Terpyridine complexes of Rhodium(I,III)
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Chapter 5

Crystal Structure of the Novel Neutral Octahedral Complex [Rh\textsuperscript{III}(Br)(Acetonyl)\textsubscript{2}(4'-(4'-Butylphenyl)-2,2':6',2''-Terpyridine)].


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Abstract

In the previous chapters, we have described the syntheses, characterisation, properties, reactivity and an application of Rh(I)-terpyridine complexes. It was found that, once the right conditions were met, the outcome of the chemistry of these complexes could be predicted to a certain degree.

Several rhodium complexes containing both a terdentate nitrogen ligand and an organic group bound to the metal are known. However, rhodium complexes of terdentate nitrogen ligands containing non-$\sigma$-bound organic groups have not been reported so far. To our surprise, during our syntheses of Rh(I)-terpyridine complexes in different organic solvents, we encountered one such species. Upon standing at room temperature, a mixture of $4$-$t$-butylphenyl-$2,2',6,2''$-terpyridine and $[\text{RhBr(COD)}]_2$ in acetone was found to deposit crystals of $[\text{Rh}^{I} \text{Br} \cdot \text{tacetonyl}]_{2} \cdot 4 (4$-$t$-butylphenyl-$2,2',6,2''$-terpyridine]). Here we report the synthesis and characterisation of this uncommon complex.
Introduction

We have synthesised several Rh(I)-terpyridine complexes in various organic solvents (ref. Chapter 2 and 3). Reaction of 4-4'-di-butylphenyl-2,2':6',2''-terpyridine and [Rh(Br)COD] in acetone, however, unexpectedly produced the Rh(I) complex [RhII(Br)acetonyl]4-[4'-di-butylphenyl]-2,2':6',2''-terpyridine] (I). Based on crystallographic studies, mass measurements (Fast Atom Bombardment and Field Desorption) and DFT calculations, we have a clear insight into its structure and composition. Each acetonyl group is σ-bonded to the Rh-metal of complex I in an axial position relative to the plane of the Tpy ligand. This is the first well-characterised example of a terdentate nitrogen metal complex with two carbon atoms σ-bonded to the metal atom.

Experimental Section

General. The 4-4'-di-butylphenyl]-2,2':6',2''-terpyridine (Tpy) ligand was synthesised and purified as described in Chapter 3. The Rh-precursor complex [Rh(Br)COD], (COD = 1,5-cyclooctadiene) was synthesised as described in Chapter 2. Acetone was freshly distilled from B.O. Complex I was formed in acetone under an inert atmosphere (purified argon), using standard Schlenk techniques. The formation of I was monitored with a UV/VIS spectrometer. Electronic absorption spectra were recorded on a HP8453 diode-array spectrophotometer. Fast atom bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX103A four-sector mass spectrometer, coupled to a JEOL MS-7000 data system. The sample was loaded in a matrix phase (glycerol) on a stainless steel probe and bombarded with xenon atoms with an energy of 3 KeV. During the high resolution FAB MS measurements a resolving power of 5000 (10% valley definition) was used. CsI and glycerol were used to calibrate the mass spectrometer. Field Desorption (FD) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP902HD/UPD system program. 10 μm Tungsten wire FD emitters containing carbon microneedles with an average length of 30 μm were used. The sample was dissolved in methanol/water and then loaded onto an emitter with the dipping or syringe
technique. An emitter current of 30 mA was used to desorb the sample. The ionsource temperature was 50 °C.

Atom numbering of complex I is done according to the following scheme:

Sythesis.

[Rh
III
(Br)(acetonyl)]
2
(4'-4-butylphenyl)-2,2':6',2''-terpyridine]. I

Acetone (40 ml) was added to 0.023 g [RhBr(COD)]
2
(0.039 mmol) and 0.029 g Tpy
a
(0.079 mmol). This mixture stood for a prolonged period (several weeks) at room temperature, without stirring. During this period, a dark blue reaction mixture was formed. Eventually, this mixture became yellow, yellow single crystals started to grow and were isolated from the mother liquor. After drying the product by removing the solvent under reduced pressure, complex I (yield ~100%) was collected as a yellow powder.

FAB' MS: m/z 604.05 [(M')-CH₃COCH₃]: FD' MS: m/z 661.08 [M'].

Due to the insolubility of complex I in various organic solvents, no NMR data could be generated. Furthermore, due to unknown reasons, elemental analysis gave no good results.

X-ray structure determination of complex I.

A crystal with dimensions 0.15x0.20x0.25 mm approximately was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated CuKα radiation and ω-2θ scan. A total of 3272 unique reflections was measured within the range -14≤h≤14, 0≤k≤28, 0≤l≤15. Of
these, 2737 were above the significance level of 4σ (1σ) and were treated as observed. The range of (sin θ)/λ was 0.044-0.625 Å⁻¹. Two reference reflections [0 3 1], [1 2 1] were measured hourly and showed 6% decrease during the 94 h collecting time, which was corrected for. Unit-cell parameters were refined by a least-squares fitting procedure using 23 reflections with 40.08<θ<42.88. Corrections for Lorentz and polarisation effects were applied. Absorption correction was performed with the program PLATON following the method of North et al. using Ψ scans of five reflections, with coefficients in the range 0.784-0.953. The structure was solved by the PATTY option of the DIF99 program system. The asymmetric unit contains half a molecule with Rh, Br, Ni(2), Cr(8), C(9), C(12) and C(13) on a special position (1 4 y 1). After isotropic refinement a synthesis revealed 4 peaks; these were interpreted as two molecules acetone of crystallisation with an occupancy factor 0.5, sharing their methyl groups; consequently C(12a) and O(1a) have an occupancy factor 0.5. The atomic displacement parameters of the methyl groups of the tBu moiety were very high and it was decided to divide these atoms into 6 C-atoms with occupancy factor 0.5. The hydrogen atoms were calculated, except those for the solvent molecule and kept fixed at their calculated positions with U = 0.1 Å². Full-matrix least-squares refinement on F, isotropic for the disordered C-atoms of the tBu and the solvent and anisotropic for the remainder of the atoms, converged to R = 0.060, Rw = 0.066, (Aσ)obs = 0.02, S = 0.84. A weighting scheme with \[ w = 0.01 \times (4σ(\text{obs})^2 + 0.01 \times σ(\text{obs})^2) \] was used. The secondary isotropic extinction coefficient \( \hat{G} \) refined to \( \hat{G} = 330(23) \). A final difference Fourier map revealed a residual electron density between -0.7 and 1.2 eÅ⁻³ in the vicinity of the Rh. Scattering factors were taken from Cromer and Mann. International Tables for X-ray Crystallography. The anomalous scattering of Rh and Br was taken into account. All calculations were performed with X-TAL3.7 unless stated otherwise. Further crystal and refinement data are listed in Table 5.1. A PLATON drawing is shown in Figure 5.1.

**Table 5.1: Crystal and refinement data for complex L.**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Formula</td>
<td>C12H16NiO2RhCl</td>
</tr>
<tr>
<td>Mol. Wt.</td>
<td>664.46</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$I2/a$</td>
</tr>
<tr>
<td>$a$, Å</td>
<td>11.990(2)</td>
</tr>
<tr>
<td>$b$, Å</td>
<td>22.679(2)</td>
</tr>
<tr>
<td>$c$, Å</td>
<td>12.044(2)</td>
</tr>
<tr>
<td>$\alpha$, deg</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$, deg</td>
<td>104.39(2)</td>
</tr>
<tr>
<td>$\gamma$, deg</td>
<td>90</td>
</tr>
<tr>
<td>$V$, Å$^3$</td>
<td>3172.3(8)</td>
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<tr>
<td>$F(000)$</td>
<td>1456</td>
</tr>
<tr>
<td>$T$, K</td>
<td>233</td>
</tr>
<tr>
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</tr>
<tr>
<td>Space group</td>
<td>P2/n</td>
</tr>
<tr>
<td>$Z$</td>
<td>4</td>
</tr>
<tr>
<td>$D_{calc}$, g/cm$^3$</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Figure 5.1. PLUTON drawing with atom labelling for complex I.
Density functional theoretical (DFT) study of complex 1.

For obtaining a better insight in the geometrical conformation of complex 1, DFT calculations were performed for model complex 1m (Figure 5.2) \([\text{Rh(Br)(-CH$_2$COCH$_3$)$_2$(Tpy)}]\) (Tpy = 2,2':6,2''-terpyridine). The atom labelling of 1m is similar to complex 1. The TURBOMOLE program was used for these calculations,\textsuperscript{[11,12]} using the BP86 functional,\textsuperscript{[13-18]} an SV(P) basis set, a medium-sized integration grid and the RI approximation.\textsuperscript{[19]} The structures of complex 1m and its cis isomer were optimized without constraints.

![Figure 5.2. Model complex 1m.](image)

UV-VIS spectroscopy of complex 1.

Electronic absorption spectra were recorded on a HP8453 diode-array spectrophotometer.
Results

Formation of $[\text{Rh}^{\text{III}}(\text{Br})(\text{acetonyl})_{2}(4'(4'-\text{butylphenyl})-2,2':6',2''\text{-terpyridine})]$ (1).

After stirring at room temperature $[\text{Rh(Br)(COD)}]_2$ (COD = 1,5-cyclooctadiene) and $4'(4'-\text{butylphenyl})-2,2':6',2''\text{-terpyridine}$ in acetone, a dark blue reaction mixture was formed. A UV-VIS electronic absorption spectrum of this mixture (Figure 5.3) showed very similar absorption bands in the visible region (metal-to-ligand and ligand-to-ligand charge transfers: MLCT and LLCT, respectively) as observed for complex $[\text{Rh}^1(\text{Br})(2,2':6',2''\text{-terpyridine})]$ in EtOH (c.f. Chapter 2). Based on these similar electronic absorption spectra, it can be suggested that the initially dark blue coloured reaction mixture in acetone contains the complex $[\text{Rh}^1(\text{Br})(\text{Tp})]$.

![Figure 5.3. UV/VIS absorption spectrum of $[\text{Rh}^1(\text{Br})(2,2':6',2''\text{-terpyridine})]$ in acetone (0.55 mM), measured after ca. 5 minutes reaction time.](image)

Upon standing at room temperature, the blue reaction mixture slowly becomes yellow and yellow crystals of complex 1 are growing. The formation of complex 1 (Scheme 5.1) is monitored for 24 hours (1 scan per hour) by UV/VIS spectroscopy (Figure 5.4). Complex 1 is air and thermally stable, and is very poor soluble in organic solvents.
Figure 5.4. a) Selected electronic absorption spectra of the formation of complex 1 (0.55 mM) for 24 hours; b) electronic absorption bands of 1 after ca. 60 hours standing at room temperature.

In Figure 5.4a, no isosbestic points can be observed, since complex 1 precipitates out of the solution.

Scheme 5.1. The in situ formation of complex 1.
Structure of complex 1: crystallographic and DFT studies.

The determination of the geometrical conformation of complex 1 was based on X-ray diffraction studies and DFT calculations. For the crystallographic studies of complex 1, the yellow crystals were not dried under vacuum, since the latter destroyed the crystals into powder; presumably because of loss of the acetone of solvation. For the DFT calculations, model complex 1m was used. Model 1m has a relatively simple ligand compared to complex 1, while both complexes should contain very similar coordination sphere around the Rh metal. Selected bond lengths and angles of complex 1 and model 1m are listed in Table 5.2 and 5.3 (respectively).

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>1</th>
<th>1m</th>
<th>Angles</th>
<th>1</th>
<th>1m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-B</td>
<td>2.576</td>
<td>2.545</td>
<td>Rh-Rh-N</td>
<td>99.5°</td>
<td>99.48°</td>
</tr>
<tr>
<td>Rh-N</td>
<td>2.058</td>
<td>2.044</td>
<td>Br-Rh-N</td>
<td>80.01°</td>
<td>79.8°</td>
</tr>
<tr>
<td>Rh-N1</td>
<td>1.954</td>
<td>1.946</td>
<td>N-Rh-N2</td>
<td>80.43°</td>
<td>80.68°</td>
</tr>
<tr>
<td>Rh-N2</td>
<td>2.058</td>
<td>2.044</td>
<td>N-Rh-N1</td>
<td>106.85°</td>
<td>106.38°</td>
</tr>
<tr>
<td>Rh-O</td>
<td>2.244</td>
<td>2.244</td>
<td>Rh-N1-C2</td>
<td>112.84°</td>
<td>113.17°</td>
</tr>
<tr>
<td>N1-C2</td>
<td>1.371</td>
<td>1.380</td>
<td>Rh-N1-C6</td>
<td>127.64°</td>
<td>127.02°</td>
</tr>
<tr>
<td>N2-C6</td>
<td>1.358</td>
<td>1.351</td>
<td>C2-N1-C6</td>
<td>119.66°</td>
<td>119.52°</td>
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<tr>
<td>N2-C2</td>
<td>1.346</td>
<td>1.397</td>
<td>Rh-N1-C2</td>
<td>119.02°</td>
<td>118.30°</td>
</tr>
<tr>
<td>N2-C6</td>
<td>1.350</td>
<td>1.397</td>
<td>Rh-N1-C6</td>
<td>119.04°</td>
<td>118.32°</td>
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<tr>
<td>C1-C14</td>
<td>1.375</td>
<td>1.375</td>
<td>C2-N1-C6</td>
<td>129.66°</td>
<td>128.42°</td>
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<tr>
<td>C1-C14</td>
<td>1.375</td>
<td>1.375</td>
<td>Br-Rh-C13</td>
<td>88.86°</td>
<td>88.36°</td>
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<tr>
<td>C1-C14</td>
<td>1.220</td>
<td>1.240</td>
<td>C1-Rh-C13</td>
<td>111.4°</td>
<td>110.7°</td>
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<tr>
<td>Rh-C13-C14</td>
<td>1.000</td>
<td>1.0769</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crystallographic and DFT data show that the methylene carbon atom of each acetonyl group is \( \sigma \)-bonded to the Rh metal of complex 1. The alternative interpretations with oxygen atoms of intact acetone molecules coordinated to the metal cannot be reconciled with the observed bond lengths. In addition, coordination of two acetone molecules via the oxygen atoms would result in a 20e-
configuration, and is therefore unlikely. According to DFT calculations, model 1m with the acetonyl groups in cis position is 5.8 kJ/Mol higher in energy than the trans analogue observed experimentally.

Within the crystals of complex 1, the shortest distance between the discrete monomers is 3.20 Å. Figure 5.5 shows the packing in the unit cell, and Figure 5.6 illustrates the π-stacking interactions between the outer terpyridine pyridyl rings and the phenyl rings of neighbouring molecules.

Figure 5.5. Packing of complex 1.

Figure 5.6. π-stacking interactions between neighbouring molecules of 1.
Discussion

Synthesis and growing crystals of complex 1.

The synthesis of complex 1 is very facile; cf. experimental section. The first step for the synthesis of complex 1 is the formation of the dark blue intermediate "RhoBr" as in Chapter 5, which is confirmed by UV-VIS spectroscopy. In contrast to the facile synthesis of 1, the mechanism for the intramolecular formation of 1 from the intermediate "RhoBr" might be complex. Based on UV-VIS spectroscopy measurements, no complete mechanism for the formation of complex 1 can be proposed.

For collecting crystals of the highly unstable complex 1, suitable for X-ray analyses, it is best not to stir the reaction mixture. The Rh precursor [RhBr(COD)]_2 is soluble in acetone, while the Lpy ligand is poorly soluble in acetone. Without stirring the mixture, the formation of complex 1 proceeds slowly, and crystals of 1 grow in a controlled manner. However, it might be that with this synthesis procedure some impurities remain which are responsible for the poor elemental analysis data.

Characterisation of complex 1.

Mass measurements (AB and HD) and DFT studies strongly support the formation and structure of complex 1 as depicted in Figure 5.1. The mass measurements, in particular the HD measurement, indicate that two acenonyl groups are attached to the Rh metal of complex 1. Both X-ray and DFT data show that bonding of contamination or oxygen atoms to the Rh metal can be excluded. Therefore, the acenonyl groups in complex 1 are 6 bonded to the Rh metal with their methylene carbon atoms.

The bond length between the Rh metal and C13 of complex 1 is ca. 1.2 Å longer than the Rh C bonds in comparable Rh(II)-bidentate nitrogen complexes described by Haarman et al. The difference in bond lengths in these related Rh(II) complexes could be caused by a different trans effect in both systems. In complex 1, C13 experiences a trans effect from an alkyl carbon atom, while in complexes of Haarman the comparable carbon atom experiences the much weaker trans effects.
effect of a chloride atom. In addition, the acetonyl group, being formally a hetero-allyl group, may show some delocalization, leading to a larger Rh-C distance.

\[ \text{Add an image of the acetonyl group here.} \]

So far, the reaction mechanism for the formation of complex 1 from [Rh(\text{Br})(2,2':6',2''-terpyridine)] in acetone is unknown.

The formation of square planar metal containing terdentate coordinated complexes with two alkyl groups trans situated onto the metal centre is highly unusual. In the coordination chemistry of terdentate nitrogen ligands, the existence of related Rh-complexes with two carbon atoms \( \sigma \)-bonded to the metal centre is even unprecedented. The results described in this and other chapters emphasise the interesting properties of Rh(I)-terpyridine complexes.

References


