Scheme 2. Preparation of (acetato)rhodium complexes **5a** and **5b**.

The IR spectra of the acetato complexes display intense absorptions for the asymmetric valence vibrations of the carboxyl groups at 1616 (**5a**) and 1624 (**5b**) cm^{-1}. The $\nu_{sym}(CO_2)$ bonds are detected between 1309 and 1366 cm^{-1}. This pattern is characteristic for monodentate carboxylato ligands.[7] The Rh–N interaction in **5a** and **5b** is retained in solution, as can be concluded from the Rh–H coupling in the ^{1}H NMR spectra [^3J(Rh,H) = 1.5 Hz].

Crystals of **5b** suitable for X-ray analysis could be obtained by concentrating a dichloromethane solution of the complex (Figure 2). Due to the weaker bonding of the acetato ligands, the Rh–N distance in **5b** [2.079(2) Å] is shorter by 0.03 Å than that in iodo complex **4b**. In the same way, the distances of the central metal to the carbon atoms of the five-membered ring are shorter than those in **4b**. The Rh–O bond lengths [2.104(2) and 2.098(2) Å, respectively] do not vary significantly from those in $(C_5Me_5)Rh(PMe_3)(CH_3COO)_2$ (Table 1).[7]

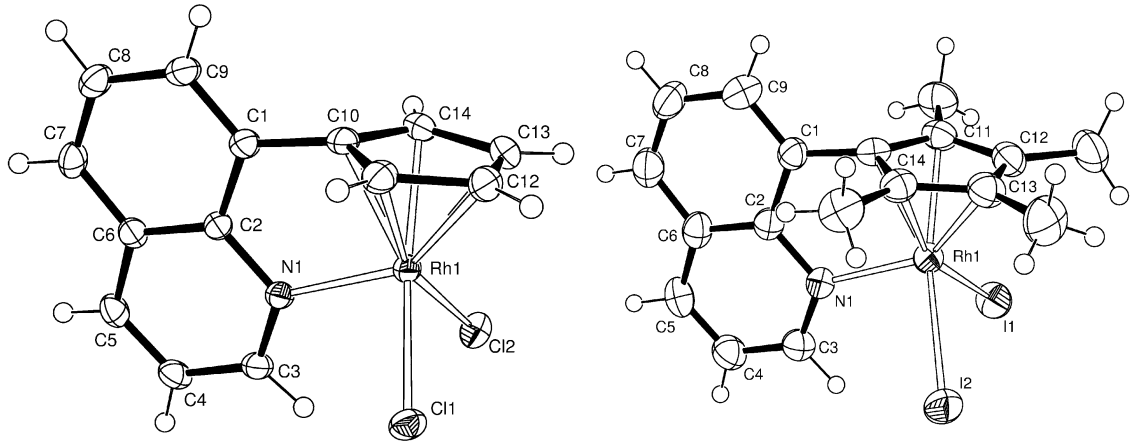


Figure 1. Solid-state molecular structure of **3a** (left) and **4b** (right).

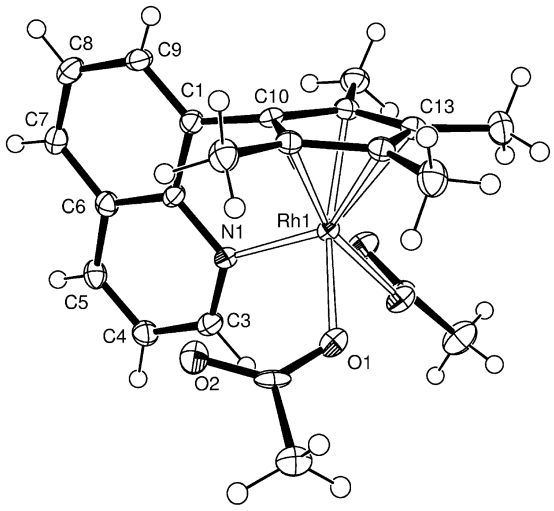
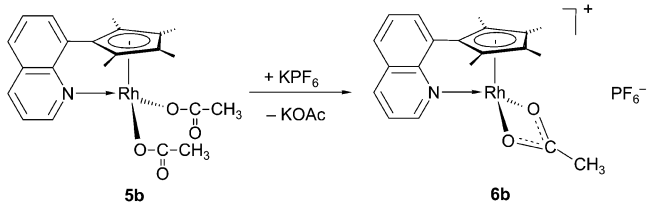


Figure 2. Solid-state molecular structure of **5b**.

Table 1. Selected bond lengths [Å] and angles [°] for **3a**, **4b**, and **5b**.

	3a (X = Cl)	**4b** (X = I)	**5b** (X = OAc)
Rh–N	2.089(1)	2.111(3)	2.079(2)
Rh–X1	2.396(1)	2.705(1)	2.104(2)
Rh–X2	2.377(1)	2.704(1)	2.098(2)
Rh–C10	2.084(2)	2.079(4)	2.067(2)
Rh–C11	2.128(2)	2.152(4)	2.114(2)
Rh–C12	2.190(2)	2.197(4)	2.177(2)
Rh–C13	2.177(2)	2.207(4)	2.177(2)
Rh–C14	2.117(2)	2.138(4)	2.123(2)
N–Rh–X1	89.7(1)	92.6(1)	96.1(1)
N–Rh–X2	91.3(1)	92.8(1)	93.4(1)
X1–Rh–X2	89.4(1)	93.7(1)	79.2(1)
C2–N–Rh	113.3(1)	113.1(3)	113.1(1)

Finally, the reaction of **5b** with KPF_6 leads to the formation of η^2-acetato[η^5-2,3,4,5-tetramethyl-(8-quinolyl)cyclopentadienyl]rhodium(III) (**6b**), as described for related complexes.[7] The chelating coordination of the carboxylato group is clearly shown by the IR spectrum, in which the intense absorptions of the monodentate carboxylato ligands are absent (Scheme 3).

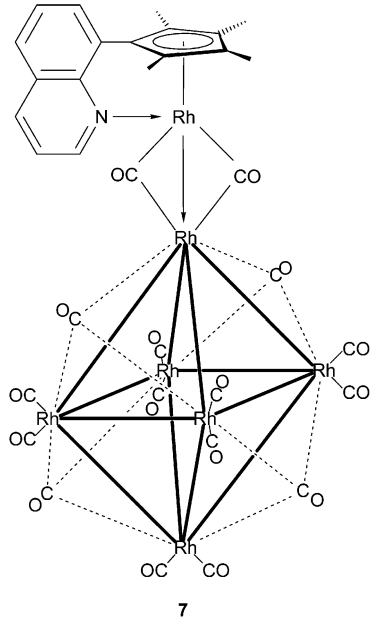


Scheme 3. Synthesis of monoacetato compound **6b**.

Catalytic Hydrogenation of 1-Hexene

Rhodium complexes play an important role as catalysts in the hydrogenation of olefinic and aromatic substrates. The first and most famous example is the well-studied Wilkinson catalyst [$Rh\{P(C_6H_5)_3\}_3Cl$].[8,9] The complex $[Cp^*RhCl_2]_2$ was synthesized and studied by Maitlis et al.[5] They showed that this compound becomes an active hydrogenation catalyst upon the addition of a base (e.g., Et_3N). More recently, a detailed kinetic investigation by Finke and Maitlis et al. proved that under mild conditions $[Cp^*RhCl_2]_2$ is a homogeneous catalyst, whereas more drastic conditions slowly lead to the formation of highly active Rh^0 nanoparticles that are able to catalyze the hydrogenation of benzene.[10]

The compounds described in this work are monomers due to the intramolecular N coordination. This coordination leads to a higher stability of the complexes. Under mild hydrogenation conditions, the formation of Rh^0 species is very unfavorable. We therefore studied their potential as hydrogenation catalysts at 40 °C, 5 bar H_2 pressure within 2 h reaction time. Rhodium complexes **3a**, **4a**, **4b**, **5a**, **5b**, and **6b**, as well as the previously described cluster **7**,[3g] were evaluated in the hydrogenation of 1-hexene. At the end of the hydrogenation reaction, all volatiles were transferred under reduced vacuum for analysis. Mass spectral analysis of the residue showed the presence of starting material.



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The analysis of the reaction products was performed by GC and GC–MS measurements. The results are listed in Table 2. All complexes show activity in the hydrogenation of 1-hexene. Beside the hydrogenation of the terminal olefin, a rearrangement to an internal olefin is catalyzed by the complexes. The highest activity in the catalytic hydrogenation reaction was found in the case of monoacetato complex **6b**. This compound also shows the lowest amount of the rearrangement product 2-hexene. This is probably due to the bidentate coordination mode of the acetato ligand, which allows the generation of a free coordination site without the decoordination of a ligand. With cluster **7**, the rearrangement reaction of the terminal olefin to 2-hexene dominates. This is probably due to a competitive rearrangement reaction at the Rh centers within the Rh_6 cluster. Halogenido complexes **3a** and **4a** show very low solubility in thf. Therefore, complete homogeneous reaction conditions could not be achieved and their activities were found

to be the lowest of all tested compounds. However, a related donor-functionalized cyclopentadienyl rhodium(III) complex is described in the literature to be completely inactive.[11]

Table 2. Results of the hydrogenation reaction of 1-hexene with the quinolyl-substituted complexes as catalysts.[a]

Catalyst	Amount		GC analysis [%][b]	
	[mg] (mmol)	hexane	1-hexene	2-hexene
3a	8.2 (0.02)	9.0	91.0	–
4a	11.2 (0.02)	10.0	90.0	–
4b	12.0 (0.02)	27.1	62.7	10.1
5a	6.6 (0.02)	31.5	41.9	26.6
5b	9.3 (0.02)	37.9	29.2	32.9
6b	8.2 (0.01)	51.3	44.1	4.6
7	37.7 (0.03)	13.2	26.6	60.2

[a] Solvent thf; no added base; glass autoclave pressurized with 5 bar H_2; 40 °C; 2 h reaction time. [b] Peak area of flame ionization detector.

Conclusions

8-Quinolylcyclopentadienyl ligands are ideally suited for chelating coordination to Rh^{III} and Ir^{III} centers. The new complexes are readily obtained by oxidation of the corresponding Rh^{I} and Ir^{I} compounds. Preliminary hydrogenation experiments show that all complexes are active in the hydrogenation of 1-hexene. However, all studied compounds also catalyze, to some extent, the isomerization of 1-hexene into internal hexenes. In comparison to the well-studied $[Cp^*RhCl_2]_2$ complex, there is no need for the addition of an external base. The best complex in this study is the acetato derivative **6b**.

Experimental Section

All experiments were carried out under an atmosphere of dry argon. Solvents were dried by using standard procedures and distilled prior to use. Complexes **1a**–**d** were prepared according to literature procedures.[4] All other reagents were used as purchased. NMR spectroscopy was performed with a Bruker DRX 200 (200.13 MHz for ^1H, 50.32 MHz for ^{13}C) instrument; ^1H NMR spectra were calibrated by using signals of residual protons from the solvent referenced to $SiMe_4$. The numbering of the assigned ^1H NMR signals of the quinoline moiety starts with H^2 for the position next to the N atom. The ^{13}C spectral chemical shifts are reported relative to the ^{13}C solvent signals (referenced to $SiMe_4$). No useful ^{13}C data were obtained for the **a** and **c** derivatives due to the very-low solubility of the complexes. MS was recorded with a Jeol JMS-700 and VG ZAB-2F.

[η^5-(8-Quinolyl)cyclopentadienyl]dichloridorhodium(III) (3a): In a Pyrex glass Schlenk tube a solution of **1a** (100 mg) in $CHCl_3$ or CH_2Cl_2 (15 mL) was irradiated for 4 d with the light of a 150-W Hg high-pressure lamp. After evaporation of the solvent, **3a** was obtained as a dark-red solid (90 mg, 0.25 mmol, 88%). Alternatively, to the photochemically induced oxidation of **1a** by the solvent, $(CH_3)_3SiCl$ (2 equiv.) in a benzene or toluene solution can be used as oxidant during light irradiation. In the latter case, the product precipitates due to its low solubility. ^1H NMR ($CDCl_3$): δ = 5.77 (m, 2 H, Cp-CH), 5.92 (pt, 2 H, Cp-CH), 7.61 [dd, $^3J(H^3,H^2)$ = 5.0 Hz, $^3J(H^3,H^4)$ = 8.4 Hz, 1 H, H^3], 7.70 [dd, $^3J(H,H)$ = 7.9 Hz, $^3J(H,H)$ = 7.3 Hz, H^6], 7.84 [dd, $^3J(H,H)$ = 7.3 Hz, $^4J(H,H)$ = 1.2 Hz, 1 H, H^5 or H^7], 7.96 [dd, $^3J(H,H)$ = 8.1 Hz, $^4J(H,H)$ = 1.3 Hz, 1 H, H^5 or H^7], 8.34 [dd, $^3J(H^4,H^3)$ = 8.5 Hz, $^4J(H^4,H^2)$ = 1.5 Hz, H^4], 8.66 [dt, $^3J(H^2,H^3)$ = 5.0 Hz, $^4J(H^2,H^4)$ = 1.6, $^3J(H,Rh)$ = 1.6 Hz, H^2] ppm. MS (FAB+): *m*/*z* (%) = 330 (100) $[M - Cl]^+$, 295 (68) $[M - 2\ Cl]^+$. $C_{14}H_{10}NRhCl_2$ (366.05): calcd. C 45.94, H 2.75, N 3.83, Cl 19.37; found C 45.65, H 2.87, N 3.82, Cl 19.33.

[η^5-2,3,4,5-Tetramethyl-1-(8-quinolyl)cyclopentadienyl]dichloridorhodium(III) (3b): A procedure analogous to that used for the synthesis of **3a**. Compound **1b** (130 mg, 0.3 mmol) in $CHCl_3$ (20 mL) afforded **3b** (90 mg, 0.21 mmol, 71%) after 4 d of irradiation as a red solid. ^1H NMR ($CDCl_3$): δ = 1.69 (s, 6 H, CH_3), 1.86 (s, 6 H, CH_3), 7.54 [dd, $^3J(H^3,H^2)$ = 5.0 Hz, $^4J(H^3,H^4)$ = 8.5 Hz, 1 H, H^3], 7.73 [dd, $^3J(H,H)$ = 7.6 Hz, $^3J(H,H)$ = 7.1 Hz, 1 H, H^6], 7.80 [dd, $^3J(H,H)$ = 7.1 Hz, $^4J(H,H)$ = 1.9 Hz, 1 H, H^5 or H^7], 7.97 [dd, $^3J(H,H)$ = 7.6 Hz, $^4J(H,H)$ = 1.7 Hz, 1 H, H^5 or H^7], 8.33 [dd, $^3J(H^4,H^3)$ = 8.5 Hz, $^4J(H^4,H^2)$ = 1.7 Hz, 1 H], 8.68 [dt, $^3J(H^2,H^3)$ = 4.9 Hz, $^4J(H^2,H^4)$ = 1.7 Hz, $^3J(H,Rh)$ = 1.7 Hz, 1 H, H^2] ppm. ^{13}C NMR ($CDCl_3$): δ = 8.8, 9.2 (CH_3); 89.5 [d, $^1J(Rh,C)$ = 9.1 Hz, quart. C_{Cp}]; 98.4 [d, $^1J(Rh,C)$ = 6.6 Hz, quart. C_{Cp}]; 107.2 [d, $^1J(Rh,C)$ = 9.1 Hz, quart. C_{Cp}]; 124.2, 127.8, 129.0, 131.0, 137.8, 154.6 ($CH_{quinoline}$); 128.3, 129.7, 157.9 (quart. $C_{quinoline}$) ppm. MS (EI): *m*/*z* (%) = 421 (1) $[M]^+$, 386 (3) $[M - Cl]^+$, 350 (3) $[M - Cl - HCl]^+$, 36 (100) $[HCl]^+$, 35 (17) $[Cl]^+$. HRMS (EI): calcd. for $C_{18}H_{18}NRh^{35}Cl_2$ 420.98712; found 420.98622. $C_{18}H_{18}NRhCl_2$ (422.16).

[η^5-(8-Quinolyl)cyclopentadienyl]dichloridoiridium(III) (3c): A procedure analogous to that used for the synthesis of **3a**. Compound **1c** (20 mg, 0.045 mmol) in $CHCl_3$ (10 mL) afforded **3c** (21 mg, 0.045 mmol, 100%) after 3 d of irradiation as an orange-brown solid. ^1H NMR ($CDCl_3$): δ = 5.77 (pt, 2 H, Cp-CH), 6.13 (pt, 2 H, Cp-CH), 7.60–7.71 (m, 2 H, $H_{quinoline}$), 7.87–7.95 (m, 2 H, $H_{quinoline}$), 8.38 [dd, $^3J(H,H)$ = 8.3 Hz, $^4J(H,H)$ = 1.4 Hz, 1 H, H^4], 8.96 [dd, $^3J(H^2,H^3)$ = 5.1 Hz, $^4J(H^2,H^4)$ = 1.5 Hz, H^2] ppm. MS (FAB+): *m*/*z* (%) = 455 (27) $[M]^+$, 420 (100) $[M - Cl]^+$, 384 (24) $[M - Cl - HCl]^+$. HRMS (EI): calcd. for $C_{14}H_{10}N^{193}Ir^{35}Cl_2$ 454.9820; found 454.9811. $C_{14}H_{10}NIrCl_2$ (455.37).

[η^5-2,3,4,5-Tetramethyl-1-(8-quinolyl)cyclopentadienyl]dichloridoiridium(III) (3d): A procedure analogous to that used for the synthesis of **3a**. Compound **1d** (30 mg, 0.06 mmol) in $CHCl_3$ (15 mL) afforded **3d** (30 mg, 0.06 mmol, 98%) as a orange-brown solid. ^1H NMR ($CDCl_3$): δ = 1.64 (s, 6 H, CH_3), 1.69 (s, 6 H, CH_3), 7.57 [dd, $^3J(H^3,H^2)$ = 5.1 Hz, $^3J(H^3,H^4)$ = 8.5 Hz, 1 H, H^3], 7.69 [dd, $^3J(H,H)$ = 7.3 Hz, $^3J(H,H)$ = 7.9 Hz, H^6], 7.83–7.93 (m, 2 H, H^5 and H^7), 8.35 [dd, $^3J(H,H)$ = 8.5 Hz, $^4J(H,H)$ = 1.5 Hz, 1 H, H^4], 9.00 [dd, $^3J(H^2,H^3)$ = 5.1 Hz, $^4J(H^2,H^4)$ = 1.5 Hz, 1 H, H^2] ppm. $C_{18}H_{18}NIrCl_2$ (511.47).

[η^5-(8-Quinolyl)cyclopentadienyl]diiodidorhodium(III) (4a): I_2 (354 mg, 1.40 mmol) was added to a solution of **1a** (490 mg, 1.40 mmol) in toluene (20 mL). The reaction mixture was stirred overnight, and the precipitated solid was recovered by filtration, washed with toluene followed by hexane, and dried in vacuo. Yield: 717 mg (1.31 mmol, 94%) as a dark-red powder. ^1H NMR ($CDCl_3$): δ = 5.84 (pt, 2 H, Cp-CH), 5.97 (m, 2 H, Cp-CH), 7.46 [dd, $^3J(H^3,H^2)$ = 5.2 Hz, $^3J(H^3,H^4)$ = 8.4 Hz, 1 H, H^3], 7.67 [dd, $^3J(H,H)$ = 7.9 Hz, $^3J(H,H)$ = 7.3 Hz, H^6], 7.83 [dd, $^3J(H,H)$ = 7.3 Hz, $^4J(H,H)$ = 1.4 Hz, 1 H, H^5 or H^7], 7.89 [dd, $^3J(H,H)$ = 8.1 Hz, $^4J(H,H)$ = 1.3 Hz, 1 H, H^5 or H^7], 8.28 [dd, $^3J(H^4,H^3)$ = 8.5 Hz, $^4J(H^4,H^2)$ = 1.5 Hz, H^4], 9.24 [dt, $^3J(H^2,H^3)$ = 5.1 Hz, $^4J(H^2,H^4)$ = 1.5 Hz, $^3J(H,Rh)$ = 1.6 Hz, H^2] ppm. MS (EI): *m*/*z* (%) = 549 (56) $[M]^+$, 422 (100) $[M - I]^+$, 295 (97) $[M - 2\ I]$.

$C_{14}H_{10}I_2NRh$ (548.95): calcd. C 30.63, H 1.84, N 2.55; found C 31.10, H 2.01, N 2.60.

[η⁵-2,3,4,5-Tetramethyl-1-(8-quinolyl)cyclopentadienyl]diiodidorhodium(III) (4b): A solution of iodine (230 mg, 0.91 mmol) in pentane (10 mL) was slowly added to a solution of **1b** (360 mg, 0.88 mmol) in pentane (20 mL). After 2 h the dark-red precipitate was filtered, washed with pentane (2 × 8 mL), and dried in vacuo. Yield: 450 mg (0.74 mmol, 85%) as a dark-red powder. ^{1}H NMR ($CDCl_3$): δ = 2.01 (s, 6 H, CH_3), 2.18 (s, 6 H, CH_3), 7.40 [dd, $^3J(H^3,H^2)$ = 5.0 Hz, $^3J(H^3,H^4)$ = 8.5 Hz, 1 H, H^3], 7.71 [dd, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 7.1 Hz, 1 H, H^6], 7.79 [dd, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.8 Hz, 1 H, H^5 or H^7], 7.92 [dd, ^3J(H,H) = 7.7 Hz, ^4J(H,H) = 1.8 Hz, 1 H, H^5 or H^7], 8.26 [dd, $^3J(H^4,H^3)$ = 8.3 Hz, $^4J(H^4,H^2)$ = 1.5 Hz, 1 H, H^4], 9.18 [dt, $^3J(H^2,H^3)$ = 5.0 Hz, $^4J(H^2,H^4)$ = 1.7 Hz, $^3J(H^2,Rh)$ = 1.7 Hz, 1 H, H^2] ppm. ^{13}C NMR ($CDCl_3$): δ = 10.7, 12.0 (Cp-CH_3); 92.5 [d, ^1J(Rh,C) = 8.2 Hz, quart. C_{Cp}]; 97.8 [d, ^1J(Rh,C) = 6.0 Hz, quart. C_{Cp}]; 108.6 [d, ^1J(Rh,C) = 8.2 Hz, quart. C_{Cp}]; 124.0, 127.6, 129.0, 130.9, 137.3, 158.8 (quinoline-CH); 128.6, 130.0, 158.7 (quart. $C_{quinoline}$) ppm. MS (EI): *m*/*z* (%) = 605 (4) $[M]^+$, 478 (100) $[M - I]^+$, 350 (35) $[M - I - HI]^+$, 175.5 (17) $[M - 2\ I]^{2+}$. HRMS (EI): calcd. for $C_{18}H_{18}INRh$ 477.95392; found 477.95687. $C_{18}H_{18}I_2NRh$ (605.06).

[η⁵-(8-Quinolyl)cyclopentadienyl]diiodidoiridium(III) (4c): A procedure analogous to that used for the synthesis of **4a**. Compound **1c** (40 mg, 0.09 mmol) and iodine (25 mg, 0.10 mmol) afforded **4c** (56 mg, 0.088 mmol, 98%) as an orange solid. MS (EI): *m*/*z* (%) = 639 (13) $[M]^+$, 512 (100) $[M - I]^+$, 384 (29) $[M - I - HI]^+$, 191 (24) $[M - 2\ I - H - Ir]^+$. $C_{14}H_{10}I_2IrN$ (638.27): calcd. C 26.35, H 1.58, N 2.19, I 39.77; found C 26.36, H 1.98, N 2.31, I 40.01.

[η⁵-2,3,4,5-Tetramethyl-1-(8-quinolyl)cyclopentadienyl]diiodidoiridium(III) (4d): A solution of iodine (57 mg, 0.22 mmol) in toluene (5 mL) was added to a solution of **1d** (111 mg, 0.22 mmol) in toluene (50 mL). After 2 h at room temperature, the product was precipitated by the addition of hexane (50 mL), separated by filtration, washed twice with a few mL of hexane, and dried in vacuo. Yield: 148 mg (0.21 mmol, 95%) as a orange powder. ^{1}H NMR ($CDCl_3$): δ = 1.88 (s, 6 H, CH_3), 2.10 (s, 6 H, CH_3), 7.40 [dd, $^3J(H^3,H^2)$ = 5.2 Hz, $^3J(H^3,H^4)$ = 8.4 Hz, 1 H, H^3], 7.69 [dd, ^3J(H,H) = 6.7 Hz, ^3J(H,H) = 8.5 Hz, 1 H, H^6], 7.84–7.91 (m, 2 H, H^5 and H^7), 8.31 [dd, $^3J(H^4,H^3)$ = 8.4 Hz, $^4J(H^4,H^2)$ = 1.4 Hz, 1 H, H^4], 9.52 [dd, $^3J(H^2,H^3)$ = 5.2 Hz, $^4J(H^2,H^4)$ = 1.4 Hz, 1 H, H^2] ppm. ^{13}C NMR ($CDCl_3$): δ = 9.9, 11.6 (Cp-CH_3); 83.7, 90.8, 99.7 (quart. C_{Cp}); 124.9, 128.1, 128.8, 132.0, 137.1, 158.8 (quinoline-CH); 129.5, 130.3, 162.2 (quart. $C_{quinoline}$) ppm. MS (EI): *m*/*z* (%) = 695 (15) $[M]^+$, 568 (100) $[M - I]^+$. HRMS (EI): calcd. for $C_{18}H_{18}I_2N^{193}Ir$ 694.9158; found 694.9123. $C_{18}H_{18}I_2NIr$ (694.38).

Diacetato[η⁵-(8-quinolyl)cyclopentadienyl]rhodium(III) (5a): To a suspension of **4a** (117 mg, 0.35 mmol) in CH_2Cl_2 (20 mL) was added silver acetate (117 mg, 0.70 mmol). The resulting mixture was protected against light and stirred for 15 h. The precipitated AgI was removed by filtration and washed with a few mL of CH_2Cl_2. After evaporation of the solvent, the residue was extracted with toluene (3×). The toluene was evaporated, and product **5a** was obtained as an orange solid. Yield 113 mg (0.27 mmol, 76%). IR (CH_2Cl_2): $\tilde{\nu}$ = 1310 (s), 1366 (s), 1593 (m), 1616 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.10 (s, 6 H, OOC-CH_3), 5.89–5.95 (m, 2 H, Cp-CH), 6.02–6.08 (m, 2 H, Cp-CH), 7.53 [dd, $^3J(H^3,H^2)$ = 5.0 Hz, $^3J(H^3,H^4)$ = 8.4 Hz, 1 H, H^3], 7.65 [dd, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 7.9 Hz, 1 H, H^6], 7.81 [dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, 1 H, H^5 or H^7], 7.90 [dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.2 Hz, 1 H, H^5 or H^7], 8.15 [dt, $^3J(H^2,H^3)$ = 5.1 Hz, $^4J(H^2,H^4)$ = 1.5 Hz, ^3J(H,Rh) = 1.5 Hz, 1 H, H^2], 8.32 [dd, $^3J(H^4,H^3)$ = 8.4 Hz, $^4J(H^4,H^2)$ = 1.5 Hz, 1 H, H^4] ppm. ^{13}C NMR ($CDCl_3$): δ = 23.6 [d, ^3J(Rh,C) = 1.5 Hz, OOC-CH_3]; 75.9 [d, ^1J(Rh,C) = 8.6 Hz, Cp-CH]; 86.1 [d, ^1J(Rh,C) = 6.9 Hz, Cp-CH]; 110.3 [d, ^1J(Rh,C) = 8.1 Hz, quart. C_{Cp}]; 123.7 [d, J(Rh,C) = 1.0 Hz], 128.0, 128.6, 130.7, 138.6, 151.1 (quinoline-CH); 129.3 [d, J(Rh,C) = 1.2 Hz], 130.2, 158.6 [d, J(Rh,C) = 0.7 Hz, quart. $C_{quinoline}$); 177.9 (OOC-CH_3) ppm. MS (FD): *m*/*z* (%) = 413 (60) $[M]^+$, 354 (100) $[M - OOC\text{-}CH_3]^+$. $C_{18}H_{16}NO_4Rh_2$ (413.23).

Diacetato[η⁵-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(III) (5b): A procedure analogous to that used for the synthesis of **5a**. Compound **4b** (290 mg, 0.48 mmol) in CH_2Cl_2 (20 mL) and silver acetate (160 mg, 0.96 mmol) afforded **5b** (216 mg, 0.46 mmol, 96%) as an orange solid. IR (thf): $\tilde{\nu}$ = 1309 (s), 1359 (s), 1590 (m), 1624 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.60 (s, 6 H, CH_3), 1.75 (s, 6 H, CH_3), 2.04 (s, 6 H, OOC-CH_3), 7.45 [dd, $^3J(H^3,H^2)$ = 5.0 Hz, $^3J(H^3,H^4)$ = 8.5 Hz, 1 H, H^3], 7.60–7.72 (m, 2 H, H^6 and H^5 or H^7), 7.90 [dd, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 2.0 Hz, 1 H, H^5 or H^7], 8.12 [dt, $^3J(H^2,H^3)$ = 5.0 Hz, $^4J(H^2,H^4)$ = 1.5 Hz, ^3J(H,Rh) = 1.5 Hz, H^2], 8.26 [dd, $^3J(H^4,H^3)$ = 8.4 Hz, $^4J(H^4,H^2)$ = 1.5 Hz, H^4] ppm. ^{13}C NMR ($CDCl_3$): δ = 9.6, 9.8 (Cp-CH_3); 24.9 [d, ^3J(Rh,C) = 1.7 Hz, OOC-*C*H_3]; 87.8 [d, ^1J(Rh,C) = 10.2 Hz, quart. C_{Cp}]; 97.8 [d, ^1J(Rh,C) = 7.3 Hz, quart. C_{Cp}]; 105.4 [d, ^1J(Rh,C) = 9.6 Hz, quart. C_{Cp}]; 123.5, 127.5, 128.8, 130.6, 137.8, 151.9 (quinoline-CH); 129.8 (2 C), 157.9 (quart. $C_{quinoline}$), 177.1 (OO*C*-CH_3) ppm. MS (FD): *m*/*z* (%) = 469 (51) $[M]^+$, 410 (100) $[M - OOC\text{-}CH_3]^+$. $C_{22}H_{24}NO_4Rh$ (469.34).

η²-Acetato[η⁵-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]-rhodium(III) Hexafluorophosphate (6b): A solution of KPF_6 (85 mg, 0.46 mmol) in water (10 mL) was added to **5b** (108 mg, 0.23 mmol) dissolved in water (20 mL). After 2 h at room temperature the mixture was extracted with dichloromethane (2×). After the removal of the solvent in vacuo, **6b** was obtained as a dark-yellow solid. Yield: 120 mg (0.22 mmol, 94%). IR (thf): $\tilde{\nu}$ = 1379 (w), 1412 (w), 1466 (s), 1507 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.50 (s, 6 H, CH_3), 1.86 (s, 6 H, CH_3), 2.15 (s, 3 H, OOC-CH_3), 7.66–7.77 (m, 2 H, H^2 and H^3), 7.85 [dd, ^3J(H,H) = 7.2 Hz, ^3J(H,H) = 8.2 Hz, 1 H, H^6], 8.13 [dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 1.2 Hz, 1 H, H^5 or H^7], 8.19 [dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.2 Hz, H^5 or H^7], 8.62 [dd, $^3J(H^4,H^2)$ = 8.0 Hz, $^4J(H^4,H^3)$ = 2.0 Hz, H^4] ppm. ^{13}C NMR ($CDCl_3$): δ = 9.2, 9.3 (Cp-CH_3); 23.8 (OOC-*C*H_3); 90.6 [d, ^1J(Rh,C) = 10.2 Hz, quart. C_{Cp}]; 100.7 [d, ^1J(Rh,C) = 7.3 Hz, quart. C_{Cp}]; 106.2 [d, ^1J(Rh,C) = 9.0 Hz, quart. C_{Cp}]; 123.5, 129.4, 130.0, 134.1, 140.9, 150.0 (quinoline-CH); 126.8, 130.4, 157.3 (quart. $C_{quinoline}$), 189.4 (OO*C*-CH_3) ppm. ^{19}F NMR ($CDCl_3$): δ = –73.3 (d, PF_6^-) ppm. ^{31}P NMR ($CDCl_3$): δ = –144.5 (sept., PF_6^-) ppm. MS (FAB): *m*/*z* (%) = 410 (31) $[M - PF_6]^+$, 350 (100) $[M - CH_3CO_2H - PF_6]^+$. $C_{20}H_{21}F_6NO_2PRh$ (555.26).

General Procedure of the Catalytic Hydrogenation of 1-Hexene: The metal complex and thf (5 mL) were placed into a glass autoclave. A solution of 1-hexene (250 mg, 2.97 mmol) in thf (5 mL) was further added, the autoclave was warmed to 40 °C in a water bath, and the hydrogen pressure was raised to 5 bar. After 2 h of stirring, the solution was cooled down to room temperature, and the pressure in the autoclave was slowly released. The solution was separated from the catalyst by condensation in vacuo and analyzed by GC and GC–MS measurements. For quantification, the peak areas from the FI detection were used. The results of the GC–MS measurements are given in Table 2.

Crystal-Structure Determination of 3a, 4b, and 5b: Crystal data of **3a** and **5b** were collected with a Bruker AXS area detector SMART 1000 and that of **4b** with a Siemens Stoe AED2 diffractometer (Mo-K_α radiation, ω-scan). The structures were solved by direct

Table 3. Crystal data and experimental details.

Compound	**3a**	**4b**	**5b**
Empirical formula	$C_{14}H_{10}Cl_2NRh$	$C_{18}H_{18}I_2NRh$	$C_{22}H_{24}NO_4Rh{\cdot}CH_2Cl_2$
Formula weight	366.04	605.04	554.26
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2(1)/c$	$P2_1/c$
Unit cell dimensions:			
a [Å]	8.4793(5)	10.421(5)	8.6340(4)
b [Å]	13.6075(7)	13.707(7)	14.2376(7)
c [Å]	10.8672(6)	12.761(6)	19.0586(9)
α [°]	90	90	90
β [°]	94.545(1)	92.58(2)	100.968(1)
γ [°]	90	90	90
Volume [Å^3]	1249.94(12)	1820.9(15)	2300.0(2)
Z	4	4	4
Density (calcd.) [g cm^{-3}]	1.945	2.207	1.601
Absorption coefficient [mm^{-1}]	1.771	4.325	1.005
F(000)	720	1136	1128
Crystal size [mm^3]	$0.41 \times 0.13 \times 0.09$	$0.40 \times 0.40 \times 0.30$	$0.42 \times 0.30 \times 0.08$
Temperature [K]	190	295	173
θ range for data collection [°]	2.40 to 32.04	1.96 to 27.99	1.80 to 28.32
Index ranges	$-12 \le h \le 12$	$-13 \le h \le 13$	$-11 \le h \le 11$
	$0 \le k \le 20$	$0 \le k \le 18$	$0 \le k \le 18$
	$0 \le l \le 16$	$0 \le l \le 16$	$0 \le l \le 25$
Reflections collected	11715	4392	15619
Independent reflections	4149 [R(int) = 0.0258]	4388 [R(int) = 0.0057]	5550 [R(int) = 0.0270]
Max. and min. transmission	1.0000 and 0.7891	0.787 and 0.603	0.8312 and 0.7270
Parameters	203	272	384
Goodness-of-fit on F^2	1.059	1.009	1.020
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0241, wR_2 = 0.0595	R_1 = 0.0280, wR_2 = 0.0552	R_1 = 0.0282, wR_2 = 0.0710
R indices (all data)	R_1 = 0.0286, wR_2 = 0.0628	R_1 = 0.0440, wR_2 = 0.0592	R_1 = 0.0397, wR_2 = 0.0750
Largest diff. peak and hole [e Å^{-3}]	1.231 and –0.317	0.828 and –0.548	0.688 and –0.510

methods and refined by full-matrix least-squares against F^2 with all reflections by using the SHELXTL program system.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located and refined isotropically. Crystal data and experimental details are listed in Table 3.[13]

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