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# First examples of [Rh(Bident)(CO)(L)] complexes where L is N-donor ligand: Molecular structure of [Rh(8-Oxiquinolinato)(CO)(NH₃)]

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## Abstract

Selective oxidation of one (*trans* to N) carbonyl group in [Rh(8-Oxiquinolinato)(CO)$_2$] with stoichiometric amount of Me$_3$NO in MeCN produces a solution containing [Rh(Oxq)(CO)(Me$_3$N)] and [Rh(Oxq)(CO)(MeCN)]. The ammonia complex, [Rh(Oxq)-(CO)(NH$_3$)], has been prepared by action of NH$_3$ gas on this solution and characterized by IR, $^1$H and $^{13}$C NMR, and X-ray data. Spectral parameters, $v$(CO), $\delta$ $^{13}$C, and $^1J$(CRh), were measured *in situ* for a series of complexes [Rh(Oxq)(CO)(L)] (L = NAlk$_3$, Py, PBu$_3$, PPh$_3$, P(OPh)$_3$, C$_8$H$_{14}$) formed upon action of L on [Rh(Oxq)(CO)(NH$_3$)] in THF. A new $v$(CO) and $\delta$ $^{13}$C based scale of σ-donor/π-acceptor properties of ligands L is proposed including NH$_3$ and CO as the natural endpoints.
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## 1. Introduction

Dozens (or perhaps hundreds) of complexes of general formula [Rh(Bident)(CO)L], where Bident is a monoanionic bidentate ligand and L is a neutral monodentate ligand, were synthesized and widely studied during the last five decades. Remarkably, all these complexes contained ligands L with more or less pronounced π-acceptor properties, such as phosphines, phosphites, arsines, olefins, or carbonyl group (soft bases, in other words). To our knowledge no complexes of this type with N-donor ligands L (or other hard bases) were described up to date. Contrary to phosphines which readily replace one carbonyl group from dicarbonyl complexes, [Rh(Bident)(CO)$_2$], N-donors are not capable of such a reaction, and this fact prevents the direct synthesis of title compounds. We report here on the spectral and structural characterization of the first [Rh(Bident)(CO)(L)] complex with N-donor ligand L in the *cis* to CO position, namely [Rh(Oxq)(CO)(NH$_3$)] (HOxq is 8-hydroxyquinoline), and present the spectral characteristics of some of its analogs, [Rh(Oxq)(CO)(Amine)] (without isolation). To obtain these complexes, we used an ordinary technique of indirect replacement of CO ligand from transition metal carbonyl complexes, stoichiometric oxidation of carbonyl group by one equivalent of trimethylamine oxide with subsequent action of ligand L [1–9].

## 2. Results and discussion

### 2.1. Preparation of parent monocarbonyl moieties

Addition of trimethylamine oxide, Me$_3$NO, (1 mole per Rh) to the suspension of partially solved [Rh(Oxq)(CO)$_2$] in acetonitrile, MeCN, (with carbonyl stretching maxima at 2080 and 2006 cm$^{-1}$) gives brownish-yellow solution.

In its IR spectrum two strong carbonyl bands of comparable intensity are present, at 1972 and 1948 cm$^{-1}$, the second of them being slightly more intense. Removal of solvent yields black solid with a kind of metallic lustre. In the IR spectrum of acetonitrile solution of this solid, the position of the absorption bands remained unchanged, but the maximum at 1972 cm$^{-1}$ showed an increase in relative intensity. Upon addition of Me$_3$N to this solution, or to the primary reaction mixture, the 1948 cm$^{-1}$ band increased in its intensity at the expense of the 1972 cm$^{-1}$ band. At the large excess of Me$_3$N only one maximum (1948 cm$^{-1}$) remained in the spectrum. We assign these bands to the monocarbonyl complexes, [Rh(Oxq)(CO)(MeCN)] (1972 cm$^{-1}$) and [Rh(Oxq)(CO)(Me$_3$N)] (1948 cm$^{-1}$), originated from the coordinatively unsaturated moiety, [Rh(Oxq)(CO)], primary product of the carbonyl ligand oxidation. The changes in the relative intensity of observed bands are obviously due to competition between Me$_3$N originated from amine oxide and solvent MeCN for the vacant coordination position in [Rh(Oxq)(CO)].

$^{13}$C NMR spectrum of the reaction mixture ($^{13}$C enriched preparation of starting dicarbonyl complex, solvent MeCN-$d_3$) showed two doublets from carbonyl carbons, $\delta$ $^{13}$C 189.8 ppm, $^1J$(CRh) 72.4 Hz and $\delta$ $^{13}$C 192.2 ppm, $^1J$(CRh) 80.0 Hz. Comparison of relative intensity variations of the doublets with variations in the IR band intensities allowed us to assign these doublets to [Rh(Oxq)(CO)(MeCN)] and [Rh(Oxq)(CO)(Me$_3$N)], respectively. Substitution of MeCN and Me$_3$N ligands for other nitrogen donors transforms these parent moieties into desired monocarbonyl complexes. For instance, addition of pyridine to the reaction mixture results in the appearance of new strong $^{13}$C doublet, $\delta$ $^{13}$C 192.2 ppm, $^1J$(CRh) 78.2 Hz, and severe decrease or almost complete disappearance of both original doublets. On the action of aliphatic tertiary amines, even in excess, incomplete Me$_3$N replacement was observed. The high values of the spin–spin coupling constants, $^1J$(CRh) > 70 Hz, for observed doublets indicate that in both parent moieties, [Rh(Oxq)(CO)(MeCN)] and [Rh(Oxq)(CO)(Me$_3$N)], carbonyl ligand is located in the *trans* position to the oxygen atom of the oxiquinolinato ligand [10,11]. Thus, we can conclude that carbonyl ligand in the starting dicarbonyl complex is oxidized selectively in the *trans* to N position.
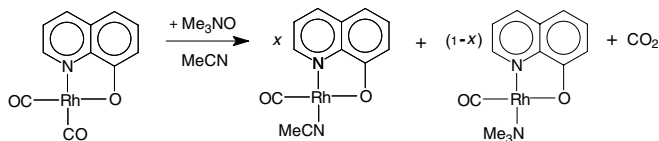
According to our preliminary observations the action of Me$_3$NO on [Rh(Acac)(CO)$_2$] in acetonitrile solution proceeds in like manner. Addition of one mol of Me$_3$NO per rhodium results in the oxidation of one carbonyl group and concurrent formation of two monocarbonyl derivatives, [Rh(Acac)(CO)(MeCN)] and [Rh(Acac)(CO)(Me$_3$N)].

## 2.2. Synthesis and characterization of [Rh(Oxq)(CO)(NH$_3$)]

On bubbling ammonia gas through a reaction mixture prepared as described in Section 2.1, a light-yellow crystalline solid precipitates. The product is soluble in acetone, ethanol, chloroform, but the intensity of carbonyl band is markedly diminished at storage of these solutions. The solution in tetrahydrofurane is more stable under inert atmosphere and thus was used for spectral measurements. The intense IR band of CO stretching vibrations has a maximum at 1942 cm$^{-1}$, a broad band with complicated shape at 3320–3170 cm$^{-1}$ is due to NH stretching vibrations of ammonia ligand. $^{13}$C NMR spectrum of complex contains one doublet at 192.4 ppm, $^1J$(CRh) 75.8 Hz. As mentioned above, the high value of $^1J$(CRh) is indicative of *trans* to O position of carbonyl group, which is in conformity with our conclusion on the structure of the parent monocarbonyl moiety. $^1H$ spectrum of complex contains a group of signals from aromatic oxiquinolinato protons in the region 6.5–8.5 ppm (6H) and a broadened singlet from ammonia protons at 3.1 ppm (3H). On the basis of elemental analysis, IR, and NMR data, we formulate this complex as [Rh(Oxq)(CO)(NH$_3$)] containing NH$_3$ ligand in the *trans* position to the nitrogen atom of oxiquinolinato ligand.

The molecular structure of ammonia complex is shown in Fig. 1. The selected bond lengths and angles are presented in Table 1.

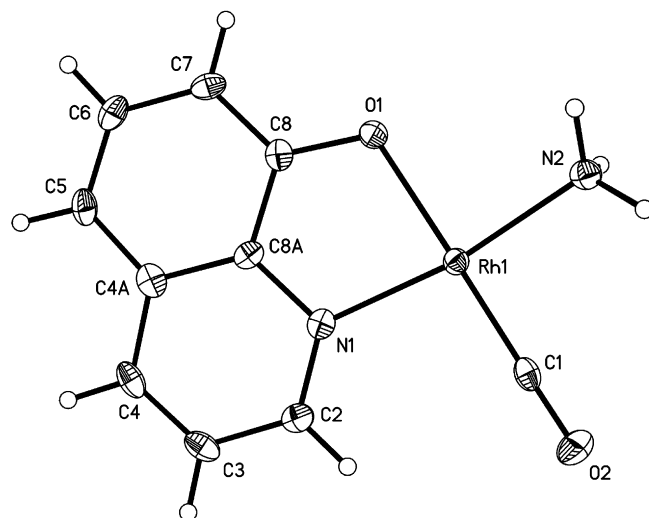Selected bond lengths in [Rh(Oxq)(CO)(L)], L = NH$_3$, PPh$_3$, and P(OPh)$_3$, with the corresponding carbonyl group frequencies are given in Table 2.



Fig. 1. The structure of [Rh(Oxq)(CO)(NH$_3$)] (50% probability ellipsoids).

Table 1
Selected bond lengths (Å) and angles (°) for the complex [Rh(Oxq)-(CO)(NH₃)] with estimated standard deviations in parentheses

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| Rh(1)–C(1) | 1.786(4) | C(1)–Rh(1)–N(1) | 97.30(14) |
| Rh(1)–N(1) | 2.024(3) | N(1)–Rh(1)–O(1) | 81.88(11) |
| Rh(1)–O(1) | 2.058(2) | C(1)–Rh(1)–N(2) | 91.72(13) |
| Rh(1)–N(2) | 2.080(3) | O(1)–Rh(1)–N(2) | 89.04(10) |
| C(1)–O(2) | 1.163(4) | N(1)–Rh(1)–N(2) | 170.67(11) |
| | | C(1)–Rh(1)–O(1) | 178.34(14) |
| | | O(2)–C(1)–Rh(1) | 179.2(3) |

It is seen that increase of π-acceptor ability of ligand L when passing from $NH_3$ to $P(OPh)_3$ leads to substantial decrease of the carbonyl C–O bond length and parallel increase of the $v(CO)$ frequency. Also it might be noticed that the phosphite complex has the longest Rh–CO bond. The lengths of bonds formed by rhodium centre with two donor atoms of oxiquinolinato ligand vary in the opposite directions: Rh–N (*trans* to L) is longest one, whereas Rh–O (*cis* to L) is shortest one for L = $P(OPh)_3$. Noteworthy is the considerable difference between two Rh–N bond lengths in the ammonia complex: 2.080(3) Å for the $sp^3$ hybridized ammonia nitrogen and 2.024(3) Å for the $sp^2$ hybridized oxiquinolinato nitrogen which is capable to π dative interaction with rhodium centre. DFT calculation made by Sizova [15] demonstrated the different order of these bonds in terms of Wiberg bond indexes: 0.333 for Rh–N(ammonia) against 0.397 for Rh–N(oxiquinolinato); the calculated bond lengths were both overestimated, 2.151 and 2.088 Å, respectively, but with remainder (0.063 Å) close to the experimental value (0.056 Å).

### 2.3. Carbonyl group frequencies and ¹³C chemical shifts in the series of [Rh(Oxq)(CO)(L)] complexes

Ammonia ligand in [Rh(Oxq)(CO)(NH₃)] is more or less easily replaced by other N-donors and cyclooctene in THF solutions; P-donors replace it readily. We used these reactions to measure IR and ¹³C NMR spectra of the [Rh(Oxq)(CO)(L)] complexes *in situ*, without isolation of reaction products. The data so obtained are given in Table 3; spectral parameters of parent dicarbonyl complex (L = CO) are included as well.

It can be seen from these data that $v(CO)$ frequencies increase markedly in order of increasing π-acceptor and decreasing σ-donor ability of ligand L from $NH_3$ to CO.

Table 3
Spectral parameters of carbonyl groups in [Rh(8-Oxiquinolinato)(CO)(L)] complexes in THF (*MeCN) solutions

| L | $v(CO)$ (cm$^{-1}$) | $\delta$ ¹³C (ppm) | ¹J(CRh); ²J(CRhP) (Hz) |
|---|---|---|---|
| NH₃ | 1942 | 192.4 | 75.8 |
| NMe₃ | 1944 | 192.5 | 80.5 |
| NMe₃* | 1948 | 192.2 | 80.0 |
| NEt₃ | 1942 | 191.9 | 79.8 |
| NBu₃ | 1942 | 192.0 | 80.0 |
| Py | 1950 | 192.2 | 78.2 |
| PBu₃ | 1952 | 192.4 | 72.2; 22.4 |
| PPh₃ | 1966 | 192.1 | 70.9; 21.8 |
| MeCN* | 1972 | 189.8 | 72.4 |
| C₈H₁₄ | 1972 | 189.4 | 73.8 |
| P(OPh)₃ | 1990 | 189.6 | 68.7; 29.9 |
| CO | 2078, 2004 | 186.5 | 71.8 |
| | | 187.3 | 65.8 |

Within the N-donor part of the series, ligands are ranked in the expected order, $NH_3$, $NR_3$ < Py < MeCN. The order of the P-donor ligands, $PBu_3$ < $PPh_3$ < $P(OPh)_3$, is also quite ordinary. In the middle part of the series, these two ranges of ligands are intermixed. The relative positions of ligands in the whole series, $NH_3$, $NR_3$ < Py, $PBu_3$ < $PPh_3$ < MeCN, $C_8H_{14}$ < $P(OPh)_3$ < CO, apparently are governed by what can be called their "net donating ability" [16] resulted from the interplay of their σ-donor and π-acceptor properties. With reference to ¹³C chemical shifts, the general trend is near to opposite: ammonia, amines, $PBu_3$ and $PPh_3$ comprise a group with high $\delta$ ¹³C values, 192.5–192.1 ppm, whereas strongest π-acceptors, MeCN, $C_8H_{14}$, $P(OPh)_3$ and CO, show markedly lower $\delta$ ¹³C values, 189.8–186.5 ppm. As would be expected, the position of the olefin ligand, $C_8H_{14}$, is close to the week σ-donor/ strong π-acceptor ends of both, $v(CO)$ and $\delta$ ¹³C, series. The endpoints of the whole series of studied ligands correspond to the ligands of antipodal π-acceptor properties: ammonia, ligand with no π-acceptor ability, and carbonyl group, the strongest one among the π-acceptor ligands. It should be remarked that the ¹J(CRh) values for complexes of $NH_3$ and aliphatic amines are considerably higher as compared with complexes of more π-acceptor ligands.

The segmental examples of rhodium(I) complexes containing carbonyl ligand in the *cis* position to two mutually *trans* N-donors were mentioned in the literature. The spectral characteristics we report here for some complexes of this structural type agree well with the data published pre-

Table 2
Selected bond lengths in the crystalline [Rh(Oxq)(CO)(L)] complexes and related carbonyl stretching frequencies (THF solutions)

| L | $v(CO)$ (cm$^{-1}$) (this work) | $r$(C–O) (Å) | $r$(Rh–C) (Å) | $r$(Rh–N) (Å) | $r$(Rh–O) (Å) | Reference |
|---|---|---|---|---|---|---|
| NH₃ | 1942 | 1.163(4) | 1.786(4) | 2.024(3)[b] | 2.058(2) | This work |
| PPh₃[a] | 1966 | 1.155(11) | 1.786(9) | 2.098(9) | 2.042(5) | [13] |
| P(OPh)₃ | 1992 | 1.146 | 1.813(3) | 2.097(2) | 2.022(2) | [14] |

[a] There are two X-ray studies of [Rh(Oxq)(CO)(PPh₃)], published in 1971 [12] and 1981 [13]. We present here the data from the latest one.
[b] 8-Oxiquinolinato nitrogen.

viously [17–19]. Notice also the parallel trends of the spectral parameters in two closely related pairs of complexes, $[Rh(Oxq)(CO)_2]$ vs. $[Rh(Oxq)(CO)(Py)]$ (see Table 3) and $[Rh(Py)Cl(CO)_2]$ vs. $[Rh(Py)_2Cl(CO)]$ [18].

## 3. Concluding remarks

The use of the carbonyl ligand as a spectral probe responding to variations in the electronic situation at the metal centre under the effect of its ligand surrounding, oxidation state, etc. has a long history. Both the CO stretching frequencies and carbonyl $^{13}C$ chemical shifts were employed to build experimental scales of σ-donor/π-acceptor ability (or net donating ability) of ligands. These scales of ligand electronic parameters, from the first ones proposed in 1960–70s, e.g. [20] and including latest one advanced in a new century [21], are reviewed and analyzed in the comprehensive analytical review [16]. Here, we put forward one more scale based on the spectral parameters of a series of rhodium(I) complexes of the general formula $[Rh(Oxq)(CO)(L)]$. We believe this scale attractive because:

(i)  It combines ligands of different classes, like N- and P-donors, olefins, CO, and seems to be prospective with regard to other ligands as well, which are incapable to replace carbonyl group directly from $[Rh(Bident)(CO)_2]$ complexes, but can be introduced into the $[Rh(Bident)(CO)(L)]$ complexes by the indirect method we described here.

(ii)  Spanning a wide range of σ-donor/π-acceptor properties of ligands L, the scale includes ammonia ligand, which seems to provide a natural zero point on the scale of π-acceptor ability.

(iii)  Like the scale [21], it is based on monocarbonyl complexes and thus makes it possible to use immediately the experimentally measured $v(CO)$ values without more or less approximate calculations of force constants. Notice that the proposed scale is based on the series of compounds, which differ from each other in a sole ligand L, not in a pair of mutually *trans* disposed ligands. This may be of some importance taking into account possible effect of changes in the L *trans* to L interaction.

## 4. Experimental

All operations were carried out in atmosphere of dry argon using classical Schlenk techniques. All solvents were purified according to standard procedures [22]. Deuterated solvents were stored over $Al_2O_3$ and distilled prior to use. Gaseous $NH_3$ was prepared by standard method [23]. $Me_3NO \cdot 2H_2O$ was used as purchased from "Avocado Research Chemicals Ltd". $[Rh(Acac)(CO)_2]$ was prepared by published procedure [24]. The $^{13}C$-enriched complex was prepared by action of 50% enriched $^{13}CO$ on a solution of $Rh(Acac)(CO)_2$ in benzene. IR spectra were recorded on a Specord 75 IR instrument ($CaF_2$ windows). NMR spectra (300.1 MHz $^1H$, 121.5 MHz $^{31}P$ {$^1H$}, and 75.5 MHz $^{13}C$ {$^1H$}) were measured on a Bruker DPX-300 spectrometer in MeCN-$d_3$ and THF-$d_8$ as solvents. The $^1H$ chemical shifts were measured with solvent residual protons as internal standard, $\delta$ $^1H$ 1.93 ppm for MeCN; $\delta$ $^1H$ 1.72 ppm for THF. The $^{13}C$ chemical shifts were measured using $^{13}CO$ enriched samples with solvent $^{13}C$ as internal standard ($\delta$ $^{13}C$ 118.10 ppm for MeCN; $\delta$ $^{13}C$ 25.26 ppm for THF). The $^{31}P$ chemical shifts were measured with 85% phosphoric acid as external standard, $\delta$ $^{31}P = 0.0$ ppm. Elemental analyses were performed with Hewlett–Packard 185 microanalyzer.

### 4.1. Synthesis of $[Rh(Oxq)(CO)_2]$

To the solution of $[Rh(Acac)(CO)_2]$ (0.516 g, 2.0 mmol) in benzene (20 ml) the solution of 8-hydroxyquinoline (0.304 g, 2.1 mmol) in benzene (5 ml) was added. The dark brown crystals with violet lustre appeared immediately. In 30 min the crystals were collected by filtration, washed with hexane and dried under reduced pressure. Yield: 0.576 g (95%). The product was identified by IR and $^{13}C$ NMR as $[Rh(Oxq)(CO)_2]$. IR ($CHCl_3$): 2084 and 2010 $cm^{-1}$ [25,26]. The $^{13}C$-enriched complex was prepared by the same way using $[Rh(Acac)(^{13}CO)_2]$. $^{13}C$ NMR ($CDCl_3$): 184.5 ppm, $^1J(CRh)$ 71.4 Hz and 186.0 ppm, $^1J(CRh)$ 67.6 Hz [27]. In THF $v(CO)$ 2078 and 2004 $cm^{-1}$; $^{13}C$ NMR (THF-$d_8$): 186.5 ppm, $^1J(CRh)$ 71.8 Hz and 187.3 ppm, $^1J(CRh)$ 65.8 Hz.

### 4.2. The interaction of $[Rh(Oxq)(CO)_2]$ with $Me_3NO$

To a suspension of $[Rh(Oxq)(CO)_2]$ (0.303 g, 1.0 mmol) in acetonitrile (10 ml) a fresh prepared solution of $Me_3NO \cdot 2H_2O$ (0.111 g, 1.0 mmol) in acetonitrile (18 ml) was added dropwise on stirring at 0 °C. The dark suspension gradually turned into brownish-yellow solution, which was then stirred throughout 1 h at room temperature. IR of the reaction mixture thus obtained (solution **I**) in the carbonyl stretching area: $v(CO)$ 1972 and 1948 $cm^{-1}$; the last band is more intense. The intensity of carbonyl bands in the spectrum of solution **I** remained unchanged for one to two days. Removal of solvent from a part of solution **I** (5 ml) yielded black solid with metallic lustre; this product, being freshly prepared, is soluble in MeCN and THF. In the IR spectrum of its solution in MeCN, the band at 1972 $cm^{-1}$ is more intense, and the band at 1948 $cm^{-1}$ is less intense then in solution **I**. IR spectrum of this product in THF shows only one $v(CO)$ band at 1944 $cm^{-1}$. The $^{13}C$ enriched sample of reaction mixture (solution **II**) was prepared in a similar manner from $^{13}C$ enriched $[Rh(Oxq)(^{13}CO)_2]$. $^{13}C$ NMR: (MeCN-$d_3$) 189.8 ppm, $^1J(CRh)$ 72.4 Hz and 192.2 ppm, $^1J(CRh)$ 80.0 Hz; (THF-$d_8$) 192.5 ppm, $^1J(CRh)$ 80.5 Hz.

## 4.3. Substitution reactions

### 4.3.1. Interaction with NMe₃

To a portion (4 ml, 0.14 mmol Rh) of the solution **I** (see Section 4.2) the solution of NMe$_3$ (0.017 g, 0.29 mmol) in MeCN (0.2 ml) was added at 0 °C (molar ratio NMe$_3$:Rh ≈ 2). In resulting reaction mixture the $v$(CO) band at 1948 cm$^{-1}$ increased in relative intensity as compared to the spectrum of solution **I**. When the large excess of NMe$_3$ was added (molar ratio NMe$_3$:Rh ≈ 10), only the strong band at 1948 cm$^{-1}$ remained. Upon replacement of solvent by THF, $v$(CO) band at 1944 cm$^{-1}$ appeared. Upon action of the large excess of NMe$_3$ on solution **II** (molar ratio NMe$_3$:Rh ≈ 10), $^{13}$C NMR (MeCN-$d_3$): 192.2 ppm, $^1J$(CRh) 80.0 Hz; (THF-$d_8$) 192.5 ppm, $^1J$(CRh) 80.5 Hz.

### 4.3.2. Interaction with NBu₃

To a portion of the solution **I** (4 ml, 0.14 mmol Rh) NBu$_3$ (0.263 g, 1.42 mmol) was added (molar ratio NBu$_3$:Rh = 10). Yellowish-brown solution was obtained. After 18 h IR (MeCN): $v$(CO) 1972 cm$^{-1}$ (weak) and 1948 cm$^{-1}$ (strong). On removal of solvent under reduced pressure yellowish-brown residue was obtained and then dissolved in THF (3 ml). IR: $v$(CO) 1942 cm$^{-1}$ (strong). The analogous operation was performed with a portion of the solution **II** (molar ratio NBu$_3$:Rh = 10). $^{13}$C NMR (THF-$d_8$): 192.5 ppm, $^1J$(CRh) 80.5 Hz (weak) and 192.0 ppm, $^1J$(CRh) 80.0 Hz.

### 4.3.3. Interaction with pyridine

To a portion of the solution **I** (4 ml, 0.14 mmol Rh) pyridine (0.023 g, 0.21 mmol) was added (molar ratio Py:Rh = 1.5). After 1 h MeCN was removed under reduced pressure. Yellowish-brown residue was obtained and then dissolved in MeCN or THF. IR: $v$(CO) 1954 cm$^{-1}$ (MeCN); 1950 cm$^{-1}$ (THF). The analogous operation was performed with a portion of the solution **II** (molar ratio Py:Rh = 1.5). $^{13}$C NMR (MeCN-$d_3$): 191.8 ppm, $^1J$(CRh) 78.8 Hz; (THF-$d_8$) 192.2 ppm, $^1J$(CRh) 78.2 Hz.

### 4.3.4. Interaction with PBu₃

To a portion of the solution **I** (4 ml, 0.14 mmol Rh) PBu$_3$ (0.028 g, 0.14 mmol) was added (molar ratio PBu$_3$:Rh = 1). After 1 h MeCN was removed under reduced pressure, and yellowish-brown residue was dissolved in MeCN or THF. IR: $v$(CO) 1954 cm$^{-1}$ (MeCN); $v$(CO) 1952 cm$^{-1}$ (THF). The analogous operation was performed with a portion of the solution **II**. At the molar ratio PBu$_3$:Rh = 0.75, $^{13}$C NMR (THF-$d_8$): 192.4 ppm, $^1J$(CRh) 72.2 Hz, $^2J$(CRhP) 22.4 Hz and weak signal 192.5 ppm, $^1J$(CRh) 80.5 Hz.

### 4.3.5. Interaction with cyclooctene

To a portion of the solution **I** (4 ml, 0.14 mmol Rh) C$_8$H$_{14}$ (0.046 g, 0.4 mmol) was added (molar ratio C$_8$H$_{14}$:Rh ≈ 3). After 1 h solvent was removed under reduced pressure, and yellowish-brown residue was dissolved in MeCN or THF. IR: $v$(CO) 1974 cm$^{-1}$ (MeCN);

$v$(CO) 1972 cm$^{-1}$ (THF). The analogous operation was performed with a portion of the solution **II** (molar ratio C$_8$H$_{14}$:Rh ≈ 3). $^{13}$C NMR (THF-$d_8$): 189.4 ppm, $^1J$(CRh) 73.8 Hz. At the molar ratio C$_8$H$_{14}$:Rh = 1, 189.4 ppm, $^1J$(CRh) 73.8 Hz and 192.5 ppm, $^1J$(CRh) 80.5 Hz.

## 4.4. [Rh(Oxq)(CO)(NH₃)]

Through the reaction mixture obtained like the solution **I** from [Rh(Oxq)(CO)$_2$] (0.727 g, 2.4 mmol) in MeCN (15 ml) and Me$_3$NO · 2H$_2$O (0.266 g, 2.4 mmol) in MeCN (42 ml) a stream of ammonia gas was passed at 0 °C during 0.5 h. A light-yellow crystalline solid precipitated gradually. The reaction mixture was left to stand for 1 h, and then the precipitate was collected by filtration under argon, washed with MeCN and dried under reduced pressure. Yield: 0.396 g (56%). After concentration of mother liquid to 5 ml, 0.050 g of product was filtered more; total yield 0.446 g (64%). Anal. Calc. for C$_{10}$H$_9$N$_2$O$_2$Rh: C, 41.12; H, 3.08; N, 9.59; Rh, 35.24. Found: C, 41.10; H, 3.31; N, 9.72; Rh, 35.84%. The crystalline complex is stable on keeping under argon atmosphere. The complex is soluble in acetone, ethanol, chloroform, THF, but only THF solution is sufficiently stable (under inert atmosphere). IR (THF): $v$(CO) 1942 cm$^{-1}$, $v$(NH) 3320–3170 cm$^{-1}$ (broad). $^1$H NMR (THF-$d_8$): a group of signals in the region $\delta$ $^1$H 6.5–8.5 ppm (oxiquinolinato protons, 6H), a broadened singlet at $\delta$ $^1$H 3.1 ppm (NH$_3$, 3H). For $^{13}$C NMR measurement was used the sample prepared by the same way from $^{13}$C enriched [Rh(Oxq)(CO)$_2$]. $^{13}$C NMR (THF-$d_8$): 192.4 ppm, $^1J$(CRh) 75.8 Hz.

## 4.5. Ammonia ligand replacement from [Rh(Oxq)(CO)(NH₃)]

### 4.5.1. Interaction with NEt₃

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) NEt$_3$ (0.010 g, 0.1 mmol) was added (molar ratio NEt$_3$:Rh = 2). After 1 h IR: $v$(CO) 1942 cm$^{-1}$. $^{13}$C NMR (THF-$d_8$): 191.9 ppm, $^1J$(CRh) 79.8 Hz (very weak) and 192.4 ppm, $^1J$(CRh) 75.8 Hz (starting complex).

### 4.5.2. Interaction with NBu₃

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) NBu$_3$ (0.018 g, 0.1 mmol) was added (molar ratio NBu$_3$:Rh = 2). After 1 h IR: $v$(CO) 1942 cm$^{-1}$. The analogous operation was performed with the solution of $^{13}$C enriched [Rh(Oxq)(CO)(NH$_3$)] (molar ratio NBu$_3$:Rh = 10). $^{13}$C NMR (THF-$d_8$): 192.0 ppm, $^1J$(CRh) 80.0 Hz (week) and 192.4 ppm, $^1J$(CRh) 75.8 Hz (starting complex).

### 4.5.3. Interaction with pyridine

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) pyridine (0.006 g, 0.076 mmol) was added (molar ratio Py:Rh = 1.5). After removal of

the solvent under reduced pressure, the residue was dissolved in THF. IR: $v$(CO) 1950 cm$^{-1}$. $^{13}$C NMR (THF-$d_8$): 192.2 ppm, $^1J$(CRh) 78.2 Hz.

#### 4.5.3.1. Direct action of pyridine on [Rh(Oxq)(CO)$_2$].

To the suspension of [Rh(Oxq)(CO)$_2$] (0.013 g, 0.043 mmol) in toluene (5 ml) pyridine (0.004 g, 0.05 mmol) (molar ratio Py:Rh $\approx$ 1.2) was added. After about 3 h at 25 °C in the IR spectrum of reaction mixture only $v$(CO) bands of starting [Rh(Oxq)(CO)$_2$] (2078, 2002 cm$^{-1}$) were observed. After heating (1 h at 80 °C), in the IR spectrum of reaction mixture along with $v$(CO) bands of [Rh(Oxq)(CO)$_2$] a new band at 1950 cm$^{-1}$ appeared. At further heating all carbonyl bands became weak. At heating [Rh(Oxq)(CO)$_2$] with excess pyridine (molar ratio: Py:Rh = 3) intensities of all $v$(CO) bands decreased rapidly.

#### 4.5.4. Interaction with PBu$_3$

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) PBu$_3$ (0.008 g, 0.04 mmol) was added; molar ratio PBu$_3$:Rh = 0.8. IR: $v$(CO) 1952 cm$^{-1}$. $^{31}$P NMR (THF-$d_8$): 34.1 ppm, $^1J$(PRh) 156.0 Hz. $^{13}$C NMR (THF-$d_8$): 192.4 ppm, $^1J$(CRh) 72.2, $^2J$(CRhP) 22.4 Hz and 192.4 ppm, $^1J$(CRh) 75.8 Hz (week, starting complex). Spectral data agree with $^{13}$C NMR parameters of [Rh(Oxq)(CO)(PBu$_3$)] obtained by action of PBu$_3$ on [Rh(Oxq)(CO)$_2$]. $^{13}$C NMR (CDCl$_3$): 190.9 ppm, $^1J$(CRh) 72.4, $^2J$(CRhP) 22.6 Hz.

#### 4.5.5. Interaction with PPh$_3$

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) PPh$_3$ (0.0104 g, 0.04 mmol) in THF (0.5 ml) was added (molar ratio PPh$_3$:Rh = 0.8). IR: $v$(CO) 1966 cm$^{-1}$. $^{31}$P NMR (THF-$d_8$): 42.4 ppm, $^1J$(PRh) 166.3 Hz. $^{13}$C NMR (THF-$d_8$): 192.1 ppm, $^1J$(CRh) 71.3 Hz, $^2J$(CRhP) 21.8 Hz and 192.4 ppm, $^1J$(CRh) 75.8 Hz (week, starting complex). Spectral data agree with reported early for [Rh(Oxq)(CO)(PPh$_3$)] [27a,28].

#### 4.5.6. Interaction with P(OPh)$_3$

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) P(OPh)$_3$ (0.0124 g, 0.04 mmol) was added (molar ratio P(OPh)$_3$:Rh = 0.8). IR: $v$(CO) 1990 cm$^{-1}$. $^{31}$P NMR (THF-$d_8$): 126.2 ppm, $^1J$(PRh) 282.2 Hz. $^{13}$C NMR (THF-$d_8$): 189.4 ppm, $^1J$(CRh) 69.0 Hz, $^2J$(CRhP) 29.9 Hz and.192.4 ppm, $^1J$(CRh) 75.8 Hz (week, starting complex). Spectral data agree with $^{31}$P NMR [14] and with $^{13}$C NMR (CDCl$_3$) for [Rh(Oxq)(CO)(P(OPh)$_3$)] obtained by action of P(OPh)$_3$ on [Rh(Oxq)(CO)$_2$]: 188.0 ppm, $^1J$(CRh) 70.0 Hz, $^2J$(CRhP) 29.4 Hz.

#### 4.5.7. Interaction with cyclooctene

To the solution of [Rh(Oxq)(CO)(NH$_3$)] (0.015 g, 0.05 mmol) in THF (2 ml) C$_8$H$_{14}$ (0.06 g, 0.05 mmol) was added (molar ratio C$_8$H$_{14}$:Rh = 1). After 1 h IR: $v$(CO) 1972 and 1942 cm$^{-1}$. $^{13}$C NMR (THF-$d_8$): 189.4 ppm, $^1J$(CRh) 73.8 Hz (week) and 192.4 ppm, $^1J$(CRh) 75.8 Hz (starting complex). At the molar ratio C$_8$H$_{14}$:Rh = 3. After 1 h IR: $v$(CO) 1972 cm$^{-1}$. In $^{13}$C NMR spectrum the same doublets, but of close relative intensities, were observed. At the molar ratio C$_8$H$_{14}$:Rh $\approx$ 10, $^{13}$C NMR (THF-$d_8$): 189.4 ppm, $^1J$(CRh) 73.8 Hz. Spectral data agree with reported early for [Rh(Oxq)(CO)(C$_8$H$_{14}$)] [29].

### 4.6. X-ray crystal structure determination

Crystal of [Rh(Oxq)(CO)(NH$_3$)] (C$_{10}$H$_9$N$_2$O$_2$Rh, $M = 292.10$) orthorhombic, space group $P2_12_12_1$, at $T = 100$ K: $a = 4.4251(8)$ Å, $b = 13.774(2)$ Å, $c = 15.956(3)$ Å, $V = 972.5(3)$ Å$^3$, $Z = 4$, $F(000) = 576$, $d_{calc} = 1.995$ g/cm$^3$, $\mu = 1.734$ mm$^{-1}$. Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1K CCD detector ($\lambda$(Mo K$\alpha$)-radiation, graphite monochromator, $\varphi$ and $\omega$ scan mode, $\theta_{max} = 27.6°$) and corrected for Lorentz and polarization effects and for absorption [30]. The structure was determined by direct methods and refined by a full-matrix least-squares technique on $F^2$ with anisotropic displacement parameters for all non-hydrogen atoms. The absolute structure was objectively determined by the refinement of Flack parameter which has become equal to 0.04(4). The hydrogen atoms were placed in calculated positions and refined in riding mode with fixed thermal parameters. The final $R$-factors are $R_1 = 0.0265$ for 2029 independent reflections with $I > 2\sigma(I)$ and $wR_2 = 0.0465$ for all 2229 independent reflections. All calculations were carried out using the SHELXTL-PLUS program (PC Version 5.10) [31].

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### Appendix A. Supplementary material

CCDC 651127 contains the supplementary crystallographic data for [Rh(Oxq)(CO)(NH$_3$)]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.09.022.

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