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Rhodium-carbonyl complexes with a quinolyl functionalized Cp-ligand: synthesis and photochemical activation

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Abstract

Dicarbonyl[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(I) (**1**) was prepared by the reaction of $[Rh(CO)_2Cl]_2$ with 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl-potassium. Irradiation of **1** in chloroform or dichloromethane as solvent leads to the formation of dichloro[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(III) (**2**). When $Rh_6(CO)_{16}$ is present, the cluster adds to the 8-quinolyl-cp-rhodium fragment and the compound [η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium-di-μ-carbonyl-hexarhodiumtetradecacarbonyl (**3**) is formed in 65% yield. The coordination sphere of the rhodium(III) atom in compound **2** and of the rhodium(I) atom in **3** is completed by a coordination of the quinolyl moiety. This was revealed by NMR spectroscopy as well as by X-ray analyses.

Keywords: *N*-Functionalized cyclopentadienyl ligands; Hemilabile ligands; Photochemical activation; Rhodium carbonyl cluster

1. Introduction

Cyclopentadienyl ligands (Cp) bearing a side chain with an additional donor function have been investigated by many research groups during the last decade [1]. Corresponding to the relative strength of interaction of strongly bonding Cp and additional weakly bonding donor groups with the complex center, these systems are classified as hemilabile ligands [2]. According to the Pearson concept [3], *N*-functionalized cyclopentadienyl ligands combine the soft Cp ligand with a hard amino or pyridyl group. This may have a great influence on the structure and the reactivity of their metal complexes. The hard nitrogen donor prefers bonding to transition metals in high oxidation states. Therefore, in 18 valence electron cyclopentadienyl rhodium complexes a nitrogen–metal interaction appears normally only in the case of Rh(III) and is unlikely for Rh(I)-complexes.

The integration of the nitrogen atom in an aromatic system such as quinoline fixes the geometry of the donor functionalized side chain. Different quinolyl functionalized cyclopentadienyl ligands were synthesized in our group and the predefined geometry allows the coordination of the nitrogen atom to the cyclopentadienyl bonded metal center which was shown in many examples [4]. For cobalt carbonyl complexes, a quinoline–metal interaction was only observed in Co(III) complexes but not in Co(I) [4d].

2. Results and discussion

Deprotonation of 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadiene with potassium hydride leads to the formation of the intensively colored 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl potassium salt

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[4a]. Its reaction with tetracarbonyldi-μ-chlorodirhodium(I) yields dicarbonyl[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(I) (**1**) after purification by chromatography as a yellow-orange solid in 56% yield. A blue, very air-sensitive byproduct is obtained as a second fraction. It is identified as the μ-carbonyl-[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]-rhodium(I) dimer (**1a**) by FD mass spectrometry (m/z = 758) and by IR spectroscopy ($\tilde{\nu}(CO) = 1738\ cm^{-1}$). The dicarbonyl complex **1** shows an absorption at $\lambda = 370$ nm in the UV/Vis spectra, whereas the peak of the blue dimer **1a** occurs at $\lambda = 594$ nm (see Scheme 1).

In the IR spectrum of **1** two intensive absorptions for the CO valence vibration ($\tilde{\nu}(CO) = 2019$ and $1955\ cm^{-1}$) are visible, proving that two CO ligands are present. Therefore, the rhodium(I) center is saturated and no coordination of the nitrogen donor can occur. This conclusion was verified by X-ray analysis. Crystals of **1** were obtained from a saturated solution of **1** in toluene at room temperature. The planes of the Cp ring and the aromatic substituent intersect at an angle of 75.4°. The distance of the metal center to the best plane of the Cp-ring is 1.91 Å, the carbonyl carbon atoms and the rhodium atom are 1.85 Å apart. As expected the values do not vary significantly from those in the related complex dicarbonyl (η^5-pentamethylcyclopentadienyl)rhodium(I) [4d] (see Fig. 1).

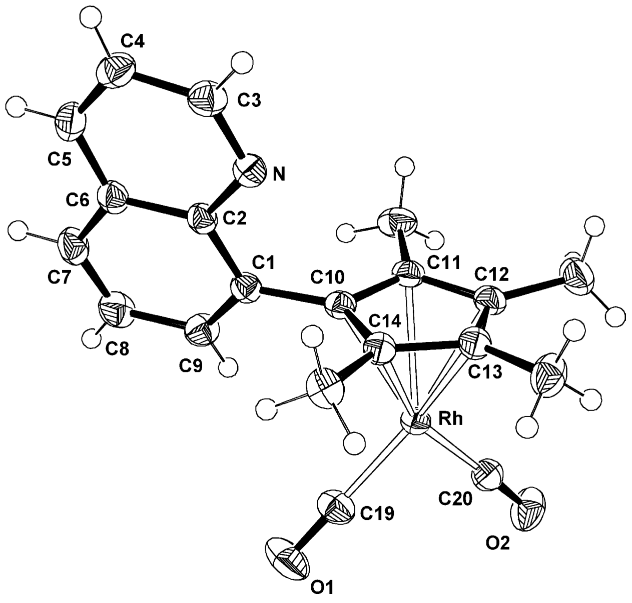
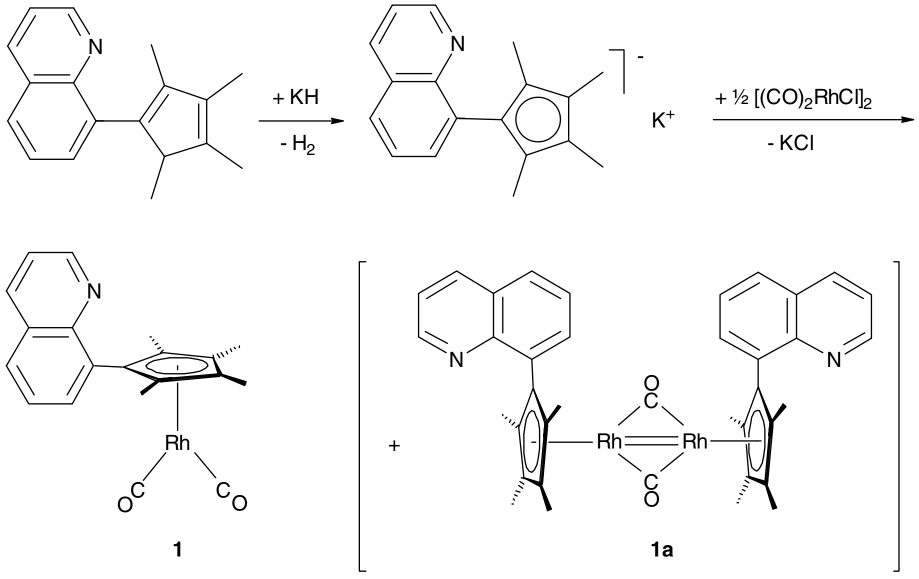


Fig. 1. Solid-state structure of **1**. Selected bond lengths (Å): Rh–C10 2.245(2); Rh–C11 2.277(2); Rh–C12 2.227(2); Rh–C13 2.308(2); Rh–C14 2.279(2); Rh–C_{CO} 1.85; C–O 1.15.

In order to allow for a coordination of the nitrogen donor to the rhodium center, a solution of **1** was irradiated in different solvents with UV light in a quartz as well as in a Pyrex glass Schlenk tube. In aromatic solvents like benzene and toluene, the yellow solution turns green after a few hours. However, ^1H NMR and IR spectroscopy show only signals of the starting compound **1**. Most probably, irradiation of **1** leads to the elimination of one CO ligand and the blue dimer **1a** is formed in a concentration which is too low for NMR and IR spectroscopic identification but high enough to turn the color of the solution from yellow to green. Prolonged irradiation did not lead to the formation of more product although vacuum was applied in order to reduce the CO concentration in solution. The photochemical reaction was followed by UV/Vis spectroscopy which shows the presence of the band at $\lambda = 594$ nm



Scheme 1. Synthesis of the carbonyl complex **1**.

which was also found in the spectrum of the isolated dimer **1a**. When chloroform or dichloromethane is used as solvent, the dichloro rhodium(III) complex **2** is formed quantitatively (see Scheme 2).

The ^{1}H NMR spectrum of **2** shows two singlets at $\delta = 1.66$ and 1.83 for the four methyl groups of the Cp ring. The signals of the quinolyl protons are observed in the typical range between $\delta = 7.51$ and 8.65. The resonance of the H atom, which is neighboring to the nitrogen, is noticeable. Besides the coupling with two aromatic protons this signal shows an additional coupling with the rhodium atom (^3J(Rh,H) = 1.7 Hz). As this coupling constant is of the same magnitude as the ^4J(H,H) coupling, the signal splits in a doublet of triplets. This proves the presence of a nitrogen rhodium interaction in solution.

This interaction was further substantiated by X-ray analysis. Crystals of **2** could be obtained from a solution in benzene at room temperature. The Rh–N distance amounts to 2.113(7) Å. This is slightly shorter than in related complexes with chelating Amino-Cp-ligands [6]. The distance of the metal center to the best plane of the Cp-ring is 1.749 Å, which is significantly shorter than in the Rh(I)compound **1**. The planes of the quinolyl moiety and the Cp ring form an angle of 83.5°. The angles around the nitrogen atom sum up to 359.9° which shows, that the coordination geometry of the nitrogen atom is ideally trigonal planar (see Fig. 2).

In another experiment a solution of compound **1** in dichloromethane or toluene is irradiated by light in the presence of $Rh_6(CO)_{16}$. After two days a dark red solution is obtained which was worked up to obtain red crystals of the new compound **3** (Scheme 2). The X-ray analysis shows that a rhodium-cluster formed where a [η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]-rhodium fragment is connected to a Rh_6-ocathedron by a metal–metal bond and by two bridging CO ligands.

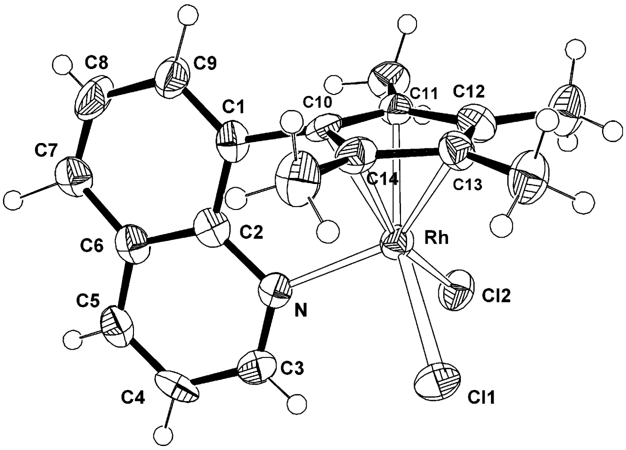
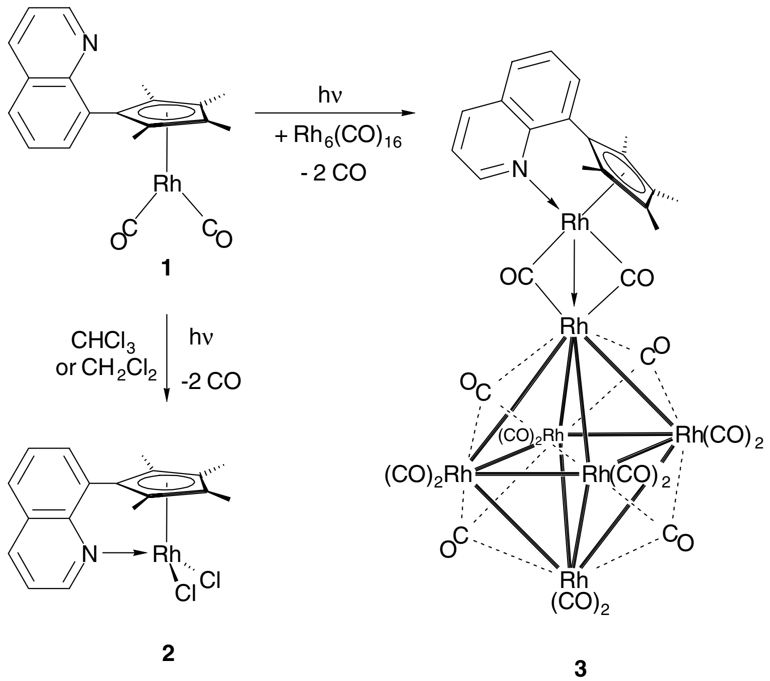


Fig. 2. Solid-state structure of **2**. Selected bond lengths (Å): Rh–N 2.113(7); Rh–Cl1 2.407(3); Rh–Cl2 2.415(2); Rh–C10 2.081(7); Rh–C11 2.121(8); Rh–C12 2.172(8); Rh–C13 2.183(8); Rh–C14 2.126(8).

The distance of the Rh1 atom to the best plane of the five-membered ring is 1.866 Å, which is in the same order as found in the Rh(I) compound **1**. The Rh1–N distance of 2.155(4) Å is significantly longer than in the Rh(III) complex **2** (2.113(7) Å) which indicates a weaker metal–nitrogen interaction in **3**. We conclude from these



Scheme 2. Synthesis of **2** and **3**.

data, that the oxidation state of the Rh1-atom can be regarded as being +I.

The distance between Rh1 and Rh2 lies with 2.761(1) Å in the upper range of the bond distances found for carbonyl bridged Rh–Rh single bonds (2.544–2.822 Å) [7]. However, most of the Rh–Rh bonds in the cluster **3** are longer (up to 2.837(1) Å).

The number of valence electrons of Rh1 amounts already to 18 electrons without the consideration of the metal–metal bond. However, the octahedral cluster framework loses two electrons through the bridging of the two carbonyl ligands, therefore it has no longer the 14 skeleton electrons which are necessary for the *closo* structure of an octahedral cluster [8]. This lack of electrons is compensated by a Rh1 to Rh2 donor bond, as it is also discussed in the literature [9–11]. Thus, the cluster receives two additional electrons from this interaction, so that the number of skeleton electrons sum up to the necessary number of 14 for a *closo* structure.

The two bridging carbonyl ligands are not symmetrical oriented but the distances of C19 and C20 to Rh2 are with 2.024(4) and 2.010(4) Å slightly shorter than to Rh1 (2.042(4) and 2.063(4) Å). This leads also to differences in the Rh–C–O angles. The values for Rh1–C–O (133.5(3)° and 131.0(3)°) and Rh2–C–O (140.9(3)° and 143.7(4)°) differ for about 10° and show the inclination of the CO groups toward the Rh1 atom. Comparable orders of the $M_2(\mu\text{-CO})_2$ unit were also found in $Cp(PPh_3)Rh(\mu\text{-CO})_2RhCp$ [10] and in $Cp^*[P(OMe)_3]Rh(\mu\text{-CO})_2RhCp^*$ [11].

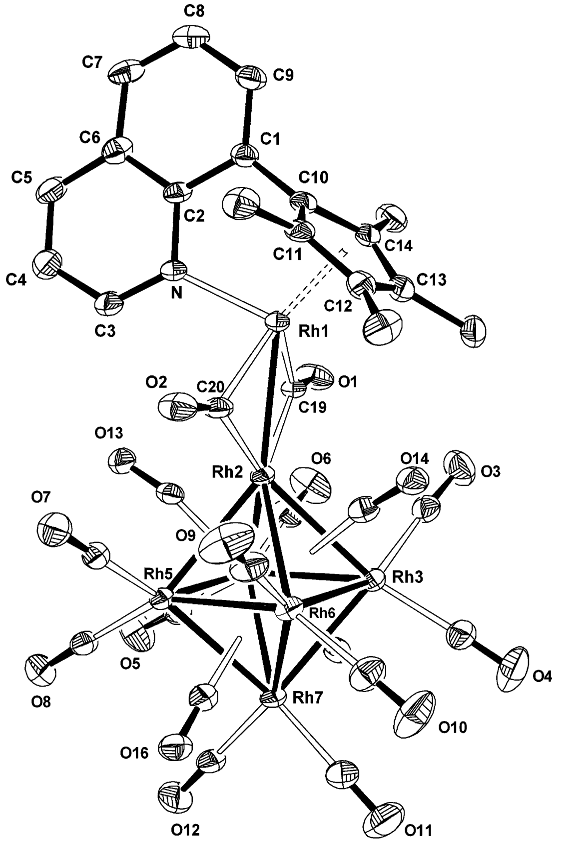


Fig. 3. Solid-state structure of **3**. H atoms are omitted for clarity. For selected bond lengths and angles see Table 1.

Table 1
Selected bond distances (Å) and angles (°) for **3**

Rh1–N	2.155(4)	Rh2–Rh3	2.819(1)	C2–N–Rh1	113.4(3)
Rh1–C10	2.123(4)	Rh2–Rh4	2.827(1)	C3–N–Rh1	129.0(3)
Rh1–C11	2.227(4)	Rh2–Rh5	2.812(1)	C2–N–C3	117.6(4)
Rh1–C12	2.309(4)	Rh2–Rh6	2.832(1)	C9–C1–C2	119.6(4)
Rh1–C13	2.280(4)	Rh3–Rh4	2.704(1)	C9–C1–C10	123.8(4)
Rh1–C14	2.255(4)	Rh3–Rh6	2.806(1)	C2–C1–C10	116.4(4)
Rh1–C19	2.042(4)	Rh4–Rh5	2.792(1)	Rh1–C19–Rh2	85.5(2)
Rh1–C20	2.063(4)	Rh5–Rh6	2.701(1)	Rh1–C19–O1	133.5(3)
Rh1–Rh2	2.761(1)	Rh7–Rh3	2.757(1)	Rh2–C19–O1	140.9(3)
Rh2–C19	2.024(4)	Rh7–Rh4	2.753(1)	Rh1–C20–Rh2	85.3(2)
Rh2–C20	2.010(4)	Rh7–Rh5	2.752(1)	Rh1–C20–O2	131.0(3)
C19–O1	1.156(5)	Rh7–Rh6	2.751(1)	Rh2–C20–O2	143.7(4)
C20–O2	1.150(5)				

Due to the additional rhodium atom Rh1 the Rh_6 cluster framework does not display the ideal octahedral geometry as the related $Rh_6(CO)_{16}$ cluster with metal-metal distances of 2.776(1) Å [12]. The Rh–Rh distances in **3** range from 2.701(1) to 2.832(1) Å, with the distances of the four rhodium atoms to Rh7 (average 2.753 Å) being significantly shorter than to Rh2 (2.823 Å) (see Fig. 3 and Table 1).

The IR spectrum shows an intense peak at 2055 cm^{-1} and three less intense absorptions at 2089, 2077 and 2023 cm^{-1} for the terminal CO ligands. At 1804 and 1777 cm^{-1} two peaks appear for the μ^2- and μ^3-bridged carbonyl ligands.

In the ^1H NMR spectrum, the four methyl groups of the Cp ring exhibit two signals at $\delta = 1.68$ and 1.81. The signal of the H-atom neighboring to the nitrogen atom lies at $\delta = 8.15$ and shows a coupling to the rhodium atom of $^3J(H,Rh) = 1.9$ Hz. This proves the presence of a metal to nitrogen coordination in solution.

3. Conclusions

In the Rh(I)-complex **1**, the nitrogen donor cannot compete with the CO ligands for metal coordination. By irradiation with visible or UV light in aromatic solvents, one CO ligand is removed and the product is stabilized by dimerization. However, the concentration of the dimer remains very low and cannot be increased by longer irradiation. In chloroform or dichloromethane the metal center is oxidized from Rh(I) to Rh(III) and the dichloro complex **2** is formed with no detectable byproduct. In the presence of $Rh_6(CO)_{16}$ irradiation leads to the cluster compound **3** in which the Cp bonded Rh atom can be regarded as Rh(I). The presence of a nitrogen-rhodium interaction was proven by NMR spectroscopy and by X-ray analysis.

4. Experimental

4.1. General remarks

All experiments were carried out under an atmosphere of dry argon. Solvents were dried by standard procedures and distilled prior to use. 2,3,4,5-Tetramethyl-1-(8-quinolyl)cyclopentadiene [4a], tetracarbonyldi-μ-chlorodirhodium(I) [13], and $Rh_6(CO)_{16}$ [14] were prepared according to the literature procedures. All other reagents were used as purchased. – NMR: Bruker DRX 200 (200.1 and 50.3 MHz for ^{1}H and ^{13}C NMR, respectively) and Bruker AC 300 (75.5 MHz for ^{13}C NMR), the ^{1}H 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 triplet ($CDCl_3$) at 77.0 ppm. – IR: Bruker IFS 28. – MS: VG Micromass 7070 H (EI) and Jeol JMS-700 (FD).

4.2. *Dicarbonyl[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(I) (**1**)*

To a suspension of 92 mg (2.3 mmol) of potassium hydride in 20 ml THF were added 570 mg (2.3 mmol) of 2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadiene. After stirring for 3 h at room temperature the violet suspension was transferred to a solution of 440 mg (1.1 mmol) of tetracarbonyldi-μ-chlorodirhodium(I) in 20 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 500 mg (1.22 mmol, 56%) of **1** as a yellow-orange solid, m.p. 103 °C. IR (toluene): ν(CO) = 2019 (s), 1955 (s) cm^{-1}. ^{1}H NMR (C_6D_6): δ = 1.74 (s, 6H, CH_3); 1.81 (d, ^3J(Rh,H) = 0.4 Hz, 6H, CH_3); 6.68 (dd, J(H,H) = 4.2 and 8.3 Hz, 1H); 7.20 (dd, J(H,H) = 7.0 and 8.2 Hz, 1H); 7.37 (dd, J(H,H) = 8.3 and 1.6 Hz, 1H); 7.51 (dd, J(H,H) = 8.3 Hz and 1.9 Hz, 1H); 8.23 (dd, J(H,H) = 7.0 and 1.6 Hz, 1H); 8.56 (dd, J(H,H) = 4.2 and 1.9 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ = 11.4, 11.7 (CH_3); 101.7 (d, ^1J(Rh,C) = 4.0 Hz, quart. C_{Cp}); 102.4 (d, ^1J(Rh,C) = 3.4 Hz, quart. C_{Cp}); 112.3 (d, ^1J(Rh,C) = 4.5 Hz, quart. C_{Cp}); 120.8, 126.2, 128.1, 136.2, 138.4, 150.1 ($CH_{quinoline}$); 128.4, 132.5, 147.6 (quart. $C_{quinoline}$); 194.3 (d, ^1J(Rh,C) = 83.6 Hz, CO). MS (EI), m/z (%): 407 (9) [M^+]; 379 (21) [$M^+ - CO$]; 351 (100) [$M^+ - 2CO$]; 249 (3) [$C_{18}H_{19}N^+$]; 244 (7); 234 (4) [$C_{17}H_{16}N^+$]; 218 (4) [$C_{16}H_{13}N^+$]; 175.5 (8) [$M^{2+} - 2CO$]; 103 (2) [Rh^+] · $C_{20}H_{18}NO_2Rh$ (407.27): Calc. C, 58.98; H, 4.45; N, 3.44. Found: C, 59.32; H, 2.56; N, 3.07%.

4.3. *Dichloro[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium(III) (**2**)*

A solution of 6 mg (0.01 mmol) of **1** in 0.5 ml of $CDCl_3$ was irradiated in an NMR tube by visible light (150 W Hg high pressure lamp). NMR measurements showed that after three days the transformation to a new product was completed. No by-product could by detected. The new product was identified as complex **2**. ^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 6H, CH_3); 1.83 (s, 6H, CH_3); 7.51 (dd, J(H,H) = 5.0 and 8.5 Hz, 1H); 7.70 (dd, J(H,H) = 7.6 and 7.1 Hz, 1H); 7.77 (dd, J(H,H) = 7.1 and 1.9 Hz, 1H); 7.94 (dd, J(H,H) = 7.6 and 1.7 Hz, 1H); 8.30 (dd, J(H,H) = 8.5 and 1.7 Hz, 1H); 8.65 (dt, J(H,H) = 4.9 Hz and 1.7 Hz, J(H,Rh) = 1.7 Hz, 1H). ^{13}C{^{1}H} 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. $C_{quinoline}$). MS (EI), m/z (%): 421 (1) [M^+]; 386 (3) [$M^+ - Cl$]; 350 (3) [$M^+ - Cl - HCl$]; 36 (100) [HCl^+]; 35 (17) [Cl^+].

4.4. *[η^5-2,3,4,5-tetramethyl-1-(8-quinolyl)cyclopentadienyl]rhodium-di-μ-carbonyl-hexarhodiumtetradecacarbonyl (**3**)*

A total of 293 mg (0.28 mmol) of $Rh_6(CO)_{16}$ was added to a solution of 112 mg (0.28 mmol) of **1** in 50 ml of dichloromethane in a Pyrex glass flask. The resulting suspension was irradiated for two days (150 W Hg high pressure lamp), in which its color changed to dark red. After evaporation of the solvent, the residue was redissolved in toluene and filtered through a reversal frit (G4). At −28 °C fine dark crystals precipitated which were filtered off and dried in vacuum; yield 255 mg (0.18 mmol, 65%). IR (toluene): ν(CO) = 1777 (m), 1804 (m), 2024 (m), 2055 (s), 2077 (m), 2089 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 6H, CH_3); 1.81 (d, J(Rh,H) = 0.5 Hz, 6H, CH_3); 7.47 (dd, J(H,H) = 5.1 and 8.4 Hz, 1H); 7.74 (dd, J(H,H) = 7.7 Hz and 7.2 Hz, 1H); 7.82 (dd, ^3J(H,H) = 7.1 and 1.8 Hz, 1H); 7.90 (dd, J(H,H) = 7.8 and 1.8 Hz, 1H); 8.15 (ddd, J(H,H) = 5.1 and 1.5 Hz, J(H,Rh) = 1.9 Hz, 1H); 8.23 (dd, J(H,H) = 8.4 and 1.5 Hz, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 50.3 MHz): δ = 8.3, 8.9 (CH_3); 102.9 (d, ^1J(Rh,C) = 5.4 Hz, quart. C_{Cp}); 106.3 (d, ^1J(Rh,C) = 4.4 Hz, quart. C_{Cp}); 121.1 (d, ^1J(Rh,C) = 6.9 Hz, quart. C_{Cp}); 123.4, 128.2, 128.9, 130.5, 138.7, 155.9 ($CH_{quinoline}$); 129.9, 130.2, 158.9 (quart. $C_{quinoline}$); 180.1–186.5 (m,

Table 2
Crystal data and experimental details

Compound	**1**	**2**	**3**
Empirical formula	$C_{20}H_{18}NO_2Rh$	$C_{18}H_{18}Cl_2NRh \cdot C_6H_6$	$C_{34}H_{18}NO_{16}Rh_7 \cdot 2C_7H_8$
Formula weight	407.26	500.25	1601.13
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	8.5251(1)	8.876(5)	11.3227(2)
b (Å)	9.2094(1)	16.904(9)	13.4111(2)
c (Å)	12.222(1)	14.891(7)	18.9848(3)
α(°)	97.932(1)	90	72.712(1)
β(°)	108.710(1)	101.26(4)	82.524(1)
γ(°)	102.293(1)	90.	69.290(1)
V (Å^3)	865.7(1)	2191(2)	2573.73(7)
Z	2	4	2
D_{calc} (g/cm^3)	1.562	1.516	2.066
T (°C)	−100	−70	−100
Absorption coefficient (mm^{-1})	0.997	1.033	2.257
$F(000)$	412	1016	1544
Crystal size (mm^3)	$0.34 \times 0.26 \times 0.25$	$0.35 \times 0.30 \times 0.15$	$0.40 \times 0.14 \times 0.12$
Θ range for data collection (°)	1.80–28.27	2.34–25.00	1.69–28.31
Index ranges	$-11 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 16$	$-10 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 20$, $0 \leqslant l \leqslant 17$	$-14 \leqslant h \leqslant 15$, $-16 \leqslant k \leqslant 17$, $0 \leqslant l \leqslant 24$
Reflections collected	11,507	3857	34,376
Independent reflections (R_{int})	4206 (0.019)	3857	12534 (0.038)
Maximum and minimum transmission	0.894 and 0.745	1.0000 and 0.8243	0.862 and 0.698
Goodness-of-fit on F^2	1.056	1.024	1.039
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0217$, $wR_2 = 0.0574$	$R_1 = 0.0443$, $wR_2 = 0.0913$	$R_1 = 0.0374$, $wR_2 = 0.0934$
R indices (all data)	$R_1 = 0.0233$, $wR_2 = 0.0583$	$R_1 = 0.0838$, $wR_2 = 0.1016$	$R_1 = 0.0558$, $wR_2 = 0.1054$
Largest difference peak and hole [e Å^{-3}]	0.718 and −0.340	0.46 and −0.42	1.493 and −1.258

$CO_{terminal}$); 221.5 (dd, ^1J(Rh,C) = 42.8 and 36.9 Hz, μ^2-CO); 235.0–237.0 (m, μ^3-CO). MS (FD), *m*/*z* (%): 1416 (100) [M^+].

5. Crystal structure determination of 1, 2, 3

The measurements for **2** were carried out on a Siemens Stoe AED2 diffractometer for **1** and **3** on a Bruker AXS SMART 1000 area detector (Mo Kα radiation, graphite monochromator, $\lambda = 0.71073$ Å, ω-scan). An empirical absorption correction was applied [15]. The structures were solved by direct methods and refined by full-matrix least-squares methods, based on F^2 (SHELXTL 5.1 programs) [16] with anisotropic displacement parameters for non-hydrogen atoms. Hydrogen atoms were located in difference Fourier syntheses (all for **2** and partly for **1** and **3**) and refined. The other hydrogen atoms were inserted in calculated positions. Complex **2** crystallizes with a benzene molecule and **3** with two toluene molecules which are severely disordered. Crystal data and experimental details are listed in Table 2.

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 234085–234087. Copies of these data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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