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Chloro(3- or 5-aminoquinoline)rhodium(I) organocomplexes showing N–H···Cl and C–H···Rh weak interactions

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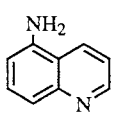
Abstract

The reaction of $[RhCl(L_2)]_2$ with 3- or 5-aminoquinoline (*n*-aqui) gives neutral tetracoordinated rhodium(I) compounds $[RhCl(L_2)(n\text{-aqui})]$ (L_2 = COD, *n*-aqui = 5-aqui **1**, 3-aqui **2**; L_2 = NBD, *n*-aqui = 5-aqui **3**, 3-aqui **4**) with *n*-aqui bonded through the heterocyclic nitrogen. Structures of complexes **1** and **2** were determined by single crystal X-ray diffraction. Both compounds show intermolecular hydrogen bond N–H···Cl linkages and contain doubly hydrogen-bonded 'dimer pairs'. In **1** additional N–H···Cl interactions between the 'dimer pairs' gives double chains along the *y*-axis. Compound **2** crystallises as diethyl ether adduct, **2**·Et_2O and the 'dimer pairs' form N–H···O hydrogen bonds with solvation molecules. For **1** a C–H···Rh interaction is observed in the crystal. In solution, compounds **1**–**4** undergo intra- and intermolecular processes that are discussed. The reaction of $[RhCl(CO)_2]_2$ with *n*-aqui gives monomers $[Rh(Cl)(CO)_2(n\text{-aqui})]$ (*n*-aqui = 5-aqui **5**, 3-aqui **6**) with *n*-aqui bonded through the heterocyclic nitrogen when Rh:*n*-aqui = 1:1 or the dimer compound with bridging ligand, $[Rh(Cl)(CO)_2]_2(\mu\text{-5-aqui})$ (**7**) when Rh:5-aqui = 2:1.

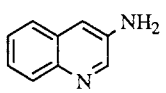
Keywords: Rhodium; Aminoquinoline; Hydrogen bonding; Fluxionality

1. Introduction

The study of weak interactions such as hydrogen bonding and C–H···M interactions is a topic of current interest. Hydrogen bond formation may promote assembly between mononuclear components and introduce a high degree of directionability that may confer special properties on the resulting molecular material [1–4]. These materials can be obtained using ligands which contain a metal-coordination site along with hydrogen donor sites if hydrogen bond acceptors are available [5], and hydrogen bonds in which coordinated halides act as acceptors are now well established [6]. The C–H···M agostic interaction in d^6-ML_5 systems is well established but the nature of the C–H···M interaction in d^8-square-planar systems remains unclear [7]. 8-substituted-quinolines appear to be suitable ligands to afford this type of interaction due to their structure and acidic properties [7–9] and recently the ability of the unsubstituted 8-quinolyl ligand to behave as η^2-chelate towards osmium has been reported [10]. We set out to study the behaviour of 8-unsubstituted, non-chelating, aminoquinoline ligands such as 3- or 5-aminoquinoline (*n*-aqui) towards rhodium(I) chlorocomplexes, in order to determine the possibility of C–H···M interactions involving the H8 of the quinoline ring and the capability of N–H···Cl hydrogen bond formation involving the chlorine bonded to the rhodium atom to afford intermolecular association. We report now on the reactions of 5- or 3-aqui with $[Rh(L_2)Cl]_2$ compounds (L_2 = 1,5-cyclooctadiene, norbornadiene; L = CO) and the solution behaviour of the obtained complexes. The crystal structures of the compounds containing 1,5-cyclooctadiene are also reported.



5-aminoquinoline (5-aqui)



3-aminoquinoline (3-aqui)

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2. Results and discussion

$[RhCl(L_2)]_2$ (L_2 = COD, NBD) react with 5-aqui or 3-aqui, irrespective of the stoichiometric ratios (Rh:*n*-aqui = 1:1 or 2:1), to afford $[RhCl(L_2)(n\text{-aqui})]$ complexes **1**–**4** that behave as non-electrolytes in acetone solution (L_2 = COD, *n*-aqui = 5-aqui **1**, 3-aqui **2**; L_2 = NBD, *n*-aqui = 5-aqui **3**, 3-aqui **4**). In all cases the absorptions due to ν(N–H) are not displaced towards lower frequencies, with respect to the free ligands and the chemical shifts of the NH_2 protons in the ^{1}H-NMR spectra are consistent with non-coordinating groups. Therefore **1**–**4** should be tetracoordinated compounds containing monodentate *n*-aqui bonded through the heterocyclic nitrogen. The appearance of several bands in the ν(N–H) region of the IR spectrum suggests the existence of hydrogen bonding. To confirm this and the possibility of the existence of C–H···Rh interactions, we solved the crystal structures of the compounds containing 1,5-cyclooctadiene, **1** and **2**.

In both compounds **1** and **2** the rhodium atom is bonded to the centroids of the double bonds of the COD ligand, to the heterocyclic nitrogen and to the chlorine atom as shown in Fig. 1 and Fig. 2, respectively. Selected bond lengths and angles are collected in Table 1. Bond lengths to the rhodium atom lie in the expected ranges [11–16], the distances of the midpoints of the double bonds from the rhodium centre, Rh–C1112 and Rh–C1516, are equal within experimental error. In compound **1**, H8 of the quinoline ring could be located in a Fourier syntheses. The Rh···H8 distance (2.452 Å) is in the range in which M···H interactions have been reported [7,8,14,17,18]. This distance in addition to the Rh···H8–C8 angle (133°) and the *trans* L–M–L angles (177.0(2) and 175.9(2)°) correspond to a weak interaction similar to those found in other rhodium(I) square-planar complexes [18,19]. Furthermore the C7–C8–H8 and C8A–C8–H8 angles of 136.2 and 105.0°, respectively, are in agreement with this interaction. In compound **2**, due to the quality of the crystallographic data it was not possible to locate and refine the position of the H8 proton from the electronic density maps. Repeated attempts to obtain more suitable crystals were unsuccessful and the crystal undergoes some decomposition under X-ray radiation. Therefore H8 was located geometrically. The Rh···H8 distance is short, 2.81 Å, and is in the range in which M···H interactions have been reported in the literature [20].

The coordination geometry at the rhodium atom can be regarded as square-planar if only the coordinated heterocyclic nitrogen, the chlorine atom and the C=C bonds are considered. In **1** the plane containing the olefinic carbons is practically perpendicular to the mean coordination plane, the corresponding angle being 88.9(2)°. The N-donor group is as expected practically planar and the N2–H2 group is almost included in this plane (C4–C4A–C5–N2 torsion angle of 2.0(6)°). The same features are observed for **2**. The close to planar aminoquinoline fragment forms a dihedral angle with the mean coordination plane of 84.04(4) and 84.9(4)° for **1** and **2**, respectively [21]. The rhodium atom is placed very slightly above ($-0.0048(4)$ Å) the plane defined by the basal donor atoms, Cl–N1–C1112–C1516 and suggest that the Rh···H8–C interaction is of the hydrogen bond type.

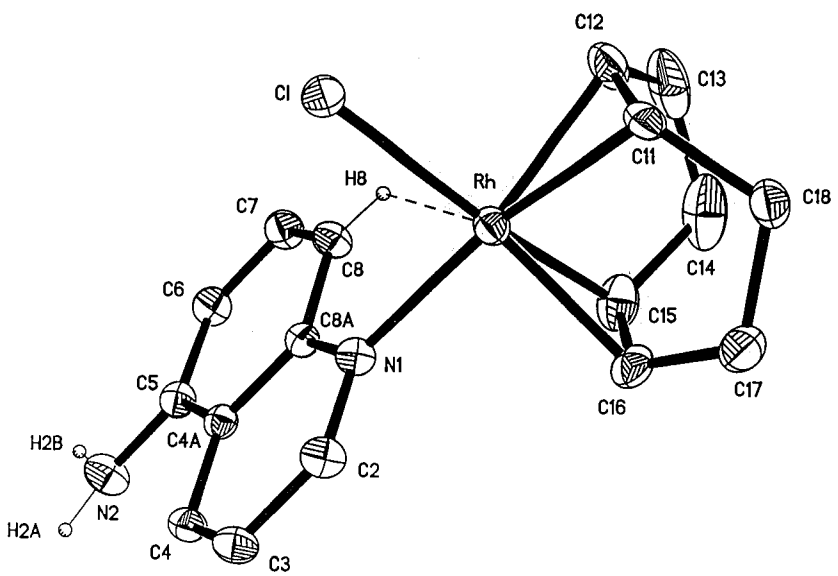


Fig. 1. ORTEP view of molecule **1** showing the atomic numbering (25% probability ellipsoids).

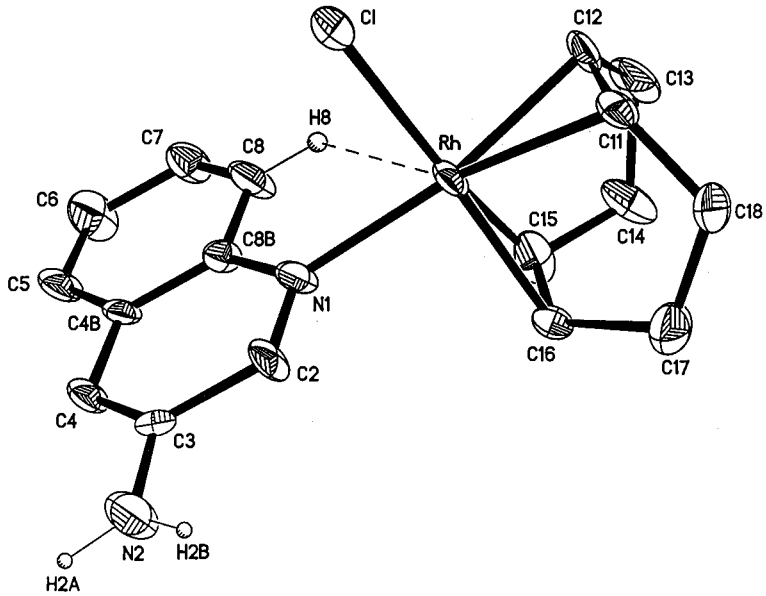


Fig. 2. ORTEP view of molecule **2** showing the atomic numbering (25% probability ellipsoids). The solvent molecule and the hydrogen atoms except three have been omitted for clarity.

The data in Table 2 confirm the existence of intermolecular hydrogen bond N–H···Cl linkages in compounds **1** and **2**. The ranges of distances and angles agree with those reported in the literature [3,6,22,23]. Compound **2** crystallises as diethyl ether solvate, $[RhCl(COD)(3\text{-aqui})]\cdot Et_2O$. Each NH_2 group forms two hydrogen bonds, one with the chlorine atom of a vicinal molecule and another one with the oxygen atom of the solvent molecule. The hydrogen bond interactions between two vicinal molecules leads to 'dimer pairs' with two N–H···Cl linking units as depicted in Fig. 3. The Cl···N distance is 3.35(2) Å (Cl···H2A, 2.55 Å) and the N–H2A···Cl angle is 155° while the N···O distance of 3.23(3) Å (H2B···O, 2.47 Å) indicates a very weak interaction and the N–H2B···O angle is 148°. In compound **1** the chlorine atoms show two interactions, so that each chlorine atom in a 'dimer pair' interacts further with one of the remaining amino hydrogens in another 'dimer pair' to give zig–zag double chains along the *y*-axis as shown in Fig. 4. The Cl···N distances are equal within experimental error, 3.482(4) and 3.476(4) Å (Cl···H, 2.58 and 2.59 Å) and the N–H···Cl angles are 167.5 and 162.5°, respectively. These results indicate that 5-aqui is more suitable than 3-aqui to give extended hydrogen-bonded double chains.

In solution these weak interactions appear to be lost, neither ^{103}Rh–H nor ^{103}Rh–C coupling constants are observed [9] and the chemical shifts are not affected by concentration changes. The disposition of the ligands as shown in Figs. 1 and 2 leads to a situation in which the

Table 1
Selected bond distances (Å) and angles (°) for **1** and **2** [a]

	1	**2**
Rh–N1	2.113(3)	2.12(2)
Rh–C11	2.137(4)	2.16(2)
Rh–C12	2.110(5)	2.12(2)
Rh–C15	2.101(4)	2.01(3)
Rh–C16	2.106(4)	2.06(2)
Rh–C1122	2.006(5)	2.01(3)
Rh–C1516	1.985(4)	1.94(4)
Rh–Cl	2.371(4)	2.359(9)
C11–C12	1.389(7)	1.43(3)
C15–C16	1.394(7)	1.30(3)
Rh···H8	2.452	2.81
C8–H8	0.95	0.92
Cl–Rh–C1112	92.6(2)	91.5(9)
Cl–Rh–C1516	177.0(2)	179(1)
N1–Rh–C1112	175.9(2)	178(1)
N1–Rh–C1516	91.4(2)	94(1)
Rh···H8–C8	133	115

[a] C1112 and C1516 are the midpoints between the olefinic bonds.

Table 2
Hydrogen bond geometry (Å) and angles (°) for **1** and **2** [a]

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	<DHA
*Compound **1***				
N2–H2A···Cl′	0.92	2.58	3.482(4)	167.5
N2–H2B···Cl″	0.92	2.59	3.476(4)	162.5
*Compound **2***				
N2–H2A···Cl‴	0.86	2.55	3.35(2)	155
N2–H2B···O23‴	0.86	2.47	3.23(3)	148

[a] (′) $-x$, $-y+1$, $-z+1$; (″) $-x$, $y-1/2$, $-z+1/2$; (‴) $-x+1$, $-y$, $-z+1$.

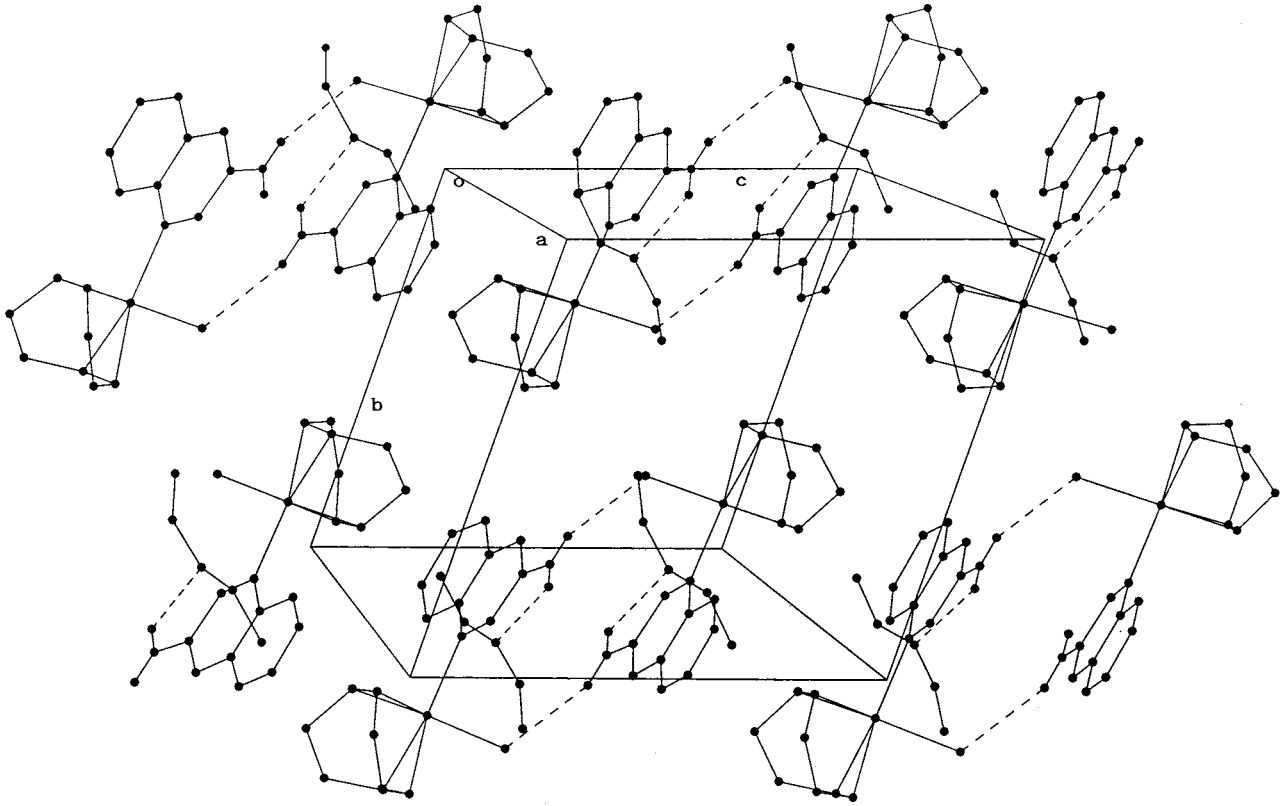


Fig. 3. Packing of the molecules showing the hydrogen bonds for **2**.

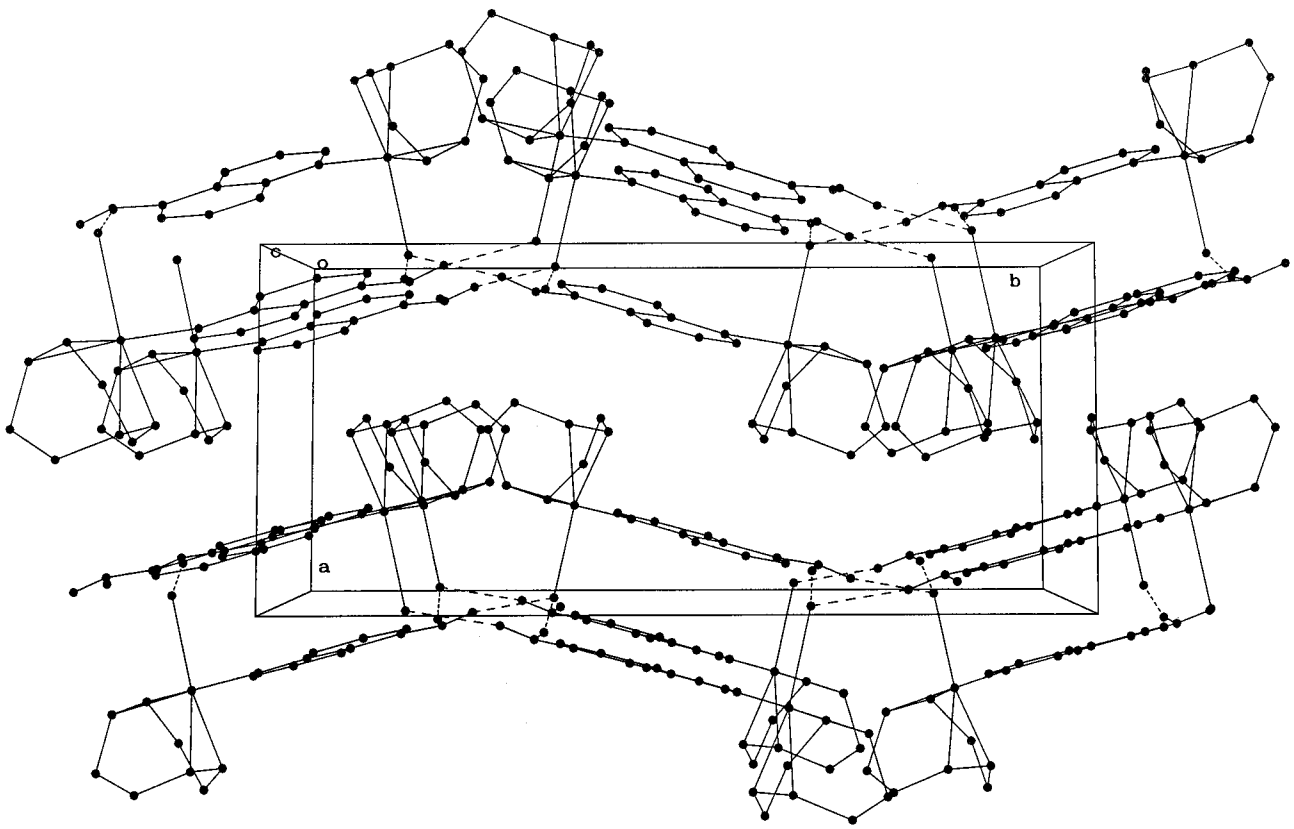
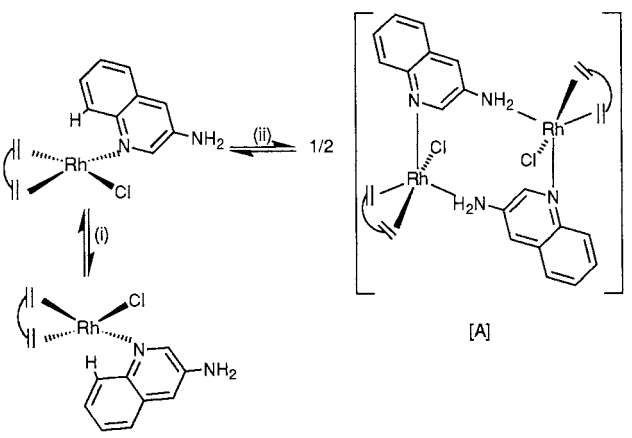


Fig. 4. Packing of the molecules viewed along the *y*-axis for **1**.

four olefinic protons are inequivalent. As would be expected for this arrangement the ^{1}H-NMR spectrum at 216 K of complex **2** shows four olefinic signals. However, complexes **1**, **3** and **4** show only two olefinic resonances. In all the complexes **1**–**4** the H8 resonance of the quinoline ring is sharp and displaced towards lower fields with respect to the free ligand by ca. 1.6 ppm, most likely due to the anisotropic effect of the metal atom. On raising the temperature the four olefinic resonances of complex **2** collapse into two resonances at 271 K. This behaviour indicates that only **2** has a rigid structure at low temperature while **1**, **3** and **4**, and also **2** at higher temperatures, undergo a fluxional process that makes the protons of each carbon–carbon double bond mutually equivalent. We believe that this process involves rotation of the aminoquinoline ligand around the Rh–N bond [16] (Scheme 1(i)). Compound **2**, containing the more sterically demanding ligands, 1,5-cyclooctadiene and 3-aqui, should have the highest activation barrier for this process. Free energy of activation for this intramolecular exchange at coalescence ($\Delta G_c^{\ddagger}$) for **2** was calculated and gives 13.6 ± 0.5 kcal mol^{-1}. Fig. 5 shows the variable-temperature ^{1}H-NMR spectra of **2**.

At higher temperatures compounds **1**–**4** undergo a second process so that at 335 K the ^{1}H-NMR spectra show only one resonance for the olefinic protons along with a broad resonance due to the H8 protons of the quinoline ring displaced towards higher fields with respect to the values at low temperature. The $\Delta G_c^{\ddagger}$ value for this second process is lower for the compounds containing norbornadiene than for complexes containing 1,5-cyclooctadiene (Table 3). In order to obtain additional information, we have used bandwidths analysis [24] of the olefinic resonances shown in Fig. 6 for complex **3**. In complex **4** overlapping of the olefinic and amino resonances occurs in the fast exchange region, therefore, in this case we used the intensities method [24] and the reference signal chosen was that due to the methine protons of norbornadiene. Linear least-squares analysis of the Eyring plots for the kinetic data provides values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (Table 3) for both compounds. The significant negative value for the entropy of activation excludes dissociation of ligands during the fluxional process and suggests an associative process. A dynamic equilibrium with a tbp intermediate such as [A], formed via coordination of the amino group can exchange effectively the olefinic moieties (Scheme 1(ii)).

The carbonylated compound $[RhCl(CO)_2]_2$ also reacts with aminoquinolines (5-aqui) or (3-aqui) but now the nature of the products depends on the stoichiometric ratios (Rh:*n*-aqui = 1:1 or 2:1) employed. When using Rh:*n*-aqui = 1:1 ratios, both ligands afford tetracoordinated $[RhCl(CO)_2(n\text{-aqui})]$ complexes that behave as non-electrolytes in acetone solution and contain the ligand linked to the metal atom via the heterocyclic nitrogen (*n*-aqui = 5-aqui **5**, 3-aqui **6**). The IR spectra show the expected absorptions due to two mutually *cis* CO groups and non-coordinated NH_2 groups. The



Scheme 1.

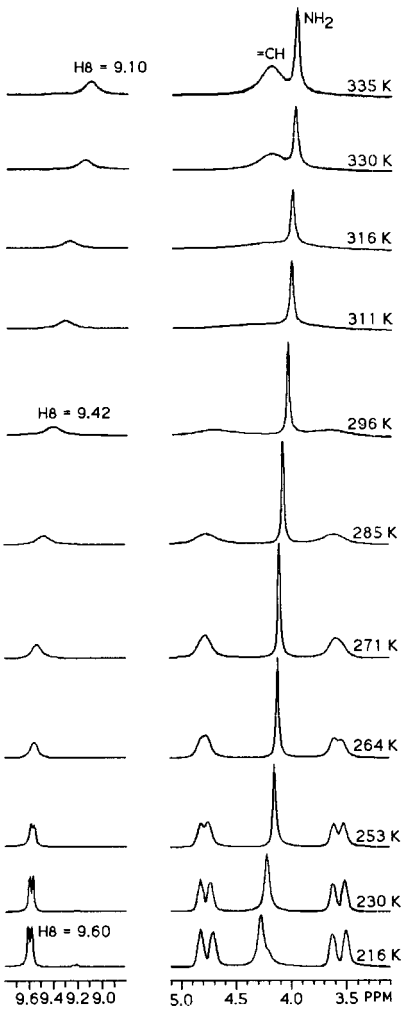


Fig. 5. Variable temperature ^{1}H-NMR study (in $CDCl_3$) at 299.949 MHz of **2** showing the H8 region of 3-aqui and the olefinic region of cyclooctadiene.

Table 3
Activation parameters for equilibrium (ii)

Complex	T_c (K)	$\Delta G_c^{\ddagger}$ (kcal mol^{-1}) [a]	$\Delta H^{\ddagger}$ (kcal mol^{-1}) [b]	$\Delta S^{\ddagger}$ (eu) [b]
RhCl(COD)(5-aqui) (**1**)	324 ± 1	14.8 ± 0.5		
RhCl(COD)(3-aqui) (**2**)	311 ± 1	14.2 ± 0.5		
RhCl(NBD)(5-aqui) (**3**)	264 ± 1	12.2 ± 0.5	9.1 ± 0.8	−12.2 ± 2.7
RhCl(NBD)(3-aqui) (**4**)	253 ± 1	11.6 ± 0.5	5.4 ± 0.6	−23.8 ± 2.8

[a] Calculated from T_c and Δv_0 with the equations $k_c = (\pi/\sqrt{2})\Delta v_o$ and $\Delta G_c^{\ddagger}/RT_c = \ln(\sqrt{2}R/\pi Nh) + \ln(T_c/\Delta v_o)$. Errors shown are propagated from the estimated errors in T_c.
[b] Calculated from the slopes and intercepts of the Eyring plots. Error ranges listed correspond to one standard deviation.

^{1}H-NMR spectra are consistent with the presence of free amino groups in solution and show the resonance due to the H8 protons of the quinoline ring sharp and are also displaced towards a lower field, though the displacement (ca. 0.8 ppm) is lower than for diolefinic compounds. Decrease of the chemical shifts of this type of protons when going from diolefinic to dicarbonylated derivatives has also been observed by other authors [19]. The corresponding ^{13}C-NMR spectra show two doublets due to two different CO groups bonded to rhodium and *trans* to chlorine or nitrogen respectively.

When using Rh:*n*-aqui = 2:1 ratios, 5-aqui affords $[Rh_2Cl_2(CO)_4(\mu\text{-5-aqui})]$ (**7**) that behaves as non-electrolyte in acetone solution and according to the analytical and spectral data is a 16-electron dimer species with bridging aminoquinoline linked to one metal atom via the heterocyclic nitrogen and to the other metal atom via the amino group. The IR spectrum shows two absorptions due to the CO groups and two absorptions due to the coordinated NH_2 at a lower frequency than in the free ligand. The ^{1}H-NMR spectrum shows the resonance of the amino group at a lower field than in the free ligand, and a resonance due to the H8 proton of the quinoline ring also displaced towards a lower field (1.0 ppm). Furthermore the H4 proton of the quinoline ring is also displaced towards a lower field (0.35 ppm) and this slight deshielding can be due to the anisotropic effects of the metal bonded to the amino group. The ^{13}C-NMR spectrum shows, at room temperature (r.t.), a broad signal due to the CO groups undergoing a dynamic process in solution; unfortunately, spectra at lower temperatures could not be obtained due to low solubility. FAB MS measurements also confirm the dimer nature of this compound.

3. Conclusions

The synthesis of $[Rh(Cl)(L_2)(n\text{-aqui})]$ containing 5- or 3-aqui ligands has been achieved. In the solid state the crystal structure of **1** shows that the H8 atom of the quinoline ring is pointing towards the rhodium centre with a Rh···H distance of 2.45 Å, in the range reported in the literature for Rh···H–C interactions. Compounds **1** and **2** show N–H···Cl hydrogen bond interactions that give 'dimer pairs'. 5-aqui is more suitable than 3-aqui to give extended hydrogen-bonded double chains via interaction of 'dimer pairs'. The diolefinic compounds undergo in solution intra- and intermolecular processes. At low temperatures rotation of aminoquinoline around the Rh–N bond occurs. At high temperatures the thermodynamic parameters exclude ligand dissociation and point to an associative process.

4. Experimental

The preparation of the metal complexes was carried out at r.t. under nitrogen by standard Schlenk techniques. $[\{Rh(L_2)Cl\}_2]$ [25] was synthesised according to known procedures. Solvents were dried by standard procedures. The ligands 3- and 5-aqui (Aldrich) were used as received.

Microanalysis were carried out using a Perkin–Elmer 240C microanalyser. Conductivities were measured in acetone solution with a Metrohm E 518 conductimeter. IR spectra were recorded on a Nicolet FTIR 740 spectrophotometer in the range 4000–50 cm^{-1} using KBr pellets or Nujol mulls between polyethylene sheets. NMR spectra were recorded with an XL-300 Varian spectrometer, ^{1}H, and ^{13}C (TMS internal standard) spectra were measured from $CDCl_3$ solutions in 5 mm tubes. The temperature of the probe was calibrated from the signals of methanol. Mass spectra were recorded on a VG Autospec, by liquid secondary ion (LSI) MS using nitrobenzylalcohol as matrix and a caesium gun (Universidad de Zaragoza).

4.1. Synthetic methods

4.1.1. [Rh(Cl)(COD)(5-aqui)] (1), [Rh(Cl)(COD)(3-aqui)] (2), [Rh(Cl)(NBD)(5-aqui)] (3), [Rh(Cl)(NBD)(3-aqui)] (4), [Rh(Cl)(CO)$_2$(5-aqui)] (5) and [Rh(Cl)(CO)$_2$(3-aqui)] (6)

These compounds were all prepared by the reaction of $[\{RhCl(L_2)\}_2]$ (0.06 mmol) (L_2 = COD or NBD; L = CO) with the stoichiometric amount (0.12 mmol) of the

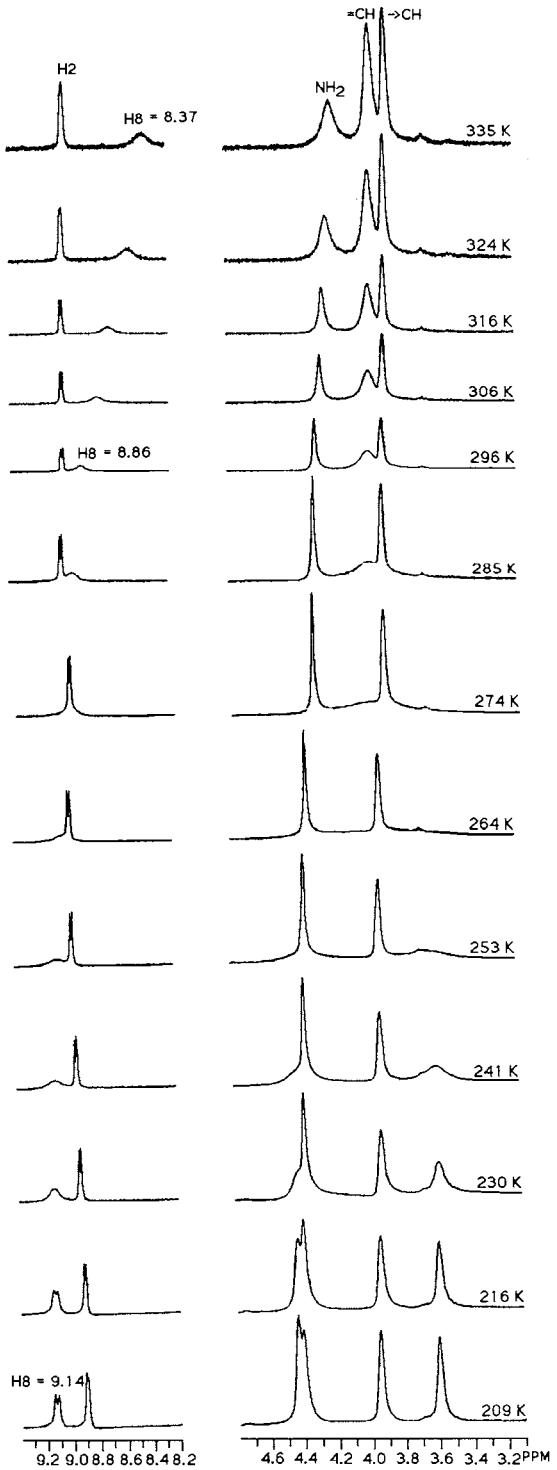


Fig. 6. Variable temperature ^{1}H-NMR study (in $CDCl_3$) at 299.949 MHz of **3** showing the H8 region of 5-aqui and the olefinic region of norbornadiene.

appropriate ligand (5-aqui or 3-aqui) in dichloromethane. Addition of diethyl ether or hexane gave yellow precipitates which were filtered off, washed with diethyl ether or hexane and vacuum dried. Yields: 60–70%.

*4.1.2. [Rh(Cl)(COD)(5-aqui)] (**1**)*

IR (KBr, cm^{-1}): 3401(m), 3316(s), 3225(m), ν(N–H); 320(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$, −55°C): δ 9.09 (m, H_8), 9.04 (m, H_2), 7.89 (m, H_4), 7.59 (m, H_7), 7.07 (m, H_3), 6.60 (m, H_6), 4.29 (s, NH_2), 4.75 (br, 2H, =CH), 3.58 (br, 2H, =CH). ^{1}H-NMR ($CDCl_3$, +60°C): δ 8.68 (br, H_8), 4.21 (br, 6H, =CH and NH_2), the other resonances are the same as that at −55°C. FAB MS Calc. for $C_{17}H_{20}^{35}ClN_2^{103}Rh$: 390. Observed: 390 [$M^+$]. Anal. Calc. for $C_{17}H_{20}ClN_2Rh$: C, 52.26; H, 5.16; N, 7.17. Found: C, 51.97; H, 5.23; N, 7.12%.

*4.1.3. [Rh(Cl)(COD)(3-aqui)] (**2**)*

IR (KBr, cm^{-1}): 3443(w), 3380(m), 3303(m), 3198(m), ν(N–H); 303(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$, −60°C): δ 9.60 (m, H_8), 8.66 (d, H_2), 7.60 (m, H_7), 7.39 (m, H_6 and H_5), 7.04 (d, H_4), 4.28 (s, NH_2), 4.82 (br, 1H, =CH), 4.71 (br, 1H, =CH), 3.63 (br, 1H, =CH), 3.51 (br, 1H, =CH). ^{1}H-NMR ($CDCl_3$, +20°C): δ 9.41 (br, H_8), 4.04 (s, NH_2), 4.71 (br, 2H, =CH), 3.64 (br, 2H, =CH), the other resonances are the same as that at −60°C. ^{1}H-NMR ($CDCl_3$, +60°C): δ 9.10 (br, H_8), 3.96 (br, NH_2), 4.19 (br, 4H, =CH), the other resonances are the same as that at −60°C. FAB MS Calc. for $C_{17}H_{20}^{35}ClN_2^{103}Rh$: 390. Observed: 390 [$M^+$]. Anal. Calc. for $C_{17}H_{20}ClN_2Rh$: C, 52.26; H, 5.16; N, 7.17. Found: C, 52.18; H, 4.99; N, 7.22%.

*4.1.4. [Rh(Cl)(NBD)(5-aqui)] (**3**)*

IR (KBr, cm^{-1}): 3401(m), 3316(s), 3225(m), ν(N–H); 320(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$, −60°C): δ 9.14 (m, H_8), 8.93 (m, H_2), 7.89 (m, H_4), 7.60 (m, H_7), 7.01 (m, H_3), 6.64 (m, H_6), 4.43 (br, NH_2), 4.40 (br, 2H, =CH), 3.59 (br, 2H, =CH), 3.95 (br, 2H, →CH). ^{1}H-NMR ($CDCl_3$, +60°C): δ 8.37 (br, H_8), 4.17 (br, NH_2), 3.93 (br, 4H, =CH), 3.84 (br, 2H, →CH), the other resonances are the same as that at −60°C. FAB MS Calc. for $C_{16}H_{16}^{35}ClN_2^{103}Rh$: 374. Observed: 374 [$M^+$]. Anal. Calc. for $C_{16}H_{16}ClN_2Rh$: C, 51.29; H, 4.30; N, 7.48. Found: C, 50.88; H, 4.08; N, 7.46%.

*4.1.5. [Rh(Cl)(NBD)(3-aqui)] (**4**)*

IR (KBr, cm^{-1}): 3394(s), 3309(s), 3204(m), ν(N–H); 310(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$, −55°C): δ 9.63 (m, H_8), 8.67 (d, H_2), 7.63 (m, H_7), 7.43 (m, H_6 and H_5), 7.04 (d, H_4), 4.24 (br, NH_2), 4.45 (br, 2H, =CH), 3.61 (br, 2H, =CH), 3.94 (br, 2H, →CH). ^{1}H-NMR ($CDCl_3$, +40°C): δ 8.97 (br, H_8), 3.96 (br, 6H, =CH and NH_2), 3.88 (br, 2H, →CH), the other resonances are the same as that at −55°C. FAB MS Calc. for $C_{16}H_{16}^{35}ClN_2^{103}Rh$: 374. Observed: 374 [$M^+$]. Anal. Calc. for $C_{16}H_{16}ClN_2Rh$: C, 51.29; H, 4.30; N, 7.48. Found: C, 50.41; H, 4.38; N, 7.40%.

4.1.6. [Rh(Cl)(CO)$_2$(5-aqui)] (**5**)

IR (KBr, cm^{-1}): 3401(m), 3330(s), 3239(w), ν(N–H); 2084(s), 2027(s), 2013(s), ν(C≡O); 310(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$): δ 8.86 (m, H_2), 8.30 (m, H_8 and H_4), 7.55 (m, H_7), 7.21 (m, H_3), 6.74 (m, H_6), 4.39 (s, NH_2). ^{13}C-NMR ($CDCl_3$): δ 183.1 (d, J(Rh–C) = 67 Hz, Rh–CO), 180.1 (d, J(Rh–C) = 73 Hz, Rh–CO). FAB MS Calc. for $C_{11}H_8^{35}ClN_2O_2^{103}Rh$: 338. Observed: 303 [$M^+ - Cl$]. Anal. Calc. for $C_{11}H_8ClN_2O_2Rh$: C, 39.03; H, 2.37; N, 8.27. Found: C, 39.16; H, 2.45; N, 8.25%.

4.1.7. [Rh(Cl)(CO)$_2$(3-aqui)] (**6**)

IR (KBr, cm^{-1}): 3436(m), 3338(s), 3218(w), ν(N–H); 2084(s), 2006(s), ν(C≡O); 310(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$): δ 8.74 (m, H_8), 8.68 (d, H_2), 7.53 (m, H_7), 7.42 (m, H_6 and H_5), 7.23 (d, H_4), 4.12 (s, NH_2). ^{13}C-NMR ($CDCl_3$): δ 183.4 (d, J(Rh–C) = 75 Hz, Rh–CO), 179.9 (d, J(Rh–C) = 69 Hz, Rh–CO). FAB MS Calc. for $C_{11}H_8^{35}ClN_2O_2^{103}Rh$: 338. Observed: 303 [$M^+ - Cl$]. Anal. Calc. for $C_{11}H_8ClN_2O_2Rh$: C, 39.03; H, 2.37; N, 8.27. Found: C, 38.97; H, 2.38; N, 7.65%.

4.1.8. [Rh$_2$Cl$_2$(CO)$_4$(5-aqui)] (**7**)

Prepared by the reaction of [{RhCl(CO)$_2$}$_2$] (0.06 mmol) with the stoichiometric amount (0.06 mmol) of 5-aqui in dichloromethane. Addition of diethyl ether gave a yellow powder which was filtered off, washed with diethyl ether and vacuum dried. Yield: 66%. IR (KBr, cm^{-1}): 3219(m), 3116(s), ν(N–H); 2091(s), 2013(s), ν(C≡O); 324(m), 316(m), ν(Rh–Cl). ^{1}H-NMR ($CDCl_3$): δ 9.02 (m, H_2), 8.52 (m, H_8 and H_4), 7.63 (m, H_7), 7.46 (m, H_3), 7.07 (m, H_6), 5.08 (s, NH_2). ^{13}C-NMR ($CDCl_3$): δ 180 (br, Rh–CO). FAB MS Calc. for $C_{13}H_8^{35}Cl_2N_2O_4^{103}Rh_2$: 532. Observed: 497 [$M^+ - Cl$]. Anal. Calc. for $C_{13}H_8Cl_2N_2O_4Rh_2$: C, 29.30; H, 1.51; N, 5.26. Found: C, 29.12; H, 1.69; N, 5.37%.

4.1.9. Crystallography

Yellow prismatic single crystals of **1** and **2** were obtained by layering dichloromethane solutions with diethyl ether. The data were collected on an Enraf–Nonius CAD 4 diffractometer for both compounds and unit cell constants refined from least-squares fitting of the θ values of 25 reflections, with 2θ range of 13–27 for **1** and 5–24° for **2**. A summary of the fundamental crystal data for both crystals is given in Table 4 Three check reflections were monitored after every 97 reflections for both compounds. For **1** no appreciable drop in the intensities of standard reflections was observed, whilst for compound **2**, 30% decay was observed.

The structures were solved by Patterson and Fourier methods. They were refined by full-matrix least-squares on F^2 (SHELXL-97) [26]. All non-hydrogen atoms have been refined anisotropically, but for compound **2** the carbon and oxygen atoms of the solvent molecule have been refined with restraints with a variable common carbon–carbon and carbon–oxygen distance. All the hydrogen atoms for compounds **1** and **2** were calculated and refined as riding on carbon atoms with common isotropic displacement parameters, except for those of the amine group and of the C8 in compound **1**, i.e. H2A, H2B and H8, respectively, which have been found as the first peaks in a difference Fourier syntheses, including fixed positions. The largest residual peak in the final difference map was 1.6 and 1.3 e Å^{-3} for **1** and **2**, respectively, in the vicinity of the Rh atom. Most of the calculations were carried out with SHELXL.

Table 4
Crystal and refinement data for [RhCl(COD)(5-aqui)] (**1**) and [RhCl(COD)(3-aqui)]Et$_2$O (**2**)

	1	**2**
Empirical formula	$C_{17}H_{20}ClN_2Rh$	$C_{21}H_{30}ClN_2ORh$
M_r	390.71	464.83
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	8.4097(8)	10.399(3)
b (Å)	18.894(1)	10.813(5)
c (Å)	10.132(3)	11.073(4)
α (°)	–	109.36(3)
β (°)	95.55(1)	111.96(3)
γ (°)	–	95.99(3)
V (Å^3)	1602.4(5)	1051.8(7)
Z	4	2
T (K)	295	295
D_{calc} (g cm^{-3})	1.62	1.46
μ (Mo–K$_\alpha$) (mm^{-1})	1.227	0.95
Crystal size (mm)	0.08 × 0.1 × 0.3	0.08 × 0.1 × 0.18
Scan technique	ω–2θ	ω–2θ
θ Range	$1 < \theta < 25$	$1 < \theta < 25$
Unique data	5615	3670
Unique data [$I > 2\sigma(I)$]	2788 [$R_{int} = 0.026$]	3475 [$R_{int} = 0.0978$]
Data/restraints/parameters	2788/0/190	3475/4/236
$R = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$	0.0301 (2122 reflections)	0.0899 (1213 reflections)
wR [a] (all data)	0.0855	0.2897

[a] $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]^{1/2}$.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CSD-116429 for compound **1** and CSD-116430 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK(fax: + 44-1223-336033 or e-mail deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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