Terpyridine complexes of Rhodium(I,III)
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Terpyridine Complexes of Rhodium(I,III)

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Terpyridine Complexes of Rhodium(I, III)

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Faculteit der Natuurwetenschappen, Wiskunde en Informatica
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Chapter 1

General Introduction.
Introduction

During the last 30 years, our group has extensively studied the coordination chemistry of bi and terdentate nitrogen ligands with late transition metals. Lately, the chemistry of Pd and Pt bidentate and terdentate nitrogen donor ligands was thoroughly investigated. In particular, we have focused on the ligands bis-tartratimiinoarephthilene (Ar-Bian), 2,2'-bipyridine (bpy), 2,2':6,2''-terpyridine (tpy), 2,6-diamino-pyridine, 2,6-(CR=N-R=CH=NR), and their derivatives.

It was found that the Pd-Ar-Bian complexes homogeneously catalyse reactions such as C-C, C-N, and C-X coupling. Pd-Ar-Bian complexes were also used in CO-alkene copolymerisation reactions, and migratory alkene insertion reactions into acyl Pd-C bonds.

Furthermore, Pd-Ar-Bian complexes were found to be successful in the selective homogeneous Pd(O) catalysed hydrogenation reactions of alkenes into Z-alkenes.

The complex [bipy-Pd(Me)Cl] was used to study the insertion of CO into the methyl Pd-C bond. To gain more insight into the mechanism of insertion reactions into Pd-C bonds, the insertion of the isoelectronic isocyanides (R-NC) into the methyl Pd-C bond of complex [bipy-Pd(Me)Cl] was studied. Observed intermediates indicate that isocyanide insertion proceeds by a fast coordination of the isocyanide to the metal via displacement of the halide atom, followed by a rate-determining migration of the methyl group to the precoordinated isocyanide.

With isocyanides, the variation of electronic and steric factors by varying the R-group on the nitrogen atom was studied. It was found that the migration rate of the methyl group to the precoordinated isocyanide increases with increasing electrophilicity of the isocyanide, which had also been observed in Pd(II) complexes. Furthermore, [bipy-Pd(Ph=NC): (R = Me, CH(O)Me, CH=CH: CH=CH; CH2=CH=O): (NC-Ph=NC): (R = Me, CH(O)Me, CH=CH: CH=CH; CH2=CH=O): (NC-Ph=NC): (R = Me, CH(O)Me, CH=CH: CH=CH; CH2=CH=O)] was used for studying migratory insertion of alkenes into Pd-alkyl and Pd-acyl bonds.

CO and alkene insertions into Pd-C bonds were also studied with [bipy-PdMeCl] complexes. The rates of CO and alkene insertions into Pd-C bonds of methylpalladium and acetyl palladium complexes, respectively, are comparable to bidentate and terdentate nitrogen ligand containing Pd-complexes. Generally, the CO and alkene insertions proceed faster for complexes containing weakly coordinated counter-ions, such as triflate (SO3Fe) and tetrakis(3,5-
bis(trifluoromethylphenyl) borate anions. This is due to the readily available coordination position for the incoming substrates.

Multidentate nitrogen ligands studied in our laboratory are able to stabilise, e.g., Rh(I), Rh(II) and Rh(IV) complexes. Recently, we were particularly interested in stabilising Rh(I) complexes with terdentate nitrogen ligands. For this purpose, we employed the terdentate (κ^2) 2,6-dimino-pyridine (2,6-CR = N-R' = C-H-N) ligands. The corresponding dark green complexes [Rh(II)Cl(2,6-CR = N-R' = C-H-N)] must be synthesised under rigorous exclusion of oxygen. Oxygen binds irreversibly to the rhodium atom, producing Rh(III) species. Haarmann et al. found that the very nucleophilic complexes [Rh(II)Cl(2,6-CR = N-R' = C-H-N)] were able to activate the relatively inert C-Cl σ-bonds of various substrates. It is generally known that breaking carbon chloride σ-bonds is only possible when very electron rich centres are used (c.f. Chapter 3 and refs. therein). The Rh(III) products, formed after oxidative addition reactions of the corresponding Rh(I) complexes with C-Cl bonds, react with hot water (100 °C) and oxygen. The complexes [Rh(II)Cl(2,6-CR = N-R' = C-H-N)] and [Rh(II)Cl(2,6-CR = N-R' = C-H-N)], formed after oxidative addition reactions with corresponding Rh(I) complexes and dichloromethane, chloroform and dichloromethyl benzene, respectively, reacted with hot water and oxygen to form complexes [Rh(III)Cl(2,6-CR = N-R' = C-H-N)]. In the case of the reaction of [Rh(II)Cl(2,6-CR = N-R' = C-H-N)] with water and oxygen at elevated temperature, also the formation of benzaldehyde and H_2O was established by 1H NMR and iodometry. In the course of the latter study, complex [Rh(II)Cl(2,6-CR = N-R' = C-H-N)] (Pr = isopropyl) was reacted with hot water (80 °C) also in the absence of oxygen, leading to [Rh(III)Cl(2,6-CR = N-R' = C-H-N)] benzaldehyde and HCl. When only oxygen reached with complexes [Rh(II)Cl(2,6-CR = N-R' = C-H-N)], stable peroxo complexes [Rh(III)OO(2,6-CR = N-R' = C-H-N)] were formed.

This interesting Rh chemistry with the terdentate 2,6-dimino-pyridine (2,6-CR = N-R' = C-H-N) ligands led us to extend the Rh research to terdentate terpyridine ligands.
Syntheses of Oligopyridines

Early syntheses of oligopyridines were low yielding and unselective. Blau prepared bipy from the distillation of a basic aqueous solution of the Cu(II) salt of 2-pyridinecarboxylate.\(^{20, 21}\) In 1928, Hein and Retter formed bipy via an oxidative coupling reaction of pyridine with Fe(III)-chloride at high temperature and pressure.\(^{24}\) The latter technique was further used by Morgan and Burstall.\(^{24, 45, 46}\) Tpy and higher oligopyridines were isolated from product mixtures containing over twenty species.\(^{24}\)

Later, in the 1950ies, the dehydrogenation reaction of pyridine over Raney nickel catalyst gave only traces of Tpy.\(^{47, 48}\) In time, the syntheses of the simple compounds bipy and 1,10-phenanthroline have been well developed.\(^{19, 55}\) However, it is only recently that the chemistry of higher oligopyridines has been systematically developed.\(^{56, 57}\) Useful syntheses of oligopyridines follow either a new interannular C-C bond formation between two extant pyridine rings, or one or more pyridine rings are prepared in a cyclisation step. The latter ring synthesis is by far the most popular strategy and will be discussed briefly.

Synthesis of Terpyridines.

The progress in developing oligopyridines was accelerated tremendously by the development of two related multistep ring syntheses by Krönke and Potts.\(^{55, 57}\) 2-Acetylpyridines are key intermediates for the formation of 2-pyridyl-enones and ylid precursors (Scheme 1.1), both important for the syntheses of oligopyridines. 2-Pyridyl-enones can be prepared directly form the reaction of a 2-acetylpyridine with an aldehyde, and ylid precursors can be prepared by the Ortleva-King reaction\(^{58}\) of a 2-acetylpyridine with iodine in pyridine.

![Scheme 1.1. Formation of 2-pyridyl-enones and ylid precursors.](image-url)
The Krönke methodology (Scheme 1.2) has been applied in the syntheses of a wide range of oligopyridines.

[Diagram of Scheme 1.2: Krönke's ring synthesis of oligopyridines]

After the reaction of A and B (Scheme 1.2), the final ring closure is achieved with ammonium acetate as the nitrogen source.

Potts and co-workers have designed a second recent methodology for synthesising oligopyridines (Scheme 1.3). After the ring closure (third step, Scheme 1.3), the remaining methylthio derivative is converted to the desulphurised product utilising alkyl magnesium bromides in the presence of catalytic amounts of bis(triphenylphosphino)nickel(II)-dichloride, i.e. nickel-catalysed Grignard displacement reaction.

[Diagram of Scheme 1.3: The Potts' synthesis of oligopyridines]

Nowadays, many desired higher oligopyridines, like the terpyridines, are relatively readily accessible in large quantities. Terpyridine ligands are used for a variety of purposes and disciplines. However, the majority of the terpyridines are used in research of fundamental academic character.
Applications

The coordination chemistry of the terpyridine ligands is widely applied for numerous main group and transition metals.\(^{[56]}\) The terpyridines are excellent in stabilising complexes with metals in high and low oxidation states, since the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of terpyridines are energetically suitable for interactions with metal d orbitals.\(^{[67, 68]}\) Complexes with metals in low oxidation states, \textit{i.e.} excess of electron density at the metal atom, are stabilised by terpyridine ligands via electron density transfer from metal to ligand (back-donation). Similarly, metals in high oxidation states, \textit{i.e.} relatively electron-poor metals, are stabilised by strong $\sigma$ electron-donation of terpyridine ligands.

Terpyridines can act as monodentate-,\(^{[69, 70]}\) bidentate-,\(^{[69, 69]}\) or terdentate\(^{[69, 70]}\) coordinating ligands. However, in the majority of their metal complexes the terdentate coordination mode is found. Brown\(^{[71]}\) described that the formation of $\text{Al}$(III)-complexes with terpyridines most probably involves three distinct steps. The mechanism for the formation of the terdentate coordinated complexes is likely to proceed firstly through a coordination of one outer pyridine unit, followed by the subsequent coordination of the center pyridine unit, and finally completion of the terdentate chelate formation. This means that the formation of a metal terpyridine complex can be a complex process involving several equilibria. Based on the findings of Brown, we expect that the mechanism of the formation of square planar $\text{Rh}$(I)-terpyridine complexes (\textbf{Scheme 1.4}) is similar to the formation of $\text{Al}$(III)-terpyridine complexes.

\begin{center}
\begin{tikzcd}
\text{RhL}_4 \quad + \quad \text{L} \quad \rightarrow \quad [\text{RhL}_3 \text{L}] \quad \rightarrow \quad [\text{RhL}_2 \text{N}] \quad \rightarrow \quad [\text{RhL} \text{N}] \quad \rightarrow \quad [\text{RhL} \text{N}] \quad \rightarrow \quad \text{[Rh terpyridine complex]}
\end{tikzcd}
\end{center}

\textbf{Scheme 1.4.} Suggested mechanism for the formation of $\text{Rh}$(I)-terpyridine complexes ($\text{L} = \text{ligand}$).
The majority of complexes containing terpyridine ligands exhibit 1:1 or 1:2 metal-ligand ratios. Numerous crystal-structural analyses of complexes with 1:1 metal-ligand ratio have been reported in literature. Frequently encountered geometries are square planar four-coordinate and six-coordinate octahedral.

So far, terpyridine ligands are mostly used in photochemical and electrochemical studies. The former are partly stimulated by the attractive photochemical and photophysical properties exhibited by complexes containing bpy and 1,10-phenanthroline. Furthermore, the multidentate nitrogen containing ligands are also frequently used for metallosupramolecular chemistry. The metallosupramolecular chemistry of the terpyridines is in various cases involved in self-assembly processes from discrete metal terpyridine monomers through aromatic ring interactions. Non-covalent interaction between aromatic ligands, i.e. π-π interaction, is a known phenomenon for metal complexes with nitrogen containing aromatic ligands. Furthermore, π-stacking is sometimes used in supramolecular crystal engineering studies. Unfortunately, π-stacking lowers the solubility of aggregated monomers. Consequently, full characterisation of these monomeric and supramolecular species is difficult.

Recently, terpyridine ligands have been used for synthesising complexes displaying lyotropic liquid crystalline behaviour. The design of lyotropic liquid crystals has attracted much interest over the last decade, since membranes of cells are considered as lyotropic liquid crystals of phospholipid bilayers in water media. The assembly of liquid crystals is based on compounds containing a rigid and a bulky highly flexible part. It is found that terpyridines can serve as excellent candidates for designing new supramolecular materials and nanostructures. The use of lyotropic metal-terpyridine complexes for medical purposes could be promising, since it is known that certain metal-terpyridine complexes are biologically active in e.g. killing bacteria and cancer cells.

Scope of this Thesis

The bidentate α-dimine and bipyridine type nitrogen ligands used by our group stabilise metal complexes in various oxidation states due to their electron donating and accepting capacities. Furthermore, the complexes showed good activities in catalytic reactions like the CO-olefin
copolymerisation. It was found that their reactivity is enhanced by relatively smaller bite angles, compared to phosphine ligands. Extension of this work to terdentate nitrogen ligands led to the study of 2,6-dimino pyridine and terpyridine ligands.

Even since the synthesis of Tpy was first time reported by Morgan and Burschka, its coordination chemistry has been extensively studied. Surprisingly, the synthesis and characterisation of RhB-terpyridine complexes has not been reported before.

In Chapter 2, we present the first successful preparation and characterisation of RhB-terpyridine complexes. Attempts have been made to increase solubility of RhB-terpyridine complexes in organic solvents by attaching bulky groups at the Tpy aromatic ring. Crystallographic studies reveal that preventing π-stacking will not automatically lead to better solubility of the studied complexes.

Numerous highly efficient (but high yielding) electro-oxidative addition reactions with the complex Rh(Br)3₄(Bu)(2,2′6,2′-terpyridine) and CBr bonds are described in Chapter 3. The oxidative addition reaction has been monitored with UV–VIS spectroscopy. Unfortunately, the obtained spectroscopic data do not suffice to establish the mechanism of the addition unambiguously. NMR data allow a consistent assignment of the product geometries.

Chapter 4 is concerned with the synthesis of a RhIII-terpyridine complex displaying isotropic liquid crystalline behaviour. For this, a dinitrile wedge containing a terminal CBr bond was oxidatively added to the Rh metal centre of the complex [RhBr(Tpy)]³⁺. In our case, the design of liquid crystalline materials is not based on substituting the aromatic rings, but on “substituting” the metal centre through simple oxidative addition reactions. This new approach of designing metal-containing materials displaying liquid crystalline behaviour offers both coordination chemists and material chemists new opportunities to strengthen each other’s work.

In Chapter 5, we report the structure of a rare neutral octahedral RhIII-hexaenone-terpyridine complex with the two alkyl groups situated trans to each other and σ-bonded to the metal.

References

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Chapter 2

Strongly Nucleophilic Rh(I) Centres in Novel Square Planar Complexes with Terdentate (κ^3) 2,2':6',2''-Terpyridine Ligands: Crystallographic, Electrochemical and Density Functional Theoretical Studies.


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Abstract

For the first time, the formation of RhI-terpyridine complexes has been unambiguously proven. The 2,2',6,2'-terpyridine (1py), 4-ethyl-2,2',6,2'-terpyridine (4CIpy), and 4-tert-butylidimethylsilyl ortho-carbomethoxy-2,2',6,2'-terpyridine (carbomethoxy-1py) ligands were used for successful syntheses and characterisation of the corresponding RhI complexes with halide co-ligands, [RhN≡X-Y-terpyridine], (X = Cl(1), Br(2); Y = H(1), 2), (Cl3), carbomethoxy(4). Full characterisation of these dark blue, highly air-sensitive compounds was hampered by their poor solubility in various organic solvents. This is mainly due to the formation of aggregates through π-stacking, as evidenced by the crystal structure of complex 1. The geometry of the neutral complexes 1-4 is square planar, with the Rh-X bonds in the plane of the 4-Y-terpyridine ligands. The π-stacking is likely not the only phenomenon hampering good solubility of RhI-terpyridine complexes in organic solvents, since the formation of discrete dimers is well possible for complex 4. Owing to the solubility problems, no acceptable NMR data could be obtained, except for complex 4 in CD2Cl2. The bonding properties of the novel RhI-terpyridine complexes were studied with single crystal X-ray diffraction, time-dependent density functional theoretical (DFT calculations, far-infrared spectroscopy, electronic absorption spectrosopy and cyclic voltammetry. From the DFT calculation it can be concluded that the HOMO of the RhI-terpyridine complexes lies predominantly on the metal centre, while the LUMO resides on the terpyridine ligand. Furthermore, the dominant absorption bands of complexes 1-4 in the visible region (400 900 nm) can be assigned to MLCT and MLCT/MLCT transitions. The relatively low oxidation potentials of complexes 1 and 2 point to a high electron density on the Rh metals. This makes the RhI-terpyridine complexes strongly nucleophile, and potentially highly reactive towards various small substrate molecules containing carbon-halide bonds.
Introduction

Currently, there is much interest in transition metal complexes containing terdentate nitrogen ligands \( \text{N-N-N} \), both in the field of supramolecular chemistry and catalysis. For example, recent investigations have shown that complexes [Pd(Me)\( \text{N-N-N} \)] react rapidly with CO and subsequently with norbornadiene to produce [Pd(C\( \text{H}_2\text{C}(\text{O})\text{Me})\text{N-N-N}])] on the road to metal-bound polyketone fragments. Unexpectedly, the highest insertion rates have been observed for complexes containing highly rigid ligands, e.g. dipyrrolid[4,3-\( h \):5,6-\( h \)]acridine. According to theoretical calculations, this is most likely due to the fact that the rigidity of the ligand causes an increased strain in the metal complex itself, thereby facilitating the intermediate bidentate coordination of the \( \text{N-N-N} \) ligands. These interesting findings prompted us to synthesize isoelectronic Rh(I) compounds. We previously reported novel compounds \([\text{Rh}(\text{Cl})\text{2.6-t-Gr} (=\text{N}-\text{R}')(\text{C}_{2}\text{H}_{4}\text{N})] \), containing fairly flexible 2,6-diamino-pyridine ligands. These complexes were found to react readily with alkyl halides and oxygen owing to a strongly nucleophilic Rh(I) centre. The present article extends the studies to stronger \( \sigma \)-donating and more rigid terpyridine ligands.

Since the first report on 2,2',6,2'-terpyridine (Tpy) by Morgan and Burstall, the coordination chemistry of this ligand and its derivatives has been widely studied. They exhibit variable coordination modes to transition metals, viz. terdentate, bidentate, or monodentate. Although complexes with many late transition metals are known, only a few examples of Rh-terpyridine complexes have been published, all of them containing Rh(I) or Rh(II). Some Rh(III) intermediates with terpyridine ligands have been proposed to participate in catalytic cycles, but the formation of such species has never been unambiguously established.

In this article, we report for the first time the synthesis, structures, spectroscopic, redox and bonding properties of four mononuclear square planar Rh(I)-terpyridine complexes. Due to the planar Tpy skeleton, these compounds exhibit strong tendency to \( \pi \)-stacking, which implies low solubility. This is the main factor that complicates their characterisation. A possible solution is to attach stericly demanding substituents at the Tpy ligand. Therefore, attempts were made to enhance the solubility of the Rh(I) terpyridine species by placing the bulky tert-butyldimethylsilyl-\( \text{ortho}\)-carboranyl group at the 4-position of the Tpy ligand.
Experimental Section

General. The syntheses of Rh(I)-terpyridine complexes and all manipulations with them were performed under an inert atmosphere of purified dry argon or nitrogen, using standard Schlenk techniques. Solvents and reagents were dried and purified by standard procedures. The $^1$H NMR measurements were performed at 294 K with a Bruker AMX 300 spectrometer operating at 300 MHz. Fast Atom Bombardment (FAB$^+$) mass spectrometry was carried out using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-7000 data system. The samples were loaded in a matrix phase (glycerol) on a stainless steel probe and bombarded with xenon atoms having 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 served as calibration standards. Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany) and Analytische Laboratorien GmbH (Lindlar, Germany).

The Tpy and 4'-chboro-2,2':6',2'-terpyridine (4'-Cl-Tpy) ligands are commercially available (Aldrich). Precursor complexes [Rh(X)(COD)]$_2$ (X = Cl, Br; COD = 1,5-cyclooctadiene) and the ligand 4'-(tert-butylidimethylsilyl-ortho-carboranyl)-2,2':6',2'-terpyridine (carboranyl-Tpy) were synthesised according to literature procedures.

Syntheses.

$[\text{Rh}^I(\text{Cl})(\text{Tpy})]$, 1

Solutions of Tpy (1.0 g, 4.3 mmol) and $[\text{Rh(Cl)(COD)}]_2$ (1.0 g, 2.0 mmol) in toluene (50 mL) were mixed and stirred together at room temperature. After five minutes, a dark blue precipitate of complex 1 was formed. After filtration, the product was washed with hot THF (3x 20 mL) and dried under reduced pressure. Yield ca. 95%. Upon gentle cooling of the collected THF phases, needle-shaped dark blue crystals were formed, which were suitable for X-ray
Synthesis, characterisation and properties of Rh(I)-terpyridine complexes

diffraction studies. A small portion of the solid was recrystallised from hot benzonitrile as dark blue leaflets that were used for elemental analysis.

FAB^* MS: m/z 371.98 [M^+].
Calculated for C_{15}H_{11}N_3RhCl (370.97): C 48.48%, H 2.98%, N 11.31%, Cl 9.54%; found: C 48.60%, H 3.04%, N 11.43%, Cl 9.80%.

[Rh^I(Br)(Tpy)], 2
A solution of Tpy (0.024 g, 0.10 mmol) and [Rh(Br)(COD)]_2 (0.03 g, 0.05 mmol) in EtOH (20 mL) was stirred at room temperature for five to ten minutes, affording a dark blue suspension. After filtration, the dark blue solid was washed with EtOH (3 x 10 mL), followed by pentane (3 x 10 mL). The product was dried under reduced pressure. Complex 2 was collected as a dark blue powder in nearly quantitative yield.

FAB^* MS: m/z 414.92 [M^+].
Calculated for C_{15}H_{11}N_3RhBr (414.92): C 43.30%, H 2.66%, N 10.10%, Br 19.20%; found: C 43.28%, H 2.66%, N 10.06%, Br 19.32%.

[Rh^I(Cl)(4'-Cl-Tpy)], 3
Solutions of 4'-Cl-Tpy (0.045 g, 0.17 mmol) and [Rh(Cl)(COD)]_2 (0.04 g, 0.08 mmol) in toluene (10 mL) were mixed at room temperature. After stirring for five to ten minutes, a dark blue solid precipitated. After filtration, the solid was washed with toluene (3 x 10 mL), followed by pentane (3 x 10 mL). The product was dried under reduced pressure. Complex 3 was collected as a dark blue powder in nearly quantitative yield.

FAB^* MS: m/z 404.93 [M^+].
Calculated for C_{15}H_{10}N_3RhCl (404.93): C 44.37%, H 2.48%, N 10.35%, Cl 17.46%; found: C 44.26%, H 2.55%, N 10.18%, Cl 17.55%.
[Rh(\text{Cl}(\text{Carboranyl-Tpy})]. 4

A solution of carboranyl-Tpy (0.2 g, 0.41 mmol) and [RhCl(COD)]\(_2\) (0.1 g, 0.20 mmol) in EtOH (100 mL) was stirred for six hours at room temperature. After standing for three weeks and decanting the dark purple supernatant liquid, dark blue crystals of 4 were collected. Yield ca. 90%.

\(^1\)H NMR (300 MHz, CD\(_2\)Cl\(_2\)): \(\delta\) 7.38 (s, 2H), 7.09 (t, 8 Hz, 2H(5.5°)), 6.94 (d, 8 Hz, 2H(3.3°)), 6.84 (t, 7 Hz, 2H(4.4°)), 0.65 (s, tert-butyl), -0.43 (s, -Si(Me)\(_2\)).

Calculated for C\(_{58}\)H\(_{55}\)N\(_4\)B\(_{10}\)SiRhCl-CH\(_3\)CH\(_2\)OH (675.27): C 44.54%, H 6.13%, N 6.23%; found: C 44.32%, H 6.03%, N 6.31%.

Complexes 1 and 3 could also be synthesised in organic solvents other than toluene, such as benzene, THF, Et\(_2\)O and EtOH. In contrast, the syntheses of complexes 2 and 4 were only successful in EtOH. Complexes 1-4 react rapidly with MeOH to produce unidentified red Rh(III) species.

X-ray structure determination of complexes 1 and 4.

A dark blue single crystal was mounted on a capillary. Intensity data were collected at room temperature with an Enraf-Nonius CAD4 diffractometer, using o-26 scan mode. Unit cell dimensions were determined from the angular setting of 25 reflections. Intensity data were corrected for Lorentz and polarisation effects. Semi-empirical absorption correction (\(\psi\)-scans)\(^{17}\) was applied. The structure was solved by the program system DIRIDIF\(^{18}\) using PATTY\(^{19}\) to locate the rhodium atom, and was refined with standard methods (refinement against \(F^2\) of all reflections with SHELXL97\(^{20}\)), with anisotropic parameters for the non-hydrogen atoms. All hydrogen atoms were placed at calculated positions and refined riding on the parent atoms. A structure determination summary is presented in Table 2.1. PLUTON\(^{21}\) drawings of complexes 1 and 4 are shown in Figures 2.1 and 2.2, respectively. Selected bond lengths and angles for both crystal structures are given in Table 2.2.
Figure 2.1. Displacement ellipsoid plot (50% probability level) of complex 1. PLUTON drawing with atom labelling.

Figure 2.2. Displacement ellipsoid plot (50% probability level) of complex 4. PLUTON drawing with atom labelling. Hydrogen atoms and the disordered ethanol solvent molecule have been omitted for clarity.
<table>
<thead>
<tr>
<th>Complex</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Unit cell dimensions</th>
<th>V, Å^3</th>
<th>(Z)</th>
<th>D, g/cm^3</th>
<th>gamma</th>
<th>F(000)</th>
<th>O range for data collection</th>
<th>(R_h) range</th>
<th>(R_h) indices</th>
<th>F(0) indices</th>
<th>DIF, peak to base, Å⁻²</th>
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**Density functional theoretical (DFT) study of complexes 1 and 2.**

Density functional theory (DFT) was employed to determine the ground state electronic structures of complexes 1 and 2, and time dependent density functional theory (TD-DFT) to describe the corresponding electronic transitions. It is important to stress that the Kohn-Sham molecular orbitals, arising from DFT calculations, are physically meaningful and that the
accuracy of excitation energies determined with TD DFT is often comparable with that of the most advanced \textit{ab initio} methods. Calculations were performed with the Amsterdam Density Functional (ADF) program \cite{ADF} for geometry optimised models of [Rh(1BrTpy)] \textit{C1m} and [Rh(2BrTpy)] \textit{C2m}. Crystallographic data of complex 1 were used to provide an initial guess for the equilibrium geometry. The atomic coordinates were then projected onto a plane, and geometry optimisation was performed for the ground state. A separate optimisation was performed for each molecule, with constrained planar geometry and C$_{2v}$ symmetry.

For all calculations, including the geometry optimisation, the following basis sets were employed: for C, N, H, Cl and Br, an uncontracted triple-$\zeta$ Sklater-type orbital (STO) basis with two polarisation functions; for Rh, an uncontracted triple-$\zeta$ STO basis with one polarisation function (5p). Core orbitals were frozen for C and N (1s), Cl (2p), Br (5p), and Rh (3s, 3d).

For the needed approximation to the exchange correlation potential, the generalised gradient approximation (GGA) was adopted that employs Becke's gradient approximation for the exchange \cite{Becke} and Perdew's approximation for correlation (ADF/BP) \cite{Perdew}. After the geometry optimisation, calculations were performed for three different fragments of each molecule: the Tpy ligand was considered as one fragment, with ClBr and Rh forming the other two. The ADF package allows the results of the fragment calculations to be used in ground state calculations for each complete molecule, and the molecular orbitals (MOs) to be analysed in terms of the fragments' orbitals. In all calculations, C$_{2v}$ symmetry was incorporated; for the terpyridine ligand and the entire molecules, for the individual atom fragments, spherical symmetry was imposed.

The ADF-RESPONSE module, an extension of ADF, was used to perform TD DFT calculations for the ground-state optimised geometry. These calculations provide excitation energies and relative contributions of individual occupied-to-virtual MO transitions to each excitation.

**UV-VIS and FTIR spectra of complexes 1 and 2.**

Electronic absorption spectra were recorded on a HP 8453 diode-array spectrophotometer. Far infrared (FTIR) spectra were recorded between 50 and 375 cm$^{-1}$ with a Bomem DA302 FTIR.
spectrometer, using a polyethylene cell filled under an argon atmosphere. In all experiments a globar light source and a lithium-cooled germanium bolometer operating at 1.2 K. were used. The spectra 128 scans were recorded at 0.5 cm^{-1} resolution. The samples were dispersed in nujol under an argon atmosphere.

Cyclic voltammetric measurement of complexes 1 and 2.

Cyclic voltammetry was performed in a gas tight cell under an inert atmosphere of dry argon. The cell was equipped with a Pt disk working electrode, apparent surface area of 0.42 mm², Pt wire auxiliary electrode, and Ag wire pseudo-reference electrode. Before each experiment, the working electrode was carefully polished with a 0.25 µm diamond paste. The redox potentials are reported against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple, used as an internal reference standard. Cyclic voltammetric experiments were performed with 10⁻² M complexes 1 and 2 in dry HPLC-grade dimethylformamide (DMF). The potential control was achieved with a PAR Model 283 potentiostat equipped with positive feedback for ohmic drop compensation.

Results

Syntheses of complexes [Rh¹{X=4'-Y-Tpy}] (X = Cl, Br; Y = H, Cl, tert-butyldimethylsilyl-ortho-carborany1) 1-4.

The novel complexes 1-4 were prepared by a ligand displacement reaction, as depicted in Scheme 2.1.
The characterisation of complexes 1-4 by means of NMR techniques was problematic due to their poor solubility. After scanning for 20 hours (using C₆D₆ as solvent), only complex 4 gave an acceptable ¹H NMR spectrum (Figure 2.3). The H(6.6') signals of 4 were hidden under the benzene signal. The B-H signals, presumably spread over the range of 2-4 ppm, are not observable. The ¹H spectrum also contained additional signals of at least one minor species, probably a degradation product, since complex 4 is far less stable in organic solvents than 1-3. The solubility of 1-4 in CD₃CN is lower than that in benzene and no acceptable ¹H NMR spectrum could be recorded. Finally, although the solubility of 1-4 in EtOH-d6 and DMF-d6 is similar to that in benzene, the ¹H NMR spectra only exhibited very broad signals.
X-ray structures of complexes 1 and 4.

The molecules of 1 (Figure 2.1) are arranged in sheets that run parallel with the crystallographic 
$h$-axis (Figure 2.4). The distance between the sheets, considered as the thickness of the molecules, is 3.508(12) Å. The neighbouring molecules in different sheets are in a staggered arrangement close to inversion symmetry. The distance between the sheets strongly indicates the presence of \( \pi \)-
stacking (Figure 2.5). Within the sheets short intermolecular distances are found between the 
chlorine atom and H5' and H3' of a neighbouring molecule: H\( \cdots \)Cl distances are 2.79 Å and 2.85 
Å. C-H\( \cdots \)Cl angles are 167° and 169°, respectively (Figure 2.6). These short distances are 
indicative of "chelating" C-H\( \cdots \)Cl hydrogen bonds that link the neighbouring molecules into a one-
dimensional intermolecular hydrogen bonding network. The hydrogen-bonded sheets are stacked in 
the crystallographic [101] direction (Figure 2.6). There are no short Rh-Rh' contacts, the smallest 
distance being 4.896(2) Å. Selected bond lengths and angles in complex 1, together with those in 
the ADF/BP-calculated model complexes 1m and 2m, for comparison, are summarised in Tables 
2.2 and 2.3.

Figure 2.4. Molecular stacking in the crystal structure of 1. Figure 2.5. The \( \pi \)-stacking between two molecules in the crystal structure of 1.
Dark blue crystals of 4, suitable for X-ray analysis, were grown from a saturated EtOH solution, after standing at room temperature for three weeks. In the solid state, the molecules (Figure 2.2) are packed in discrete dimers around the inversion centres (Figure 2.7), with Rh-Rh' distances of 3.1503(13) Å. The packing of the dimers appears to be dominated by intermolecular hydrophobic interactions of the carborane residues, and by hydrophilic interactions of the Rh-Cl residues with the disordered ethanol molecules also present in the structure. Apart from the interaction between the two halves of each dimer, no π-stacking is observed (Figure 2.8).
Figure 2.7. Dimer formation in the crystal structure of complex 4. Symmetry operation i: -x, 1-y, 1-z.

Figure 2.8. Perpendicular view on the aromatic system of complex 4.
Table 2.2. Selected bond lengths \( \text{A} \) for complexes 1 and 4, and for geometry-optimised 1m and 2m models.

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<thead>
<tr>
<th>Bond distance</th>
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<th>2m</th>
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<td>2.3540</td>
<td>2.4871</td>
</tr>
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<td>Rh1N</td>
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<td>2.1185</td>
<td>2.0151</td>
<td>2.0563</td>
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<td>Rh-N2</td>
<td>1.8900</td>
<td>1.8904</td>
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<td>Rh1-N3</td>
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<td>2.0116</td>
<td>2.0421</td>
<td>2.0505</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.3352</td>
<td>1.3380</td>
<td>1.3207</td>
<td>1.3405</td>
</tr>
<tr>
<td>N1-C5</td>
<td>1.3484</td>
<td>1.3411</td>
<td>1.3583</td>
<td>1.3808</td>
</tr>
<tr>
<td>N2-C6</td>
<td>1.3666</td>
<td>1.3603</td>
<td>1.3533</td>
<td>1.3609</td>
</tr>
<tr>
<td>N2-C10</td>
<td>1.3535</td>
<td>1.3447</td>
<td>1.3773</td>
<td>1.3609</td>
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<tr>
<td>N3-C11</td>
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<td>1.3708</td>
<td>1.3873</td>
<td>1.3808</td>
</tr>
<tr>
<td>N3-C15</td>
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<td>1.3504</td>
<td>1.3207</td>
<td>1.3503</td>
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</tbody>
</table>

N = C1 for 1, 4 and 1m, and Rh for 2m

Table 2.3. Selected bond angles \( ^\circ \) for complexes 1 and 4, and for geometry-optimised models 1m and 2m.

<table>
<thead>
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<th>Angles</th>
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<th>1m</th>
<th>2m</th>
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</thead>
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<td>99.54</td>
<td>99.62</td>
<td>99.84</td>
<td>100.20</td>
</tr>
<tr>
<td>N-Rh-N2</td>
<td>175.12</td>
<td>175.12</td>
<td>181.00</td>
<td>180.20</td>
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<tr>
<td>N-Rh-N3</td>
<td>99.13</td>
<td>99.25</td>
<td>99.34</td>
<td>100.20</td>
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<td>N1-Rh-N2</td>
<td>80.79</td>
<td>80.93</td>
<td>80.76</td>
<td>79.80</td>
</tr>
<tr>
<td>N1-Rh-N3</td>
<td>161.29</td>
<td>160.74</td>
<td>160.32</td>
<td>169.64</td>
</tr>
<tr>
<td>N2-Rh-N3</td>
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<td>Rh-N1-C1</td>
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<td>129.08</td>
<td>127.05</td>
<td>127.78</td>
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<td>Rh-N1-C5</td>
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<td>113.38</td>
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<td>Cl1-N1-C5</td>
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<tr>
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<td>Rh1-N2-C10</td>
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<td>120.18</td>
<td>119.20</td>
<td>119.18</td>
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<tr>
<td>Cl6-N1-C10</td>
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<td>122.00</td>
<td>121.60</td>
<td>122.23</td>
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<td>Rh-N2-C11</td>
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<td>114.95</td>
<td>113.88</td>
<td>113.64</td>
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<td>Rh-N2-C15</td>
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<td>128.40</td>
<td>127.65</td>
<td>127.78</td>
</tr>
<tr>
<td>Cl1-N3-C15</td>
<td>117.93</td>
<td>117.97</td>
<td>118.34</td>
<td>118.50</td>
</tr>
</tbody>
</table>

N = C1 for 1, 4 and 1m, and Rh for 2m
DFT study and electronic absorption spectra of complexes 1 and 2.

Density functional theoretical calculations have been performed on complexes 1 and 2, restricted to a $C_{2v}$-symmetric square planar arrangement. Only orbital contributions above 10% are incorporated in Table 2.4.

Table 2.4. Characters and one-electron energies of the levels HOMO-8 to LUMO+4 (HOMO and LUMO in bold) of $[\text{Rh}^1(\text{X'})\text{ppy}]$ (1: X = Cl; 2: X = Br) as calculated by the ADF/BP program.

<table>
<thead>
<tr>
<th>MO</th>
<th>X</th>
<th>Energy (eV)</th>
<th>Terpyridine</th>
<th>Rh</th>
<th>X</th>
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<tr>
<td></td>
<td></td>
<td>unoccupied orbitals</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24a1</td>
<td>Cl</td>
<td>-1.170</td>
<td>31.3% (18a1)</td>
<td>55.5% (d,z,z)</td>
<td>—</td>
</tr>
<tr>
<td>26a1</td>
<td>Br</td>
<td>-1.350</td>
<td>30.2% (18a1)</td>
<td>54.3% (d,z,z)</td>
<td>—</td>
</tr>
<tr>
<td>11b2</td>
<td>Cl</td>
<td>-1.463</td>
<td>95.9% (8b2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>12b2</td>
<td>Br</td>
<td>-1.490</td>
<td>95.9% (8b2)</td>
<td>—</td>
<td>—</td>
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<tr>
<td>7a2</td>
<td>Cl</td>
<td>-2.057</td>
<td>92.1% (6a2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>8a2</td>
<td>Br</td>
<td>-2.084</td>
<td>92.2% (6a2)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>10b2</td>
<td>Cl</td>
<td>-2.131</td>
<td>96.7% (7b2)</td>
<td>—</td>
<td>—</td>
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<tr>
<td>11b2</td>
<td>Br</td>
<td>-2.149</td>
<td>96.6% (7b2)</td>
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<td>—</td>
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<tr>
<td>6a2</td>
<td>Cl</td>
<td>-2.998</td>
<td>95.8% (5a2)</td>
<td>—</td>
<td>—</td>
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<tr>
<td>7a2</td>
<td>Br</td>
<td>-3.026</td>
<td>95.7% (5a2)</td>
<td>—</td>
<td>—</td>
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<tr>
<td>9b2</td>
<td>Cl</td>
<td>-3.079</td>
<td>75.4% (6b2)</td>
<td>18.3% (d,α)</td>
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<tr>
<td>10b2</td>
<td>Br</td>
<td>-3.115</td>
<td>76.0% (6b2)</td>
<td>17.6% (d,α)</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td></td>
<td>occupied orbitals</td>
<td></td>
<td></td>
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<tr>
<td>23a1</td>
<td>Cl</td>
<td>-4.119</td>
<td>—</td>
<td>77.6% (d,z)</td>
<td>—</td>
</tr>
<tr>
<td>25a1</td>
<td>Br</td>
<td>-4.129</td>
<td>—</td>
<td>78.0% (d,z)</td>
<td>—</td>
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<tr>
<td>19b1</td>
<td>Cl</td>
<td>-4.514</td>
<td>—</td>
<td>56.0% (d,α)</td>
<td>34.3% (p,α)</td>
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<tr>
<td>20b1</td>
<td>Br</td>
<td>-4.500</td>
<td>—</td>
<td>49.6% (d,α)</td>
<td>41.1% (p,α)</td>
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</table>
The DFT calculations prove that variation of the ligand X (CI and Br) for complexes 1 and 2, respectively, results only in small differences between orbital characters and energies as shown in Table 2.4 and Figure 2.9. The MO diagrams of complexes 1 and 2 clearly show that the comparable predominantly Rh d-orbitals of 1 and 2 (HOMO-1, 2, 3) have the same energies except for empty d_{z^2} orbitals, which is also the case for the Tpy-centred orbitals (Figure 2.9). Thus, the only comparable orbitals of 1 and 2 differing in energy are the orbitals with a predominantly halide (p_e) character (Figure 2.9). The variation of X in complexes 1 and 2 is reflected in the HOMO-4, HOMO-5 and HOMO-7 (X = CI) and HOMO-6 (X = Br). These predominantly halide (X) orbitals are ca. 0.3 eV lower in energy for complex 1 than for complex 2 (X = CI and Br, respectively).

According to the DFT calculations, the HOMO-1, HOMO-4 and HOMO-5 of 1 and 2 have significantly mixed Ntp_e/Rh d_† characters. The HOMO-2 of 1 and 2 have a strongly mixed Tpy_r/Novp_e/Rh d_† character. In contrast to this, the HOMO and HOMO-3 of 1 and 2 have a predominant Rh d_† and Rh d_† character, respectively, while the HOMO-7 (X = CI) and HOMO-6 (X = Br) has predominantly a halide (p_e) character. As expected, the LUMO of 1 and 2 reside on
the $\pi^*$ (Tp) system, with some Rh(d$_{z^2}$) contribution. The higher-lying virtual orbitals of 1 and 2 are also almost exclusively located on the $\pi^*$ (Tp) system, except for (LUMO+5) Rh(d$_{z^2}$,2).

Relevant electronic transitions (transition energies, wavelengths, oscillator strengths) of complexes 1 and 2 and their characters obtained from TD-DFT calculations are presented in Tables 2.5 and 2.6, respectively. Apart from the first three excitations, only electronic transitions with oscillator strengths > 0.015 are incorporated in Tables 2.5 and 2.6.

![Diagram](image_url)
Table 2.5: Single-electron transitions of complex I, as calculated by the XAD-1P program.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Energy (eV)</th>
<th>Wavelength (nm)</th>
<th>Oscillator strength</th>
<th>Character</th>
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</tr>
<tr>
<td>2</td>
<td>1.066</td>
<td>1033</td>
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<td>MLCT/MLCT</td>
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<td>920</td>
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</tr>
<tr>
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<td>MLCT/MLCT</td>
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<tr>
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Table 2.6: Selected characteristics of the 2000 AEC BFI iron.
The first seven single-electron transitions in Tables 2.5 and 2.6 are the same excitations from the comparable d(Rh) orbitals of complexes 1 and 2. Single-electron transitions at higher energies are less readily comparable with each other owing to different characters of the molecular orbitals involved.

Experimental UV-VIS spectra and calculated electronic transitions for complexes 1 and 2 are shown in Figures 2.10 and 2.11, respectively. The lowest seven single-electron transitions are highlighted, except for the forbidden transitions nr. 1 of very low oscillator strengths.

Figure 2.10. Electronic absorption spectrum of 7.27·10⁻⁵ M 1 in EtOH. Major electron transitions of 1, as calculated by the ADF/BP method (Table 2.5).
Figure 2.11. Electronic absorption spectrum of 1.36·10⁻⁴ M 2 in EtOH. Major electron transitions of 2, as calculated by the ADF/BP method (Table 2.6).

The assignment of the absorption bands in the UV-visible region (250-900 nm) is facilitated by DFT calculations. The calculated electronic transitions of complex 1 match fairly well with the experimental electronic absorption spectrum, except for the calculated transition 7 (Table 2.5). For complex 2 the deviations in the UV region are larger. The intense absorption bands in the region 250-350 nm are predominantly due to intraligand Tpy transitions. The pronounced composed absorption bands in the region 450-700 nm encompass mixed MLCT/XLCT (6, 5) and MLCT (4) transitions. The minor absorption bands in the region 700-900 nm belong to symmetry-forbidden (in a perfect square planar coordination) MLCT (3), MLCT/XLCT (2) and MLCT (1: HOMO-to-LUMO) transitions.
Cyclic voltammograms of complexes 1 and 2.

Under an argon atmosphere, freshly prepared solutions of 1 and 2 in neat DMF show very similar cyclic voltammograms. Therefore, only the cyclic voltammogram of complex 1 is depicted in Figure 2.12.

![Cyclic voltammogram of complex 1 in DMF at a Pt disk electrode, $\nu = 100$ mVs$^{-1}$.](image)

**Figure 2.12.** Cyclic voltammogram of complex 1 in DMF at a Pt disk electrode, $\nu = 100$ mVs$^{-1}$. a) Partially reversible one-electron oxidation of the Rh(I) centre to Rh(II) at $T = 293$ K; b) reversible one-electron reduction of the Tpy ligand at $T = 233$ K; c) complete cyclic voltammogram at $T = 293$ K. Asterisk denotes the Fe/Fe$^+$ couple.

The anodic peak of complexes 1 and 2 is associated with one-electron oxidation of the formal Rh(I) centre to the corresponding Rh(II) product, being partly chemically reversible on the time scale of cyclic voltammetry ($\nu = 100$ mVs$^{-1}$) at room temperature (Figure 2.12). Further oxidation of 1$^+$ and 2$^+$ to corresponding Rh(III) species was not observed. Comparison of the oxidation potentials of 1 and 2 shows negligible difference: $E_{1/2}$ (1) = -0.84 V vs Fe/Fe$^+$; $E_{1/2}$ (2) = -0.83 V vs Fe/Fe$^+$. This result agrees with the DFT-calculated energies of the HOMO for both complexes, which differ merely by 0.01 eV (Table 2.4).

The reduction of 1 and 2 is reversible (Figure 2.12) on the time scale of cyclic voltammetry at $T = 233$ K ($\nu = 100$ mV/s), being predominantly localised on the lowest $\pi^*$ (Tpy) level (Table 2.4). It is therefore understandable that also the reduction potentials of both complexes are nearly identical.
(E_{1/2} (1) = -1.98 V and E_{1/2} (2) = -1.97 V vs Fe/Fe^+). The calculated LUMO energies of 1 and 2 differ slightly more (0.036 eV).

**Far-infrared (FIR) spectra of complexes 1 and 2.**

Generally, the assignment of IR $\nu$(Rh-X) (X = Cl, Br) modes of pseudo-octahedral Rh$^{III}$X$_3$-terpyridine complexes is difficult.\(^{[34]}\) The complexity of the FIR spectra of these complexes is for a great deal attributed to the coupling of $\nu$(Rh-X) and $\nu$(Rh-N) modes, and to the difference between the $\nu$(Rh-X) modes of the *cis* and *trans* halides. On the other hand, for square planar Rh$^{III}$(X)-terpyridine complexes is the assignment easier. The FIR spectra of complexes 1 and 2 are similar, except for the $\nu$(Rh-Cl) and $\nu$(Rh-Br) bands, as shown in **Figure 2.13**.

![Figure 2.13. Far IR spectra of complexes 1 (a) and 2 (b) dispersed in nujol.](image)

The assignment of $\nu$(Rh-X) (X = Cl, Br for 1 and 2, respectively) is straightforward: $\nu$(Rh-Cl) at 256-260 cm$^{-1}$ and $\nu$(Rh-Br) at 188 cm$^{-1}$. The assignment of $\nu$(Rh-Cl) is also supported by the
observation of the chlorine isotope splitting: the experimental value of 4 cm⁻¹ 256 and 260 cm⁻¹ for ^35Cl and ^37Cl, respectively, is comparable with the calculated isotope splitting of 5 cm⁻¹ (K = 6.33 × 10⁻¹⁰ dyn/cm for Rh-Cl).

The band pattern observed for 1 at 120 and 138 cm⁻¹ is also considerably shifted to smaller wavenumbers for 2 (85 and 96 cm⁻¹). These bands are most likely the Rh-N bending vibrations out-of-plane and in-plane.

Other absorption bands observed for 1 at 300-320 cm⁻¹, 220-230 cm⁻¹ and 153 cm⁻¹ show only a minor shift to smaller wavenumbers for 2, i.e., 295-302 cm⁻¹, 214-226 cm⁻¹ and 141 cm⁻¹. These bands are assigned to Rh-N vibrations.

Discussion

Syntheses of complexes 1-4.

The syntheses of the studied Rh-terpyridine complexes are fairly simple with nearly quantitative yields, as soon as the right reaction conditions, in particular the suitable solvent, are found. The dark blue RhI-terpyridine species are highly air-sensitive and readily oxidised to yellow/red RhIII species.

After having prepared complex 1 in toluene and washed it subsequently with hot THF, crystals were formed after gentle cooling of the combined THF phases. However, this method was not successful for the crystallisation of the other studied RhI-terpyridine complexes. In contrast to complex 1, complex 2 could not be synthesised in toluene: instead, only orange RhII species were formed. Complex 2 was only obtained in EtOH. Similar to complex 1, complex 3 could be prepared in various organic solvents such as benzene, THF, EtO and EtOH. Attempts to synthesise the Rh-Br complex analogous to 3 gave only red products. Finally, despite the instability of the carbonanyl-Tpy unit in various organic solvents, complex 4 was found to be stable for several weeks in EtOH and could crystallize upon standing at room temperature.
X-ray crystallographic studies of complexes 1 and 4.

In contrast to the facile syntheses of the studied Rh(I)-terpyridine complexes, their characterisation is hampered due to their low solubility in organic solvents. It is well documented that the crystal packing of various square planar d-transition metal complexes with aromatic ligands is dominated by \( \pi \pi \) stacking interactions, leading to poor solubility and hampering full characterisation. The distance between the sheets is 3.50 Å in the crystal of 1 is due to this type of \( \pi \) stacking (Figure 2.3 and Figure 2.4).

Complex 4, bearing the bulky carborane group, \( \text{C}_{6} \text{B}_{11} \text{H}_{13} \text{H} \), was prepared in the hope of preventing such \( \pi \) stacking. In the crystal, molecules of 4 are packed in discrete dimers with a Rh-Rh distance of 3.450(4) Å. This is too long for a single bond, but rather short for a non-bonding contact. \( \text{C}_{6} \text{B}_{11} \text{H}_{13} \text{H} \) is clear that the introduction of the carborane group has resulted in a structure without strong \( \pi \)-stacking, the dimeric structure being apparently the highest degree of association possible with this ligand. Unfortunately, even this non-\( \pi \)-stacked complex does not dissolve well in organic solvents. Thus, preventing \( \pi \) stacking is not a sufficient condition for increased solubility of Rh(I)-terpyridine complexes.

Despite the dramatic difference in the packing of complexes 1 and 4, the coordination geometries of the mononuclear units are very similar and comparable with isoelectronic RhII and RhIII-terpyridine complexes. The corresponding bond lengths (Table 2.2) and angles (Table 2.3) are almost the same. The Rh-N distances for both complexes 1 and 4 (1.894(6) - 2.026(6) Å) are significantly shorter compared to \( \text{RhIII-terpyridine} \), \( \text{RhII-dimine} \), and \( \text{RhII-terpyridine} \). For Rh(I) chloride complexes with the diminepyridine ligands 2,6-bis(R)diminepyridine and 2,6-bis(R)methylidipyridine (R = \( \text{Pt} \)) it was shown by Haas and \( \text{I} \), that the angle between the N-N plane and the Rh-Cl axis is a clear measure of steric interactions between the R groups and the chlorine atom. In our study, these angles are 62.5(7)° for 1 and 34.3(4)° for 4. These values are much smaller than those found by Haas and \( \text{I} \) (53.4(10)° - 113.5(1)°). We can therefore conclude that steric interactions between the terpyridine ligand and the chlorine atom in complexes 1 and 4 are insignificant.
Bonding properties of complexes 1 and 2.

A good agreement is found between the experimental and corresponding DFT calculated bond lengths and angles in complexes 1 and 2 (Tables 2.2 and 2.3). This confirms that the used GGA functional (Becke-Perdew), for geometry determination, and the chosen basis set for the DFT calculations, run by the ADF program, are adequate.

From the DFT calculations, it is clear that the HOMO of complexes 1 and 2 is mainly located on their rhodium d- orbital. This, combined with the strong electron donating nitrogen atoms-coordinated on the Rh(III) metal centre, makes complexes 1 and 2 extremely nucleophilic and thereby very reactive towards e.g. oxygen and carbon-halogen bonds. While the HOMO of 1 and 2 has a strong metal character, the LUMO is predominantly located on the π^* system of the Tpy ligand. The HOMO-1 and HOMO-2 can be characterised as antibonding combinations (π-interactions) of p(N) + X = Cl, Br and d(Rh) orbitals. Both orbitals are destabilised in comparison with the HOMO-3, which has predominantly a Rh d-character. The HOMO-4 and HOMO-5 are bonding orbitals, π-interactions between p(N) and d(Rh) orbitals. HOMO-6 + X = Cl/HOMO-7 (X = Br) have exclusively a ligand Tpy character (like HOMO-8). The HOMO-7 + X = Cl/HOMO-7 (X = Br) have predominantly a halide character (σ-interactions).

Data in Tables 2.5 and 2.6 reveal that complexes 1 and 2 have comparable electronic transitions from orbitals of the same characters. The lowest seven excitations in both complexes correspond mutually very well. At higher energies, there is no longer a one-to-one relationship between the composition of the excited states of the Cl and Br complexes (1 and 2, respectively) in terms of one-electron transitions. After the seventh excitation, the Br p orbitals play a more dominant role in the single electron transitions for complex 2 than the Cl p orbitals for complex 1. This is mainly due to the difference in energy of the halide p-orbitals (Figure 2.9).

Regarding the differences, for complex 2 an extra electronic transition (viz. nr. 9, Table 2.6) has been calculated by the ADF/BP program, which has no counterpart in complex 1. Furthermore, for complex 1, the electronic transition nr. 8 has a predominant MLCT character (Table 2.5), while the corresponding electronic transition nr. 8 in complex 2 can better be assigned as NLECT (Table 2.6).

The MO diagrams of complexes 1 and 2 are very similar. Only the unoccupied predominantly Rhd. 3d and occupied halide molecular orbitals of 1 and 2, viz. LUMO+5, HOMO-4, HOMO-5 and HOMO-7 (X = Cl/HOMO-6 + X = Br), slightly differ in energies (ca. 0.3 eV), as displayed by
their molecular orbital distributions. Figure 2.9. This rationalizes the fact that complexes 1 and 2 exhibit similar UV-Vis spectra and cyclic voltammograms. The assignments of the UV-Vis absorption bands of complexes 1 and 2 to particular types of electronic transitions are done with a high certainty, on grounds of the TD-DFT calculations. The most intense absorption bands in the UV region 280-380 nm are solely assigned as Py intraligand transitions. The dominant and minor absorption bands and shoulders in the visible region 450-600 nm are assigned to mixed electronic transitions that vary in nature from pure MLCT to mixed MLCT-MILCT charge transfers (Tables 2.5 and 2.6). The HOMO-LUMO transition is not symmetry allowed (Table 2.4), resulting in a very low oscillator strength (Tables 2.5 and 2.6). Exclusive Rh-centred d-d, H transitions are not observed. The only notable contribution, yet of limited significance (1%) to transition in n, has been calculated for complex 1, see Table 2.5.

Complexes 1 and 2 have fairly negative oxidation potentials, strongly indicating that the Rh metal centres accommodate high electron densities. The one-electron oxidation of formally Rh(I) to Rh(II) at room temperature is partly reversible on the time scale of seconds. The relative stability of the Rh(II) species can be ascribed to the high electron donating capacity of the coordinated Py and nitrogen ligands. It is noteworthy that the subsequent oxidation of Rh(II) to Rh(III) was not observed in the available potential window.

At room temperature, the initial one-electron reduction of complexes 1 and 2 in DMF is also partly chemically reversible. Fully reversible scan ∆ν = 100 mV s−1 can be achieved at T = 233 K. The one lifetime of the radical cations of 1 and 2 results from the accommodation of the added electron in the 2,4-Py LUMO, as evidenced by the DFT calculations. The following thermal relaxation of the radical cations most likely involves release of the ligand ligand to compensate for the high electron density at the metal centre. Slow ligand dissociation is known to occur also in the case of the radical cation of the much less electron-rich complex [Rh(CO)3(PPh3)2] (2-dipropylphenyl)imidazol-2-ylidene). For the extremely air-sensitive complexes 1 and 2, no spectroelectrochemical study was performed.

**FTIR spectra of complexes 1 and 2.**

The Rh–N–terpyridine complexes contain only a single Rh-N bond. This facilitates the analysis of their far-IR spectra compared to those of Rh(I)-Py species. The assignment of ν-Rh-N
for 1: 250–260 cm\(^{-1}\) and 2: 188 cm\(^{-1}\) is straightforward from the comparison of the IR spectra. Bands at 120–138 cm\(^{-1}\) and 85–96 cm\(^{-1}\) are tentatively assigned to Rh–X bending vibrations. The influence of the Rh metal oxidation state and of the absence/presence of axial halides on the \(\nu_{\text{Rh–X}}\) modes for \(\text{Rh}^{1+}\text{X}^*\text{tpy}\) and \(\text{Rh}^{1+}\text{X}^*\text{tpy}\) has not been thoroughly studied yet. The Rh–X bonds are generally weaker than Rh\(^{11}\)–X bonds due to stronger \(\pi\)-donation from X to Rh\(^{11}\) than to Rh\(^{11}\) metal ions. Therefore, the larger \(\nu_{\text{Rh–X}}\) wavenumbers reported for \(\text{Rh}^{1+}\text{Cl}^*\text{tpy}\) (360–380 cm\(^{-1}\)) and \(\text{R}_{\text{Br}}\text{Br}^*\text{tpy}\) (205–209 cm\(^{-1}\)) are reasonable.

Conclusions

For the first time, we report the successful syntheses, characterisation and properties of neutral rigid square planar Rh(II)-terpyridine complexes (1–4). For the syntheses, the use of an appropriate solvent for each individual complex is of crucial importance. Characterisation is difficult, primarily due to their low solubility (formation of \(\pi\)-stacked aggregates and discrete dimers) and high reactivity, promoted by the high electron density on the Rh centre. The studied Rh(II)-terpyridine complexes show no steric repulsion between the halides and the tpy ligand, as evidenced by the crystal structures. The variation of the halide ligand in complexes 1 and 2 (Cl and Br, respectively) has no significant influence on the electronic structure. Their HOMO is predominantly located on the Rh(I) centre in 1, and the LUMO resides on the tpy ligand.

References


Chapter 3

Oxidative Addition Reactions of $[\text{Rh}^1(\text{Br})(\text{TpY}^*)] \quad (\text{TpY}^* = 4'-(4-\text{tbutylphenyl})-2,2':6',2''\text{-terpyridine})$ with Alkyl Bromides.

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Abstract

Oxidative addition reactions with the highly nucleophile complex Rh(CO)₄(4-butylenylphenyl-2,2'-6,2'-terpyridine), 1, and alkyl halides containing chlorine and bromine atoms gave mixtures of uncharacterised products. In contrast to this, oxidative addition reactions with complex [Rh(Br)₄(4-butylenylphenyl-2,2'-6,2'-terpyridine)] · 2 and various alkyl bromides, containing mainly terminal carbon-bromine bonds, gave clean single products in almost quantitative yield. The corresponding air stable yellow Rh(III) terpyridine complexes are, in contrast to the parent Rh(I)terpyridine complex, soluble in various organic solvents. Consequently, these products are further characterised by means of 1H, 13C, 19F, 1Rh and 2D NMR techniques. NMR techniques were also used to determine the geometry of the studied Rh(III)terpyridine complexes, which was found to be octahedral with the alkyl moiety axially positioned with respect to the Rh terpyridine plane except for complexes 3 and 4. The oxidative addition reaction of complex 2 with 1-bromo decane in ethanol was monitored by UVVIS spectrometry. The recorded electronic absorption spectrum of this reaction showed two distinct isosbestic points in the visible region. It is most likely that firstly the carbon-bromine bond of 1-bromo decane is activated by the Rh metal (d HOMO, cf. Chapter 2), followed by the arrangement of the alkyl moiety in axial position. Unfortunately, based on our findings, no single mechanism for this oxidative addition reaction can be suggested.
Introduction

Oxidative addition reactions are a general synthetic method for the formation of carbon-metal σ-bonds. Most reported syntheses of carbon-metal σ-bonds involve the reaction of alkyl iodides and bromides with compounds of gold, platinum, palladium, iridium and rhodium. In particular, the oxidative addition reaction of MeI to carbonyl rhodium complexes has been studied in great mechanistic detail, since it is the key step in the catalysed carbonylation of methanol on an industrial scale. Furthermore, rhodium-alkyl complexes are considered to be key intermediates in major industrially important catalytic processes like hydrogenation and hydroformylation.

Oxidative addition reactions of carbon-halogen bonds to transition metal complexes are also applied in a number of other industrially important catalytic processes. Examples of these are the cross-coupling and carbonylation reactions of aryl halides for e.g., the syntheses of drugs and fragrances. More recently, since compounds containing carbon halogen bonds have been used in large amounts over the last century (agriculture, industry, home products, etc.), their potential danger for the environment has created considerable concern. Therefore, it is very important to develop catalysts to transform compounds with carbon halogen bonds into harmless molecules in order to neutralise the potential danger of organohalide pollutants. This can be achieved by either stoichiometric reactions or biological processes, which can be facilitated by catalysts and enzymes respectively.

Based on the many mechanistic studies using e.g., square-planar d6 metal complexes, several mechanisms have been proposed for the oxidative addition reaction of alkyl halides. The most common referred mechanisms in literature are the Sz2 and the concerted cis-addition mechanisms, and mechanisms involving free alkyl radical intermediates. Recent theoretical studies of the oxidative addition reaction of MeX (X = Cl, Br to Pd, Rh and Ir complexes suggest that the preferred pathway is Sz2. In addition, kinetic studies on the oxidative addition reaction of many carbon halogen bonds to a RhIr complex suggest a general Sz2 like mechanism.

The reactivity of metal-containing complexes towards oxidative addition reactions with carbon halogen bonds is highly dependent on the electron density of the metal centre. For example, breaking carbon chloride σ-bonds is only possible when very electron rich centres are used. Therefore, compared to alkyl iodides and bromides, oxidative addition reactions of the less reactive...
alkyl chlorides are more scarce. The design of complexes with electro-donating metal centres is based on the use of strongly electron-donating ligands. Tendencate ligands containing ligands have proven to be very successful in this respect. Bish et al. studied the oxidative addition of alkyl chlorides with rhodium complexes using the [RhCp*<sub>2</sub>Cl] <sub>2</sub> precursor and the 2,6-bis-1,4-dimethyl-1,2,4-triazolin-3-yl pyridine-3,4-pyrazol ligand. Furthermore, Haarmann et al. successfully showed that the very electron-rich complexes [RhC<sub>2</sub>H<sub>5</sub>(OR)<sub>2</sub>]<sup>+</sup>(N<sub>3</sub>)<sub>2</sub> with tendencate pyridine-dimine ligands are highly reactive towards various substrates containing carbon-chloride σ-bonds. It was found that chloroform, dichloromethane, benzyl chloride and 1,2-dichloroethane readily undergo oxidative addition reactions even at low temperatures (50 °C). The tendencate pyridine-dimine ligand is not only increasing the reactivity of the Rh centre, but due to its chelating capability also stabilises the oxidative addition product facilitating its full characterisation. Finally, crystallographic studies strongly indicated that the Rh-C σ bond formed after the oxidative addition reaction with CHCl<sub>3</sub> or CH<sub>3</sub>Cl and [RhC<sub>2</sub>H<sub>5</sub>(OR)<sub>2</sub>]<sup>+</sup>(N<sub>3</sub>)<sub>2</sub> has a metal carbene (Rh-C=CH-) character.

These interesting features displayed by the square planar complexes [RhC<sub>2</sub>H<sub>5</sub>(OR)<sub>2</sub>]<sup>+</sup>(N<sub>3</sub>)<sub>2</sub> towards oxidative addition reactions with alkyl halides prompted us to study similar rhodium complexes of terpyridine ligands. Unlike the work of Haarmann et al., the oxidative addition reactions with [Rh(N<sub>3</sub>)<sub>2</sub>Py] and CH<sub>3</sub>Cl or Br for complexes 1 and 2 respectively gave chlorocarbons that formed mixtures of unidentified products. Only oxidative addition reactions with Rh-Br-<sub>2</sub> and mainly primary alkyl bromides afforded the formation of clean single products 4. Here we report the successful oxidative addition reactions between complex 2 and numerous reagents containing primary terpyridine C-Br bonds.
Experimental Section

**General.** The 4′-4′-butylphenyl 2,2′:6′,2′-terpyridine (tpy) ligand was synthesised according to literature procedures, while its purification was executed differently, i.e., column chromatography with silver; using an eluent mixture of toluene:diethyl ether:hexane = 6:1:4. The syntheses of the complexes 1-24 were performed in an inert atmosphere of purified argon, using standard Schlenk techniques. For the syntheses of these complexes, 0.028 g [RhBr(COD)]_2 (0.048 mmol), COD = 1,5-cyclooctadiene and 0.035 g Tpy (0.096 mmol) were used. The yield of the products 1-23 was practically quantitative, while the yield of 24 was ca. 70%. Solvents were dried and purified by standard procedures. The bromine reagents, used for the synthesis of complexes 3-24, were purchased from Aldrich. The H and C NMR spectra were recorded at 294 K with Bruker AMX 300, Bruker DRX 300, Varian Mercury 500 and Varian Inova 500 spectrometers. All H and C NMR signal assignments of complexes 3a, 3b and 4-24 are based on NMR studies for the signal assignments of complex 10 using also mathematical simulations and 2D NMR techniques such as COSY (H-H), and HMQC (H-C) measurements. The 15N NMR spectra were recorded using the PFG HMQC sequence in a Bruker DRX 300 spectrometer equipped with a 5 mm triple resonance inverse probe with a gradient, operating at 30.42 MHz 15N frequency, a second 300 MHz decoupler giving a 90° 15N pulse of 10 μs. Spectra were recorded without decoupling 15N in t. Spectral width in t was 500 ppm and 32 increments were used. Three values for J (1 H, 15N) 2.5, 5, 10 Hz were used to determine the 15N resonance, after finding the 15N resonance the final experiment was done with a spectral width in t of 50 ppm and between 64 and 128 increments. This resulted, after linear prediction in t, a better resolution than 0.2 ppm for 15N resonance. Chemical shifts were referenced to external trimethylsilane = 0 ppm, negative chemical shifts are reported for lower frequencies. Spectra were recorded at 296 K. The 1H NMR measurements were performed as part of the characterisation of the RhIII terpyridine complexes.

Rh measurements were carried out on a Bruker DRX 300 spectrometer under temperature control at 298 K using a 5 mm triple resonance inverse probehead: 1H, 13C, 19F with a 1 gradient coil 90° H = 7.2 ms, 90° Rh = 10.5 ms using the PFG HMQC sequence. The acquisition time was 30.90 minutes for the final experiment. The spectral width was 10 ppm for 1H. In the first measurement, the spectral width for 1H was 9000 ppm which was covered by 128 increments.
16 dummy scans were used. To exclude loading and improve resolution, a second and sometimes
third measurement with modified 3rd order values and smaller spectral widths were carried out. the
final experiment was 500 ppm in \( \tau \) and using 256 increments. The digital resolution of the
Rh was at least 3.7 Hz per. After a linear prediction in the \( \tau \) direction, the \( 512 \times 512 \) matrix was transformed
applying a sinc band weighting function. The Rh spectra are obtained in \( \tau \) and the H spectra in \( \tau \).
The absolute 34Rh ppm values are referenced to 2.256 MHz. Signals at higher frequencies are
taken as positive. Last Atom Bombardment (FAB), mass spectrometry was carried out using a
FAB-MS SX-102a four sector mass spectrometer, coupled to a JEOI MS-7100 data system.
The samples were loaded in a matrix phase glycerol on a stainless steel probe and bombarded with
ion atoms with an energy of 5 KeV. During the high resolution FAB-MS measurements a
resolving power of 5000:1 for a valley definition was used. Cel and glycerol were used to calibrate
the mass spectrometer. Elemental analyses were carried out by H. Kolle Mikroanalytisches,
Laboratorium (Meling an der Ruhr, Germany) and Analytische Laboratorium GmbH (Lindlar,
Germany).

For the syntheses of the RhIII-terpyridine complexes the following reactants were used:

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<th>Table 3.1. Reactants for variable coordination.</th>
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Atom numbering of the Rh(III)-terpyridine complexes for the assignment of NMR signals is done according to the following scheme:

\[
\text{[Rh}^\text{III}(\text{Cl})(\text{Tpy})\text{]}, \ 1
\]

Toluene (40 ml) was added to 0.030 g [RhCl(COD)]_2 (0.061 mmol) and 0.044 g Tpy (0.12 mmol). This mixture was stirred at room temperature for about 5 minutes, after which a dark blue precipitate was formed. After decanting the supernatant liquid, the solid residue was washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, 0.06 g of complex 1 (yield ca. 99%) was collected as a dark blue powder.

FAB' MS: \( m/z \ 503.07 \ [M^+] \).
[Rh(1-Br)(Tpy\textsuperscript{\textregistered})], 2

Ethanol (30 ml) was added to 0.023 g [RhBr(COD)]\textsubscript{2} (0.039 mmol) and 0.029 g Tpy\textsuperscript{\textregistered} (0.079 mmol). This mixture was stirred at room temperature, and after ca. 10 minutes a dark blue precipitate was formed. After decanting the supernatant liquid, the remaining solid residue was washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, 0.043 g of complex 2 (yield ca. 99\%) was collected as a dark blue powder.

FAB\textsuperscript{+}MS: \textit{m/z} 547.01 [M\textsuperscript{+}].

[(2-(N-isopropylimino)phenyl)Rh\textsuperscript{III}(X)(Tpy\textsuperscript{\textregistered})]\textsuperscript{+}Y\textsuperscript{-}, 3a and 3b

Ethanol (40 ml) was added to 0.028 g [RhCl(COD)]\textsubscript{2} (0.057 mmol) and 0.041 g Tpy\textsuperscript{\textregistered} (0.11 mmol). This mixture was refluxed for 5 minutes, and 1 precipitated out of the solution. After cooling the mixture to ca. 35°C, >100 equivalents of 2-(N-isopropylimino)bromobenzene were added to this mixture. Upon stirring the reaction mixture for 2-3 minutes, a yellow suspension was formed. The product mixture was poured into pentane (150 ml). After decanting the supernatant liquid, the remaining solid residue was washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, 0.078 g of product mixture 3a:3b = 30:70 (yield ca. 90\%) was collected as a yellow powder (3a: X = Cl; 3b: X = Br; Y = Cl or Br). With a FAB mass measurement masses of 649.16 and 693.11 were detected for 3a (-Br) and 3b (-Cl) respectively.

\textsuperscript{1}H NMR (300 MHz Varian Mercury 300, CD\textsubscript{3}OD, 298K, δ): 9.11 (d, \textit{J}(Rh.H) = 3.0 Hz, 1H (19)), 9.03 (s, 2H (3.5`)), 8.78 (d, 8.1 Hz, 2H (3.3`)), 8.22 (2H (4.4`)), 8.20 (d, 7.5 Hz, 2H (6.6`)), 8.14 (d, 8.4 Hz, 2H (8.8`)), 7.75 (d, 8.1 Hz, 2H (9.9`)), 7.74 (1H (17`)), 7.62 (t, 6.8 Hz, 2H (5.5`)), 7.05 (t, 7.2 Hz, 1H (16`)), 6.89 (t, 7.1 Hz, 1H (15`)), 6.31 (3a, d, 7.8 Hz, 1H (14`)), 6.23 (3b, d, 7.5 Hz, 1H (14`)), 5.30 (3b, t, 6.6 Hz, 1H (20`)), 5.13 (3a, t, 6.3 Hz, 1H (20`)), 1.85 (d, 6.6 Hz, 6H (21`)), 1.44 (s, 9H (tributyl)).

FAB\textsuperscript{+}MS: \textit{m/z} 649.16 [(M\textsubscript{3a\textsuperscript{+}})-Br], 693.11 [(M\textsubscript{3b\textsuperscript{+}})-Cl].
Carbon-bromide bond activation by Rh(I)-terpyridine complexes

\[\text{[(2-(N-isopropylimino)phenyl)Rh}^{III}\text{(Br)(Tpy)}^{6}]^{+}\text{Br}^{-}, \text{4}\]

A solution of [RhBr(COD)]\textsubscript{2} and Tpy\textsuperscript{6} in 20 ml ethanol was refluxed for 10 minutes, giving [Rh'(Br)(Tpy\textsuperscript{6})] (3) as a dark blue solid. After cooling, this mixture was added >100 equivalents of 2-(N-isopropylimino)-bromobenzene. After several minutes of stirring a yellow emulsion was formed. The product mixture was poured into pentane (150 ml). After decanting the supernatant liquid, the remaining solid residue was washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, complex 4 (yield ca. 95%) was collected as a pale yellow powder.

1\textsuperscript{H} NMR (500 MHz, Varian Inova 500, CD\textsubscript{3}OD, 298K, δ): 9.11 (d, \textsuperscript{3}J(Rh-N-H) = 3 Hz, 1H (19)), 9.03 (s, 2H (3',5')), 8.78 (d, 8.0 Hz, 2H (3,3'')), 8.22 (t, 8.5 Hz, 2H (4,4'')), 8.20 (d, 6.0 Hz, 2H (6,6'')), 8.14 (d, 8.0 Hz, 2H (8,8'')), 7.74 (t, 8.5 Hz, 2H (9,9'')), 7.74 (d, 8.0 Hz, 1H (17)), 7.62 (t, 6.5 Hz, 2H (5,5'')), 7.05 (t, 7.5 Hz, 1H (16)), 6.90 (t, 7 Hz, 1H (15)), 6.23 (8 Hz, 1H (14)), 5.29 (m, 6.5 Hz, 1H (20)), 1.85 (d, 6.5 Hz, 6H (21)), 1.44 (s, 9H (rbutyl)).

\textsuperscript{13}\textsuperscript{C}{\textsuperscript{1}H} NMR (125 MHz, Varian Inova 500, CD\textsubscript{3}OD, 298K, δ): 174.23 (C19), 165.94 (d, \textsuperscript{1}J(Rh,C13) = 29.5 Hz), 157.24 (C2',C6'), 154.92 (C2,C2''), 154.42 (C10), 153.49 (C4'), 152.07 (6,6''), 145.35 (C18), 140.23 (4,4''), 133.16 (C7), 131.77 (C15), 130.75 (C17), 130.15 (C14), 128.28 (C5,C5''), 127.65 (C8,C8'), 126.61 (C9,C9'), 125.45 (C3,C3''), 125.01 (16), 121.81 (C3',C5'), 60.00 (C20), 34.70 (C11), 30.41 (C12), 22.78 (C21).

\textsuperscript{103}Rh NMR (3.16 MHz, 300 Bruker DRX, CD\textsubscript{3}OD, 298K, δ): 3220.75.

\textsuperscript{15}N NMR (30.42 MHz, 300 Bruker DRX, CD\textsubscript{3}OD, 298K, δ): -112.16 (N2), -140.55 (N1'), -151.92 (N1,N1').

Calculated for C\textsubscript{53}H\textsubscript{35}N\textsubscript{4}RhBr\textsubscript{2}: C 54.28 (%), H 4.56 (%), N 7.23 (%), Br 20.64 (%); found C 54.15 (%), H 4.48 (%), N 7.12 (%), Br 20.59 (%).

FAB\textsuperscript{+}MS: m/z 693.11 [(M\textsuperscript{+})-Br].
Chapter 3

\[\text{[Rh}^{III}(\text{Br})_3(\text{Tp}^{\circ})_2]\], 5

At room temperature 100 equivalents of \(\text{Br}_2\) were added to a deep dark blue mixture of 2 (0.079 mmol) and EtOH (20 ml). Instantaneously, a yellow emulsion was formed. The product mixture was poured into pentane (150 ml). After decanting the supernatant liquid, the remaining solid residue was washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, complex 5 (yield ca. 99%) was collected as a yellow powder.

\[\text{H NMR (300 MHz, 300 Bruker AMX, CD}_2\text{Cl}_2, \delta): 9.68 \text{ (d, 4.5 Hz, 2H (6.6\,')}, 8.36 \text{ (s, 2H (3',5')}, 8.28 \text{ (d, 8.4 Hz, 2H (3',3'))}, 8.13 \text{ (t, 7.8 Hz, 2H (4.4'))}, 7.79 \text{ (d, 8.7 Hz, 2H (8.8'))}, 7.72 \text{ (t, 8.0 Hz, 2H (5.5'))}, 7.68 \text{ (d, 8.7 Hz, 2H (9.9'))}, 1.41 \text{ (s, 9H (2butyl)).}\]

\[\text{\text{Rh NMR (3.16 MHz, 300 Bruker DRX, CD}_2\text{Cl}_2, \delta): 4530.13.}\]

Calculated for \(\text{C}_{26}\text{H}_{23}\text{N}_2\text{RhBr}_3\) (704.85): C 42.41 (%), H 3.27 (%), N 5.93 (%), Br 33.85 (%); found C 42.36 (%), H 3.22 (%), N 5.84 (%), Br 33.78 (%).

\[\text{FAB' MS: m/z 627.93 [(M')-Br].}\]

\[\text{[(R)Rh}^{III}(\text{Br})_2(\text{Tp}^{\circ})_2]\], 6-24

At room temperature ca. 100 equivalents of \(\text{Br}-\text{R}\) (Table 3.1) were added to a deep dark blue mixture of 2 (0.079 mmol) and EtOH (20 ml). After completion of the reaction a yellow solution (10-13, 16, 18-21, 23-24) or emulsion (6-9, 14, 15, 22) was formed. The product mixture was poured into pentane (150 ml). After decanting the supernatant liquid, the remaining solid residue was washed with pentane (3×10 ml). After drying the precipitate by removing the solvent under reduced pressure, the product was collected as a yellow powder (yield ca. 99% for 6-23 and ca. 70% for 24).

**Table 3.2.** Reaction time (Rt) for complex 2 (0.079 mmol) and ca. 100 equivalents of alkyl bromides in EtOH (20 ml); FAB/mass (m/z) data for complexes 6-23 and elemental analyses for 6, 13 and 21.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>reaction time</th>
<th>FAB' MS ([(M')-\text{Br}])</th>
<th>Elemental Analyses (%), calculated for:</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>instantaneously</td>
<td>562.04</td>
<td>(\text{C}<em>{26}\text{H}</em>{23}\text{N}_2\text{RhBr}_3) (640.95): 48.55 (C), 4.07 (H), 6.53 (N), 24.85 (Br); found 48.62 (C), 4.15 (H), 6.39 (N), 24.78 (Br)</td>
</tr>
</tbody>
</table>
Carbon-bromide bond activation by Rh(I)-terpyridine complexes

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>7</td>
<td>5 minutes</td>
<td>576.05</td>
</tr>
<tr>
<td>8</td>
<td>15 minutes</td>
<td>590.07</td>
</tr>
<tr>
<td>9</td>
<td>30 minutes</td>
<td>604.08</td>
</tr>
<tr>
<td>10</td>
<td>1 hour</td>
<td>618.10</td>
</tr>
<tr>
<td>11</td>
<td>1 hour</td>
<td>632.12</td>
</tr>
<tr>
<td>12</td>
<td>1 hour</td>
<td>660.15</td>
</tr>
<tr>
<td>13</td>
<td>12 hours</td>
<td>688.18</td>
</tr>
</tbody>
</table>

C\(_{25}\)H\(_{32}\)N\(_4\)RhBr\(_2\) (796.52): 54.63 (C), 5.76 (H), 5.46 (N), 20.77 (Br); found 54.56 (C), 5.70 (H), 5.49 (N), 20.69 (Br)

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<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
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<tr>
<td>15</td>
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<td>18</td>
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<tr>
<td>19</td>
<td>2 hours</td>
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<tr>
<td>20</td>
<td>2 hours</td>
<td>660.15</td>
</tr>
<tr>
<td>21</td>
<td>12 hours</td>
<td>700.18</td>
</tr>
</tbody>
</table>

C\(_{26}\)H\(_{33}\)N\(_4\)RhBr\(_2\) (779.11): 55.33 (C), 5.86 (H), 5.38 (N), 20.45 (Br); found 55.24 (C), 5.61 (H), 5.35 (N), 20.56 (Br)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>72 hours</td>
<td>624.05</td>
</tr>
<tr>
<td>23</td>
<td>instantaneously</td>
<td>640.07</td>
</tr>
<tr>
<td>24</td>
<td>instantaneously</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.3. Atom numbering of complexes 6-24.

<table>
<thead>
<tr>
<th>Saturated</th>
<th>Unsaturated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me(C(_{13}))Rh (6)</td>
<td>(7)</td>
</tr>
<tr>
<td>Rh</td>
<td>(14)</td>
</tr>
<tr>
<td>Rh</td>
<td>(8)</td>
</tr>
<tr>
<td>Rh</td>
<td>(9)</td>
</tr>
</tbody>
</table>
Complexes 4-24 are air-stable and soluble in various organic solvents (e.g. MeOH, EtOH and dichloromethane). However, in various cases (5, 7-9, 14, 15, 17, 18, 22) a few drops of trifluoroethanol (CF₃CH₂OH) were added to enhance their solubility in deuterated dichloromethane for NMR studies.

Table 3.4. ¹H NMR data of complexes 6-24. For atom numbering cf. Table 3.2.

<table>
<thead>
<tr>
<th>Nr.</th>
<th>¹H NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>δ 9.53 (d, 5.4 Hz, 2H (6,6')), 8.24 (s, 2H (3, 5)), 8.21 (d, 8.1 Hz, 2H (3, 3')), 8.00 (t, 7.8 Hz, 2H (4,4')), 7.76 (d, 8.7 Hz, 2H (8, 8')); 7.60 (d, 9Hz, 2H (9, 9')); 7.59 (m, 2H (5, 5')); 1.41 (s, 9H (butyl)); 1.11 (d, 3J(Rh,H) = 2.4 Hz, 3H (13))</td>
</tr>
<tr>
<td>7</td>
<td>δ 9.53 (d, 5.5 Hz, 2H (6,6')); 8.28 (s, 2H (3, 5')); 8.25 (d, 8.0 Hz, 2H (3, 3')); 8.02 (t, 7.8 Hz, 2H (4, 4')); 7.81 (d, 8.5 Hz, 2H (8, 8')); 7.63 (d, 8.5 Hz, 2H (9, 9')); 7.62 (m, 2H (5, 5')); 2.22 (dq, 3J(H,H) = 7.5 Hz, 3J(Rh,H) = 3 Hz, 2H (13)); 1.44 (s, 9H (butyl)); 0.22 (t, 7.5 Hz, 3H (14))</td>
</tr>
<tr>
<td>8</td>
<td>δ 9.45 (d, 5.5 Hz, 2H (6,6')); 8.25 (s, 2H (3, 5'); 8.22 (d, 7.5 Hz, 2H (3, 3')); 8.02 (t, 7.8 Hz, 2H (4, 4')); 7.79 (d, 8.5 Hz, 2H (8, 8')); 7.62 (d, 8.5 Hz, 2H (9, 9')); 7.60 (t, 7.5 Hz, 2H (5, 5')); 2.17 (dt, 3J(H,H) = 8.5 Hz, 3J(Rh,H) = 2.5 Hz, 2H (13)); 1.43 (s, 9H (butyl)); 0.63 (m, 8.5 Hz, 2H (14)); 0.58 (t, 6.8 Hz, 3H (15))</td>
</tr>
<tr>
<td>9</td>
<td>δ 9.47 (d, 5.4 Hz, 2H (6,6')); 8.23 (d, 7.6 Hz, 2H (3, 3')); 8.21 (s, 2H (3, 5')); 7.90 (t, 7.1 Hz, 2H (4, 4')); 7.76 (d, 7.6 Hz, 2H (5, 5')); 7.60 (t, 7.3 Hz, 2H (6, 6')); 7.55 (t, 7.3 Hz, 2H (7, 7')); 2.17 (dt, 3J(H,H) = 8.5 Hz, 3J(Rh,H) = 2.5 Hz, 2H (13)); 1.43 (s, 9H (butyl)); 0.63 (m, 8.5 Hz, 2H (14)); 0.58 (t, 6.8 Hz, 3H (15))</td>
</tr>
</tbody>
</table>
Monitoring the formation of complex 13 with UV/Vis spectroscopy.

A standard cuvet was filled with 4 ml of an ethanolic solution of complex 2 at 23.10¹¹ M under nitrogen atmosphere glovebox. To this solution 5 μl of 1-bromo decane (50 equivalents) was added for the oxidative addition reaction, which was monitored with a diode array HPS453 spectrophotometer at 298 K. In total, 75 electronic absorption spectra were recorded with sixty seconds interval between each single measurement (6,500 seconds total measurement time). The first spectrum was recorded after 2 minutes reaction time. 1 Bromo decane shows no absorption in the relevant UV region.

Monitoring the formation of complex 13, in presence of 2-methylphenol, with UV/Vis spectroscopy.

A standard cuvet was filled with 4 ml of an ethanolic solution of complex 2 at 5.75 10⁻¹¹ M and 1 g 2-methylphenol (ca. 40 equivalents) under nitrogen atmosphere glovebox. To this solution, 24 μl of 1-bromo decane (50 equivalents) was added for the oxidative addition reaction, which was monitored with a diode array HPS453 spectrophotometer at 298 K. In total, 90 electronic absorption spectra were recorded with sixty seconds interval between each single measurement (5,400 seconds).
total measuring time). The first spectrum was recorded after 1 minute and 50 seconds reaction time. 2-Methylphenol shows no absorption in the relevant visible region.

Results

Syntheses of complexes 1-24.

For the synthesis of complex 1 various solvents can be used (e.g. toluene, benzene, THF and EtOH), while the synthesis of complex 2 is found to be most successful when using EtOH as the solvent (Scheme 3.1). Complexes 1 and 2 are highly air sensitive like the Rh(I) terpyridine complexes described in Chapter 2. They react with oxygen instantly to form mixtures of uncharacterised red Rh(III) species, as evidenced by $^1$H NMR measurements of the products.

$$\text{[RhX(COD)]}_2 + \text{Tp}^* \rightarrow \text{solvent} \rightarrow \text{room temperature}$$


The synthesis of 2 in toluene and MeOH gave uncharacterised red products, while in THF uncharacterised pale yellow coloured products were formed. The synthesis of 2 in benzene resulted in the formation of uncharacterised gray species. Hence, since EtOH is a suitable solvent for the syntheses of both complexes 1 and 2, all oxidative addition reactions involving complexes 1 and 2 were performed in situ in EtOH.
The first studied reactions were the oxidative addition reactions with complex 1 (ca. 0.01 mmol) and 1-1000 equivalents of CHCl₃ and CH₂Cl₂ (Scheme 3.2).

\[
\text{[RhCl(COD)]}_2 + \text{Tp}^* \xrightarrow{\Delta \text{EtOH}} \text{1} \xrightarrow{\text{Reactant}} \text{product}
\]

\textbf{Scheme 3.2.} Reaction procedure of 1 with CHCl₃ and CH₂Cl₂.

Unfortunately, the oxidative addition reactions involving 1 and chloroform or dichloromethane gave only mixtures of uncharacterised products. This is also the case in reactions of 1 with O₂, HCl, C₂Cl₆, benzylchloride, 2-(N-isopropylimino)benzenechloride, silicon chlorides, benzylbromide and MeBr. However, in the oxidative addition reaction of 1 and 2-(N-isopropylimino)-bromobenzene two isomeric products (Scheme 3.3) were formed, which could be identified by means of NMR techniques and mass spectrometry.

\[
\text{[RhCl(COD)]}_2 + \text{Tp}^* \xrightarrow{\Delta \text{EtOH}} \text{1} \xrightarrow{\text{Reactant}} \text{product}
\]

\textbf{Scheme 3.3.} Reaction procedure of 1 with 2-(N-isopropylimino)-bromobenzene.

The majority of \(^1\)H signals of the two isomers of 3 in the NMR spectrum of the product mixture are overlapping each other. Only two pairs of non-overlapping signals indicate the presence of two different species in the measured sample (Figure 3.1). The presence of two different compounds in the product mixture is also confirmed by FAB-mass measurement. Masses of 649.16 and 693.11 are
detected, representative for 3a (m/z [M⁺]-Br) and 3b (m/z [M⁺]-Cl) respectively. The composition of the product mixture is 3a:3b = 30:70 according the ¹H NMR integrals.

Figure 3.1. ¹H NMR spectrum of the isolated mixture 3a + 3b (Varian Mercury 300 MHz, CD₂OD, 298K).

To avoid the formation of mixtures, 2-(N-isopropyliminoo)-bromobenzene was oxidatively added to complex [Rh(I)(Br)(Tpy*)] (2). As expected, this reaction gave only one product [(2-N-isopropyliminophenyl)(Tpy*)(Rh(III)Br)²⁺Br⁻] (4) (Scheme 3.4).
This success prompted us to perform oxidative addition reactions with complex 2 and ca. 100 equivalents of various alkyl bromides (Table 3.1). As indicated earlier, all reactions were carried out in situ using EtOH as the solvent (Scheme 3.5). The atom numbering of complexes 6-24 is shown in Table 3.2, while reaction time, mass and elemental analyses of complexes 6-24 are summarised in Table 3.3.
\(^{15}\)N NMR spectroscopy of complex 4, Tpy\(^{2+}\) and 2-N-isopropylimino-bromobenzene.

The \(\delta^{15}N\) of complex 4 have significantly shifted upfield compared to the \(\delta^{15}N\) of the corresponding free Tpy and isopropyl ligands (Table 3.6). This means that all nitrogen atoms of 4 are coordinated to the rhodium metal. In view of this finding and the elemental composition of complex 4, it is likely that it is an octahedral ion: \(\text{RhIII-terpyridine complex with a bromide acting as a counter-ion}\), as indicated in Scheme 3.4.

**Table 3.6.** \(\delta^{15}N\) chemical shifts of complex 4, Tpy and 2-N-isopropylimino-bromobenzene.

<table>
<thead>
<tr>
<th></th>
<th>(\delta^{15}N) (ppm)</th>
<th>(\delta^{15}N) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4, CDOD</td>
<td>Tpy, CDCl₃</td>
<td>2-N-isopropylimino-bromobenzene</td>
</tr>
<tr>
<td>31.9, N₂</td>
<td>85.4 N₂</td>
<td>34.3 N₂, CDOD</td>
</tr>
<tr>
<td>100, N₂</td>
<td>73.3 N₂</td>
<td>25.5 N₂, CDCl₃</td>
</tr>
<tr>
<td>112.2 N₂</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{103}\)Rh NMR spectroscopy of complexes 4-7, 9, 13-17 and 22.

Transition metal NMR shifts can nowadays easily be measured by modern 2D pulse techniques and serve as a probe into electronic and steric effects of ligands and substituents in metal complexes. \(^{15}\) The influence of these effects on \(\delta^{103}\)Rh for complexes 4-7, 9, 13-17, 22 and \((\text{R}^2\text{Rh}^{11}+\text{Cl}_2,6-\text{Gr}=-\text{N} \cdot \text{R} \cdot \text{C} \cdot \text{H} \cdot \text{N})\) has been studied with PFG HMQC II and \(^{103}\)Rh NMR techniques.

The \(\delta^{103}\)Rh of complexes 4-7, 9, 13-17 and 22 (Table 3.7) are comparable with the \(\delta^{103}\)Rh of similar complexes \((\text{R}^2\text{Rh}^{11}+\text{Cl}_2,6-\text{Gr}=-\text{N} \cdot \text{R} \cdot \text{C} \cdot \text{H} \cdot \text{N})\) for which \(^{103}\)Rh NMR data are available \(^{18}\) (Table 3.8).
Table 3.7. \(^{109}\)Rh chemical shifts in CD\(_2\)Cl\(_2\) measured at room temperature.

<table>
<thead>
<tr>
<th>Complex (R)</th>
<th>ppm ((\delta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>3221</td>
</tr>
<tr>
<td>5 (Br)</td>
<td>4540</td>
</tr>
<tr>
<td>6 (Me)</td>
<td>3366</td>
</tr>
<tr>
<td>7 (ethyl)</td>
<td>3365</td>
</tr>
<tr>
<td>9 (butyl)</td>
<td>3380</td>
</tr>
<tr>
<td>13 (decal)</td>
<td>3375</td>
</tr>
<tr>
<td>14 (ethenyl)</td>
<td>3415</td>
</tr>
<tr>
<td>15 (2-propenyl)</td>
<td>3533</td>
</tr>
<tr>
<td>16 (2-Me-2-propenyl)</td>
<td>3545</td>
</tr>
<tr>
<td>17 (3-butenyl)</td>
<td>3396</td>
</tr>
<tr>
<td>22 (phenyl)</td>
<td>3548</td>
</tr>
</tbody>
</table>

* Measured in CD\(_2\)OD at room temperature.

---

Table 3.8. \(^{109}\)Rh chemical shifts in CD\(_2\)Cl\(_2\) measured at room temperature.

<table>
<thead>
<tr>
<th>Complex(^{[4]})</th>
<th>Nr.</th>
<th>(R^1)</th>
<th>(R^2)</th>
<th>(R^3)</th>
<th>ppm ((\delta))(^{[5]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>H</td>
<td>iPr</td>
<td>CH-Cl</td>
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<tr>
<td>B</td>
<td>H</td>
<td>Cy</td>
<td>CH-Cl</td>
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<tr>
<td>C</td>
<td>H</td>
<td>tBu</td>
<td>CH-Cl</td>
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<tr>
<td>D</td>
<td>H</td>
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<td>CH-Cl</td>
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<tr>
<td>E</td>
<td>CH(_3)</td>
<td>p-An</td>
<td>CH-Cl</td>
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<td>H</td>
<td>iPr</td>
<td>CH-Ph</td>
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<tr>
<td>G</td>
<td>H</td>
<td>iPr</td>
<td>Cl</td>
<td></td>
<td>4923</td>
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</table>

iPr = isopropyl; Cy = cyclohexyl; tBu = isobutyl; p-An = paraanisyl.
Monitoring the formation of complex 13 with UV/VIS spectroscopy.

Besides the electronic absorption spectra of isolated 2 and 13 (Figure 3.2), also the formation of complex 13 was monitored by means of UV/VIS spectrometry (Figure 3.3). From the monitoring, two distinct isosbestic points can be observed in the absorption spectra of the oxidative addition reaction (Figure 3.3). Monitoring the formation of complex 13 in the presence of 2-methylphenol (o-cresol) rendered similar absorption spectra as observed without 2-methylphenol.

![Figure 3.2. Electronic absorption spectra of complex 2 and 13 in ethanol (as indicated).](image-url)
Discussion

Syntheses of complexes 1-24.

Like the syntheses of complexes $[\text{Rh}(X)(2,2':6',2''-\text{terpyridine})]$ ($X = \text{Cl, Br}$), as described in Chapter 2, the syntheses of complexes 1 and 2 (blue) were rather simple once the right reaction conditions were found. Complexes 1 and 2 are air sensitive, and form red Rh(III) species with air.

Various oxidative addition reactions with 1 and carbon chloride bonds gave mixtures of uncharacterised products. Based on $^1$H NMR studies (only broad signals) and mass measurements (only the fragment $[\text{RhCl}(\text{Tpyp})]$ could be detected with some certainty), it is impossible to characterise the different products. It is likely that one side product is a Rh(III) trichloride species. It is known that oxidative addition reactions between Rh(I)-chlorides and alkyl chlorides, in
particular CHCl and CHCl in EtOH can also give RhIII-trichloride species as decomposition products together with diethoxyalkyl compounds.

Furthermore, the oxidative addition reactions with 1 and carbon bromide bonds gave also mixtures of uncharacterised products. Except when 2- N-isopropylimino-bromobenzene was used as reactant, forming a mixture of complexes 3a and 3b. Reaction between complex 2 and 2- N-isopropylimino-bromobenzene gave one single product complex 4. The 1H chemical shifts of complexes 3b and 4 are identical.

Similar to the synthesis of complex 4, oxidative addition reactions in EtOH with complex 2 and carbon hydrogen bromides gave clean products (complexes 5-24) in almost quantitative yields. In contrast to the dark blue coloured complexes 1 and 2, all synthesised RhIII-terpyridyl species are air stable and yellow. Primary sp and vinylic sp carbon-bromide bonds reacted faster with complex 2 than the secondary sp carbon-bromide bond of bromobenzene, as indicated by their reaction time (Table 3.3). Furthermore, generally, smaller saturated and terminal unsaturated alkyl bromides reacted faster than the larger ones (Table 3.3). Under the applied reaction conditions (see experiments), only bromomethane, benzylbromide and diphenylbromomethane reacted instantaneously with complex 2.

Complexes 5-24 dissolved sufficiently to excellently in deuterated dichloromethane, and rather poorly in deuterated methanol. In contrast, complexes 3a, 3b and 4 dissolved very well in deuterated methanol and not in deuterated dichloromethane. Their charged character can rationalize the high solubility of the latter three complexes in methanol.


Since attempts to grow crystals of complexes 3-24 failed, the determination of their geometry is based on their 1H and 13C NMR spectra. 15N NMR experiments of complex 4 and NOE 2D + 1H NMR experiments of complex 22.

The δ15N of complex 4 = 112.16, 140.55 and 151.92 ppm is not too different from the δ15N of complexes [Pd(N₂CH[CH₃])₂][N] (NO₂) = 110 phenanthroline = phen; 3.4,7,8 tetramethyl-1,4,6 phenanthroline = tm-phen; X = OTH triflate. Pd (δ15N) = 125.6 and 130.8 ppm for pmc and tm-phen derivatives, respectively, described by Niliari et al. The coordination shifts, i.e. the differences in δ15N between the free ligands and relevant complexes of 4 and [Pd(N₂CH[CH₃])₂][N] (NO₂),

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NMR spectroscopy.

Transition metal nuclei generally offer very large changes in their chemical shifts (several 100 or 1000 ppm) depending on molecular structure, hence good sensitivity to subtle structural perturbations, due to a large sensitivity to small changes in the ligand field. In general, transition metal complexes containing metal bonded groups with more electron withdrawing and/or bulky substituents show lower shielding of the metal nuclei. The deshielding effect correlates with the difference in ligand field energy, i.e. a lower electron density on the metal correlates with a
smaller ligand field splitting, and hence a more positive chemical shift of the metal nuclei. The steric deshielding effect correlates among other things with the metal-carbon bond length, and thus also the weakening of this bond, and hence also a more positive chemical shift of the metal nuclei with increasing M-C bond length. However, it must be noted that the individual influences of the electronic and steric effects are difficult to separate. Furthermore, for the transition metal chemical shift, the ligand field electronic and steric chemical environments of transition metal containing complexes is a more dominant factor than the actual charge of the transition metal.

This is clearly evidenced for complex 4. Although complex 4 contains a cationic Rh(III) metal, suggesting an electron poor metal centre, complex 4 has the lowest $\delta^{\text{II}}$Rh of the studied Rh(III)-terpyridine complexes. This can be explained by the fact that complex 4 contains an additional N-atom instead of a bromide, which accounts for the somewhat lower $\delta^{\text{II}}$Rh compared to e.g. 6 or 14.

The Rh metal nucleus has a great sensitivity to (small) changes in its coordination environment. This has been amply demonstrated in previous studies, and is also observed by comparing the $\delta^{\text{III}}$Rh of octahedral Rh(III) complexes 4-7, 9, 13-17, 22 and [R$^2$]RhIII(2,6-[C(R)]=N-R$^2$-C-H-N)]. The $\delta^{\text{III}}$Rh of [R$^2$]RhIII(2,6-[C(R)]=N-R$^2$-C-H-N] is generally more positive than for complexes 4-7, 9, 13-17, and 22. This is most probably due to the fact that chloride is lower in the spectrochemical series compared to bromide (R'. Table 3.8). Furthermore, the imine nitrogens in [R$^2$]RhIII(2,6-[C(R)]=N-R$^2$-C-H-N] must be regarded as higher in the spectrochemical series as compared with the pyridine nitrogens in Rh(III)-terpyridine complexes, since the former are better $\pi$-acceptors.

Apart from relatively small mutual differences, complexes 4-7, 9, 13-17, 22 and [R$^2$]RhIII(2,6-[C(R)]=N-R$^2$-C-H-N] show similar trends in chemical shifts within their respective series in relation to deshielding of the nuclei. As has been shown before and was discussed above, the nuclear deshielding correlates qualitatively at least with the relative ligand field energy, i.e. a lower electron density on the metal correlates with a smaller ligand field splitting, and hence a more positive chemical shift of the metal nuclei.

For compounds A-G (Table 3.8), the following qualitative assessment can be made. Compound G contains a halide directly coordinated to Rh, hence a much higher chemical shift compared to the strong field C-H-N moiety of the other compounds in this sub-series. The shift of C relative to A and
B is explained by the fact that the coordination angles within the complexes are far from optimum, especially in C. Hence the ligand field splitting is less for this complex resulting in a higher chemical shift. Other differences are rather small and cannot be explained even qualitatively.

The complexes [R-Rh(CN)2](6) and [CN]- are N, R, C, H, N, and 4, 7, 9, 13, 17 and 22 show similar trends. This is best evidenced by comparing the δ R of complexes 5 and of complexes 6, 7, 9, 13, 17, 22. Like complex 6, complex 5 contains three RH-X σ-bonds. N = Br and has by far the most positive δ R within the sub-series. So complexes 4, 6, 7, 9, 13, 17 and 22 contain only two RH-Br σ-bonds. Furthermore, complexes 14, 16 and 22 have more positive δ R than complexes 6, 7, 9 and 13. Apparently, allyl and propyl groups induce a lower ligand field than alkyl groups.

Monitoring the formation of complex 13 with EVAIS spectrometry: mechanistic aspects.

On monitoring the formation of complex 13 from complex 2 and 1-bromo decanoate, no absence of α-cresol, basse points in the electronic absorption spectra are clearly observable. (Figure 3.3) However, the involvement of possible formal intermediates during the synthesis of complex 13 cannot be excluded. Radicals as intermediates can be excluded, since monitoring the oxidative addition reaction in the presence of α-cresol gave similar electronic absorption spectra as without.

HF-DHF calculations have shown that the HOMO of complex 2 is entirely located on the α-diketone of the Rh metal. This doubly occupied HOMO then nucleophilically attacks the bromine-bearing carbon bond and forms the new Rh-carbon bond concurrently with the breaking of the carbon bromine bond. So for complexes 6, 24 the new Rh-carbon bond is axial, at position 4 with respect to the equatorial Rh-Ipyr. plane [157], as evidenced by NMR. In complexes 3 and 4 the Rh-carbon bond is in equatorial position.

However, based on the results, it is not possible to unequivocally propose a mechanism of the overall oxidative addition of the carbon halogen bonds to Rh(I) terpyridine complexes.

References


[References]


81. "The products to be separated disagree, but do not diffuse very well in solution. Diffusion rates of products are adequate. However, enhanced separation at each single product, firstly, a greenish oil, diazene, and ammonium. Finally, the diazene intermediate was completely converted to the dipyrroldizine. The latter two products are colorless orange, white."
The used bromine reagents provided by Aldrich were superior to Acros Chimica. Deliveries from Acros Chimica gave always mixtures of products, instead of single clean products when reagents were purchased from Aldrich.


[105] To be published.
Chapter 4

[Rh\(^1\)(Br)(2,2':6',2''-Terpyridine)]: Easy Access to the Synthesis of Neutral Octahedral Rh(III)-based Metallomesogens Displaying Lyotropic Mesomorphism with Dichloromethane.

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Abstract

RhI-terpyridine complexes are rigid (Chapter 2) and reactive towards carbon halide bonds (Chapter 3). These two properties of complex Rh-Bu2,2′,6,2′-terpyridine (1) were used to synthesise lyotropic liquid crystals. Fo this, complex 1 was reacted with the highly flexible dendrimer wedge [BrCH=SN-CH=SiCH2CH2CH=]n (G2). The oxidative addition reaction of 1 with G2 gave complex [BrCH=CH-CH=SiCH2CH2CH=]nRh(nBu)2(py) (2) + py = 2,2′(6,2′-terpyridine). Complex 2 showed lyotropic liquid crystalline behaviour in the presence of small amounts of CHCl3. Possible stacking interactions between monomers of complex 2 in CDCl3 were studied with 1H NMR techniques.

Within the liquid crystalline phases, the Rh-terpyridine moiety of complex 2 is responsible for a degree of orientational order through anisotropic intermolecular interactions, while the dendrimer part of complex 2 is responsible for some flexibility (disorder). The order of the molecules in the lyotropic liquid crystalline phase lies between that of completely ordered solid crystalline phases and fully isotropic liquid phases. The lyotropic liquid crystals of complex 2 were studied with a polarised optical microscope and X-ray (powder) diffraction techniques. The space group and unit-cell volume of complex 2 could be determined (Pna21 and ca. 12,100 A³, respectively), while the orientation of the correlating monomers 2 in the lyotropic liquid crystalline phase is unknown.

Based on the obtained results and semi-empirical calculations, the structure and intermolecular orientation of the lyotropic liquid crystals has been simulated.
Introduction

Since the synthesis of the Ni-based mesomorphic dithiolene complexes was reported by Giroud-Godquin and Mueller-Westerhoff in 1977, many metal-containing liquid crystals have been synthesised by complexing metals with mesomorphic organic ligands. The rapid growth in number of metallomesogens is due to the expected advantages of combining the properties of liquid crystal phases with those of the incorporated metals. Accordingly, specific properties such as colour, paramagnetism, electric conductivity, and chirality can be more easily obtained with metal-organic complexes than with purely organic compounds. Molecular properties such as polarizability or hyperpolarizability can be enhanced by the presence of metals. Furthermore, the inclusion of metals into mesogenic materials enables the formation of new molecular geometries (octahedral, trigonal bipyramidal, etc.), and consequently the formation of new metastable phase types.

Up till now, the standard approach towards new metal-containing liquid crystal systems involved modification of promising ligands to obtain materials displaying mesomorphic behaviour. Frequently used ligands for this purpose are mesomorphic oligopyridines, since they easily form well-defined chelate complexes with many metals. The use of modified 2,2',6,2'-terpyridines for the synthesis of metal-containing liquid crystal phases has not received much attention in literature. The vast majority of mesogenic metal-containing complexes exhibiting liquid crystal behaviour are derived from d^8 transition metals. A few examples of rhodium-based liquid crystals have been described, including dicarbonylrhodium(1,5)-1,10-diketonates, RhI(4′-alkoxyaniline) and RhI(4′-alkoxyxylazine) complexes. Furthermore, RhI dimetallic complexes with Schiff base-salen type ligands have been modified to promote mesomorphism. The use of RhIII metallomesogens is mostly restricted to the synthesis of liquid crystals of fatty acids. These binuclear metal-metal bonded compounds are known as rhodium soaps of the general formula [CH₂CH₂CO₂]Rh₃. Organometallic liquid crystals based on octahedral RhIII metallomesogens have only been mentioned by Rourke et al.

In general, liquid crystals are materials exhibiting intermediate structures. The characteristic order of liquid crystals lies between the fully ordered solid crystalline phases and the completely isotropic liquid phases. There are many different types of liquid crystalline phases. These phases are
characterised and classified according to molecular ordering that constitutes the phase structure. 

Two of them are relevant for the present study. The so-called nematic phase is characterised by an absence of positional order and the orientation of the long axis of the molecules along a given direction. The smectic phase exhibits the same type of orientational order, with in addition a positional order in one direction. This means that the molecules form layers. Different types of order inside the layers are possible. The molecules can for instance be perpendicular to the layers, as in smectic A phases, or tilted with respect to the layers as in smectic C phases. In all liquid crystalline phases, the mean orientation of the molecules, also called director, defines the optical axis of the material.

One strategy to obtain metallomesogenic liquid crystals is the incorporation of a flexible and a rigid part in the building block. The metal-containing rigid part provides strong enough anisotropic intermolecular interactions to induce orientational order. In contrast, the flexible part provides the material structure with the necessary disorder to have some degree of translational freedom. The observation that RhBr-terpyridine complexes undergo oxidative addition very easily with 1-Bralkanes (Chapter 3), prompted us to investigate the simple oxidative addition reaction of the rigid complex [RhBr(Tpy)] (1, Tpy = 2,2':6,2'-terpyridine) and the highly flexible dendrimer wedge G2 ( [Br(CH₃)Si(CH₃)₂]CH₂Br ) [Si(CH₃)₂CH₂CH₂] (Scheme 4.1). We expected that the product could exhibit liquid crystalline behaviour, since it contains rigid and flexible parts. Surprisingly, the use of oxidative addition reactions with a range of alkyl halides to prepare metallomesogens has not been thoroughly investigated yet, although it is known that the oxidatively added ligands on metals of metallomesogenic liquid crystalline materials can dramatically alter the liquid crystalline properties. 

In this chapter we report the synthesis and properties of the neutral octahedral RhIII complex 2 ([CH₂=CHCH=CH₂]Si(CH₃)₄ [Si(CH₃)₂CH₂Br]Br·Tpy) (Scheme 4.1). We observed that lyotropic liquid crystals of complex 2 were formed, when solutions of 2 in CH₂Cl₂ were almost completely dried under air atmosphere (i.e., high concentrations of complex 2). To investigate if molecules of 2 interact with each other also at relatively low concentration, possible stacking interactions (i.e., indefinite self-association) were studied with 1H NMR techniques. During the evaporation of the solvent, these interactions could be partly responsible for the formation of the lyotropic liquid crystals.
Upon prolonged standing at room temperature under air atmosphere, lyotropic liquid crystals changed into pure solid crystals suitable for X-ray powder diffraction studies, from which the crystal symmetry and cell-unit could be determined.

\[
\text{COD} = 1,5\text{-cyclooctadiene}
\]

In order to gain more insight in the criteria to be met, in respect to the relationship between size of dendrimer wedge and successful formation of liquid crystals, two other complexes were synthesised comprising a smaller and larger generation (respectively) of the G family. For this purpose, we have synthesised complexes \([\text{[CH}_2\text{=CHCH}_2\text{]}_3\text{Si(CH}_2\text{)}_3\text{Rh(Br)}_2\text{(Tpy)} \text{]} \text{ (3) and [[(CH}_2\text{)}_3\text{Si(CH}_2\text{)}_3\text{Si(CH}_2\text{)}_3\text{]}_3\text{Si(CH}_2\text{)}_3\text{Rh(Br)}_2\text{(Tpy)} \text{]} \text{ (4) (Scheme 4.2), using dendrimer wedges [Br(CH}_2\text{)}_3\text{Si(CH}_2\text{CH}=\text{CH}_2\text{]} \text{ (G1) and [Br(CH}_2\text{)}_3\text{Si[[(CH}_2\text{)}_3\text{Si(CH}_2\text{)}_3\text{Si(CH}_2\text{)}_3\text{]}_3 \text{ (G3), respectively.}}\]
Experimental Section

General. The *in situ* syntheses of complexes 2-4 were performed in an inert atmosphere (purified argon), by using standard Schlenk techniques. Solvents were dried and purified by standard procedures. Attempts have been made to purify complex 4 by size-exclusion chromatography (SEC) over BioBeads-SX-1, using CH$_2$Cl$_2$ as an eluent. $^1$H NMR spectra of complex 2-4 were recorded at 294K, with a Varian Mercury 300 spectrometer operating at 300 MHz for $^1$H. Assumed stacking interaction (self-association) of complex 2 was studied with a Varian Inova 500 spectrometer operating at 500 MHz for $^1$H. $^{13}$C NMR spectrum of complex 2 was recorded at 294 K, with a Varian Inova 500 spectrometer operating at 125.6 MHz for $^{13}$C. The assignment of $^1$H NMR signals of complex 2-4 is partly based on 2D NMR techniques. Fast Atom Bombardment (FAB$^+$) mass spectrometry was carried out using a JEOL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-7000 data system. The samples were 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 FABMS measurements a resolving power of 5000 (10% valley definition) was used. CsI and glycerol were used to calibrate the mass spectrometer. Elemental analyses were carried out by H. Kolbe Mikroanalytisches Laboratorium (Mülheim an der Ruhr, Germany).

Syntheses.

![Complex 2-4](image)

[\{[(\text{CH}_2=\text{CHCH}_2)_3\text{Si(CH}_2)_3\text{Si(CH}_2)_3\text{Rh}^{III}(\text{Br})_2(\text{Tpy})]\}, \text{2}]

At room temperature, a solution of 0.130 g of [Rh(Br)(COD)]$_2$ (0.22 mmol) and 0.163 g of Tpy (0.45 mmol) in EtOH was refluxed for 10 minutes. After cooling to room temperature, 3.5 g of G2 (4.8 mmol) was added to the dark blue suspension of complex 1. After stirring overnight at room temperature, a yellow suspension was formed. The solids were precipitated by centrifugation. After decanting of the supernatant liquid, the solids were washed with pentane (3x10 ml). The remaining solids were purified from uncharacterised brown side-products by dissolving selectively (based on difference in
solubility in mixtures of CH2Cl2 and pentane) the yellow products. After filtering the side products, the product was dried by removing the solvent under reduced pressure (10⁻⁵ bar) for 16 hours. 0.46 g of complex 2 (90% yield) was collected as a yellow powder.

1H NMR (300 MHz Mercury, CD2Cl2, δ): 9.52 (d, 5.7 Hz, 2H(6,6")), 8.18-8.10 (m, 5H(3,3";3',5';4")), 8.02 (t, 8.4 Hz, 2H(4,4")), 7.62 (t, 6.6 Hz, 2H(5,5")), 5.78 (m, 9H(16)), 4.86 (m, 18H(17)), 2.06 (dt, 8.7 Hz, 2J(Rh,H) = 2.7 Hz, 2H(7)), 1.59 (m, 2H(8)), 1.55 (d, 8.1 Hz, 18H(15)), 1.14 (m, 6H(12)), 0.63 (m, 2H(9)), 0.52 (t, 8.4 Hz, 6H(11)), 0.27 (t, 8.4 Hz, 6H(13)). 13C{1H} NMR (500 MHz Inova, CD2Cl2, δ): 156.62 (C2,C6'), 155.41 (C2,C2'), 155.01 (C6,C6'), 138.21 (C4,C4'), 137.26 (C4'), 134.82 (C16), 127.98 (C5,C5'), 123.40 (C3,C3'), 122.64 (C3',C5'), 113.45 (C17), 34.63 (C7), 26.45 (C8), 19.87 (C13), 18.26 (C12), 17.47 (C11), 16.63 (C15), 14.28 (C9).

FAB+MS: m/z 1064.36 [M+Br].

Calculated for C85H80N3Si5RhBr12 (1146.29): C 56.58%, H 7.03%, N 3.67%, Si 9.80%, Br 13.94%; found C 56.51%, H 7.11%, N 3.63%, Si 9.75%, Br 13.85%.

[(CH2=CHCH2)3Si(CH2)3Rh(Br)2(Tpy)], 3

At room temperature, a solution of 0.006 g of [Rh(Br)(COD)]₂ (0.01 mmol) and 0.005 g of Tpy (0.02 mmol) in EtOH was refluxed for 10 minutes. After cooling to room temperature, 0.2 g of G1 (0.73 mmol) was added to the dark blue suspension of complex 1. After stirring overnight at room temperature, a yellow suspension was formed. The solids were precipitated by centrifugation. After decanting of the supernatant liquid, the solids were washed with pentane (3×10 ml). After drying the product by removing the solvent under reduced pressure, 0.012 g of complex 2 (0.017 mmol = 87% yield) was collected as a yellow powder.

1H NMR (300 MHz Mercury, CD2Cl2, δ): 9.51 (d, 2H(6,6")), 8.15 (m, 5H(3,3";3',5';4")), 8.10 (t, 8.4 Hz, 2H(4,4")), 7.63 (t, 6.6 Hz, 2H(5,5")), 5.51 (m, 3H(12)), 4.65 (m, 6H(13)), 2.09 (dt, 8.7 Hz, 2J(Rh,H) = 2.8 Hz, 2H(7)), 1.29 (d, 8.1 Hz, 6H(11)), 0.63 (m, 2H(8)), 0.32 (m, 2H(9)).

FAB+MS: m/z 608.06 [M+Br].
Chapter 4

\[\{(\text{CH}_3)\text{Si}((\text{CH}_2)_{2})\text{Si}((\text{CH}_2)_{2})\text{Si}((\text{CH}_2)_{2})\text{Rh}((\text{Br})_{2})(\text{Tp}y)\}\]

At room temperature, a solution of 0.016 g of \[\text{[Rh}((\text{Br})_{2})(\text{COD})_{2}\text{]}\] (0.03 mmol) and 0.013 g of Tpy (0.06 mmol) in EtOH was refluxed for 10 minutes. After cooling to room temperature, 0.4 g of G3 (0.30 mmol) was added to the dark blue suspension of complex 1. After stirring for several days, a yellow suspension was formed. After centrifuging the mixture, the wet phase was separated from the brownish solids (side products). After removing the solvent under reduced pressure, the remaining yellow oil was purified by SEC (cf. experimental section). After removing the eluent (CH\textsubscript{2}Cl\textsubscript{2}) under reduced pressure, 0.01 g of a mixture of complex 4 and another uncharacterised product (A) was collected as a yellow oil. \(^1\)H NMR measurement of this mixture reveal a product distribution of \(4\):A = 70:30 (9.4% yield).

\(^1\)H NMR (300 MHz, Mercury, CD\textsubscript{2}Cl\textsubscript{2}, \(\delta\)): 9.51 (d, 5.4 Hz, 2H(6.6″)), 8.14-7.85 (m, 7H(3.3″;3.3″;4.4″;4.4″)), 7.60 (m, 2H(5.5″)), 2.05 (m, 2H(7)), 1.70 (m, 2H(8)), 1.32 (m, 18H(16)), 1.06 (m, 6H(12)), 0.54 (m, 38H(17,15,9)), 0.39 (m, 6H(13 or 11)), 0.21 (m, 6H(13 or 11)), -0.04 (s, 81H(19)).

FAB\(^{+}\)MS: \(m/z\) 1734 [M\(^+\)-Br]. Due to complications (e.g. impurity), no absolute mass could be found for complex 4.

**Determination mesogenic textures of complex 2.**

The textures of metallomesogenic phases were observed under a Leica DM IRB polarising optical microscope at room temperature. Solutions with different concentrations of complex 2 dissolved in CH\textsubscript{2}Cl\textsubscript{2} (0.08-0.2 M) were prepared. Drops of these solutions were placed on glass slides. The drying processes were monitored under the optical polarising microscope between crossed polarisers. Isotropic materials appear then dark while anisotropic materials transmit some light with an intensity depending on the degree of anisotropy and the orientation of the optical axis with respect to the polarisers of the microscope. The different structures of liquid crystalline phases lead to characteristic optical textures that can be used to identify these phases.\(^{[27]}\)
Possible stacking interaction (self-association) of complex 2.

The formation of lyotropic liquid crystals of complex 2 in the presence of CHCl₃ occurs at relatively high concentrations of complex 2 (weight ratio complex 2:solvent > 1:2.5). To investigate intermolecular interactions of complex 2 molecules in solvent at lower concentrations, the assumed self-association through stacking interactions was monitored by ¹H NMR techniques. The latter interactions should influence certain ¹H chemical shifts of complex 2, compared to those of the non-self-associated molecules of 2. The stacking interactions could be partly responsible for the formation of the observed lyotropic liquid crystals when solvent evaporated.

X-ray powder diffraction measurement of complex 2.

In order to measure the powder diffractogram of complex 2, three different instruments have been used.

**Guinier-Johannson camera**

This instrument was used because of its excellent resolution, combined with easy sample preparation. The Guinier-Johannson camera makes use of an incident Johannson monochromator, which is a large single crystal, cut and oriented to diffract the Kα₁ component of the incident radiation. This monochromator is also bent and its curvature is designed to use the whole surface of the crystal to diffract simultaneously, thus yielding a large diffracted intensity. As a consequence of this curvature and the orientation of the crystal, the monochromator not only separates Kα₁ from Kα₂ easily, but converts the divergent incident beam to an intense convergent diffracted beam focussed onto a sharp line. The monochromator is placed in such a way that this line coincides with the photographic film. In the Guinier camera the convergent Kα₁ beam irradiates the sample that is located on the same circle where the film is placed. As a consequence of the focussing of the primary beam, also all diffracted beams will be focussed on the film, resulting in a high-resolution diffraction diagram (full width at half maximum = ca. 0.06° 2θ).

The amount of material needed is small; usually ca. 5 mg, if needed even less.
Aperf Probe Camera, Bruker

This instrument was used because the specimen is measured in reflection using the so-called Bruel-Brentano geometry, while the Guinier-Johansson camera measures the specimen in transmission, by application of the Seemann-Bohlin geometry. Therefore, any deviation of the randomness of the orientation of the crystallographic texture will be shown in differences in diffraction intensities between the two measurements. For this, two different specimens were prepared.

X-ray powder-diffraction patterns were measured at the high-resolution powder diffractometer from the Swiss-Norwegian CRG beam line SXBL 3 BM 14 at the European Synchrotron Radiation Facility (ESRF) Grenoble, France, with a h = 0.7894 Å. For data collection a capillary with a diameter of 10 mm was filled with powder and rotated during exposure. Continuous scans were made from 0.5° to 38.0° 2θ. Instead of measuring every 20° range the same time, the higher angle regions of the patterns were measured several times in order to mimic a single-crystal measurement as much as possible, so it was tried to give every reflection the same data collection time. After data collection, the scans were binned at 0.008° 2θ and scored. Full pattern decomposition (FPD) with a split type pseudo-Voigt peak profile function was converged to Rp (1.10), Rw (1.50).

Results

Synthesis of complexes 2-4.

Complex 2 was synthesised at room temperature in situ using freshly distilled H1OH from sodium as drying agent as solvent (Scheme 4.1). The synthesis of 2 is most successful when using also freshly prepared dendrimer wedge G2, since G2 is prone to polymerrisation. Complex 2 dissolves very easily in various organic solvents other than alkane and prone polar solvents e.g.
CHCl₃, CH₂Cl₂, benzene, toluene, Et₂O, THF). At high concentrations (> 0.2 M in CH₂Cl₂), complex 2 forms nematic lyotropic liquid crystal phases as observed using an optical polarised microscope.

The synthesis of complex 3 is almost instantaneously. Like complex 2, complex 3 is also a yellow solid. However, in contrast to complex 2, complex 3 is poorly soluble in organic solvents, and showed no liquid crystalline behaviour.

The complete conversion of starting material to complex 4, under the applied reaction conditions, takes several days. To separate complex 4 (yellow oil) from G3 (colourless oil), the SFC technique was used. Unfortunately, the purification of complex 4 was not possible, since the unknown compound A co-eluted with complex 4. Based on very similar ¹H NMR signals and the co-elution of A with 4, both products must be fairly similar in structure and size. Complex 4 dissolves in many organic solvents, and the mixture complex 4 and compound A showed no liquid crystalline behaviour.

Complexes 2–4 are air and thermally stable.

Observation of metalmesogenic textures of complex 2 with CH₂Cl₂.

When drops of solution of complex 2 in CH₂Cl₂ were drying, the isotropic liquid phase was found, under polarised optical microscope, to change into a liquid crystal phase (Figure 4.1). This was best observed starting with highly concentrated solutions of 2 (> 0.2 M in CH₂Cl₂). The solution in the isotropic phase is black and the dried liquid crystalline phase left behind by the evaporation of CH₂Cl₂ is brightly coloured (blue). When the solvent evaporates (weight ratio material:solvent > 1:2.5), the front line between the solution and the dried area migrates in the direction of the white arrow (Figure 4.1). Close to the dried phase, in the solvent-rich phase small areas of liquid crystalline phases are already observable as light regions (e.g., the region at the start of the white arrow in Figure 4.1). A flow could be observed in the solvent-poor phase close to the front line between the solution and dried phase. This indicates that these anisotropic regions are liquid.
Figure 4.1. Formation of a liquid crystalline phase.

When the solvent is fully evaporated, the texture of the liquid crystalline phase is immobilized by the glass substrate. This substrate-induced memory effect is a known phenomenon for both thermotropic and lyotropic liquid crystals. The resulting texture depends on the concentration of the solution deposited on the glass. When a drop of dilute solution of complex 2 (<0.05 M in CH$_2$Cl$_2$) is dried at room temperature in air (Figure 4.2a), a texture appears at the edge of the initial droplet, while the rest remains dark. This texture is reminiscent of the one observed in very thin films of thermotropic nematic liquid crystals. When drops of a more concentrated solution of 2 (0.05-0.1 M in CH$_2$Cl$_2$) are dried, similar patterns can be observed at the edge of the droplet (left upper corner Figure 4.2b). However, moving towards the centre of the droplet, another type of texture can be observed. The latter can be characterised as Schlieren texture, and appears in the optical microscopy of bulk nematic and smectic C liquid crystalline phases under crossed polarisers when the director field exhibits defects. The dark streaks or brushes, which are typical for Schlieren textures, appear around disclinations, i.e. line defects arising from singularities in director field. At even higher concentrations of the initial solutions, the whole dried drop presents a
Schlieren texture (Figure 4.2c). The latter shows under the microscope a different pattern than in Figure 4.2b, because of a larger thickness of material left behind after the drying process.

Figure 4.2a. Texture formed after drying drop (<0.05 M). The white bar is 100 µm long.

Figure 4.2b. Texture formed after drying drop (0.05-0.1 M). The white bar is 100 µm long.

Figure 4.2c. Texture formed after drying drop (0.1-0.2 M). The white bar is 100 µm long.

Drying a highly concentrated drop of sample 2 (0.2 M in CH₂Cl₂) renders the formation of various different types of textures along the radius of the drop (Figure 4.3a-d). This is possibly caused by the thickness gradient along the radius, and also the different drying history at different positions in the drop. At the edge of the dried drop (Figure 4.3b-c), similar textures are observed as seen in Figure 4.2a-c. In the middle of the radius of the dried drop, large areas with the same director orientation can be observed. This is evidenced by the appearance of rather large areas with a relatively uniform intensity (Figure 4.3d). In the centre of the dried drop, most probably, very small single crystals are grown (Figure 4.3a, inner part of the white circle).

All observed characteristics of the various studied textures of dried solutions of 2 in CH₂Cl₂ under the optical polarising microscope clearly indicate the formation of nematic or smectic lyotropic liquid crystalline phases of 2 in the presence of small amounts of CH₂Cl₂.

Attempts to observe thermally induced phase transitions of nearly dry liquid crystalline phases of complex 2 using DSC (Differential Scanning Calorimetry) (7 = 20-200 °C) failed. No degradation
or melting of complex 2 was observed, indicating a high thermal stability and a melting point higher than 200 °C for complex 2. During DSC experiments, it is almost certain that all CH₂Cl₂ solvent molecules have evaporated out of the liquid crystalline phases at elevated temperatures.

As mentioned earlier, after drying, the studied lyotropic liquid crystal phase of complex 2 changed eventually into a dry solid phase containing very small single crystals, which were used for
Synthesis of lyotropic liquid crystals with Rh(I)-Tpy complex and dendrimer-wedge powder diffraction studies *(vide infra)*. Finally, after several months of standing at room temperature in air, larger crystals could be observed under the polarised microscope (*Figure 4.4*). Unfortunately, these single crystal plates were too thin for X-ray measurements.

*Figure 4.4. A representative single crystal plate of complex 2, formed after more than 30 days. The white bar is 100 μm long.*

**Monitoring self-association of complex 2.**

At different concentrations of complex 2, the chemical shifts of the aromatic protons H(5,5") and H(6,6") of complex 2 were measured (*Table 4.1*). The NMR signals of H(5,5") and H(6,6") shift slightly downfield with lowering in concentration of complex 2. The chemical shifts of H(5,5") and H(6,6") do not shift significantly at concentrations below 0.0025 M for complex 2. At different concentrations of complex 2, only aromatic ¹H NMR signals shifted slightly, while the ¹H NMR signals of the dendrimer moiety did not shift at all.

**Table 4.1.** Chemical shifts (ppm) of H(5,5") and H(6,6") in CDCl₃ at different concentrations of complex 2 (M).

<table>
<thead>
<tr>
<th>Concentration</th>
<th>0.075</th>
<th>0.015</th>
<th>0.0075</th>
<th>0.005</th>
<th>0.0025</th>
<th>0.0015</th>
<th>0.00015</th>
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<tr>
<td>δH(5,5&quot;)</td>
<td>7.622</td>
<td>7.645</td>
<td>7.650</td>
<td>7.652</td>
<td>7.656</td>
<td>7.656</td>
<td>7.658</td>
</tr>
</tbody>
</table>
Complex 2 seems to undergo self-association with the involvement of the 1py ligands in the studied concentration domain. The self-association process is possibly facilitated by \( \pi-\pi \) stacking interactions between the aromatic ring systems of monomers of complex 2.

The possible unstacked and stacked units (built from monomers) in solvent are in rapid equilibrium; the designations unstacked and stacked describe an average over many unspecific conformations. The average association constant for molecules of complex 2 in solvent has been calculated with curve-fitting software: \( k = 4.2 \times 10^{-9} \text{ mol}^{-1} \). The relative amounts of bound species varies from 50\% at the lower concentration studied (0.00015 M) to 36\% at the higher concentration (0.075 M). The calculated chemical shifts for \( \text{H}6.5\) and \( \text{H}6.6\) obtained from the fitting procedure are 7.66 and 9.56 ppm for the free monomers and 7.57 and 9.45 ppm for the bound species.

X-ray powder diffraction study of crystalline complex 2.

The determination of crystal structures from single-crystal data has become routine, provided it is possible to grow suitable crystals (0.1-0.5 mm). If only polycrystalline powder is available then structure determination becomes complicated. In the last decade a number of groups have tried to tackle this problem and a couple of program packages that enable the calculation of the structure from the X-ray powder diffraction diagrams exist nowadays, for instance POWSIM (9) and SIRPOW (9). The main problem in structure determination is the number of "single" reflections that can be extracted from a powder diffractogram. Especially for lower symmetries (up to orthorhombic) and larger structures the overlap of reflections prevents the extraction of reliable intensities especially at higher \( 2 \theta \) values.

Ideally, the polycrystalline material consists of many randomly oriented crystallites with dimensions of ca. 0.1-10 \( \mu \)m. To measure a powder diffractogram, suitable for a structure determination, the crystallites should not be smaller than 0.1 \( \mu \)m, because this would cause broadening of the reflection profiles leading to a decrease in resolution. Also crystallites larger than 10 \( \mu \)m result loss in resolution. A decreasing number of crystallites will affect the crystal statistics.
and thus the reliability of the reflection intensities. Furthermore, the crystallites should have a random orientation in the specimen. Presence of texture will again affect the reliability of the intensities. Finally, the diagram should represent one single phase, although traces of contamination with a second phase does not present major problems.

X-ray powder diffraction studies of dried crystals of complex 2 have been done with three different techniques (Guinier-Johansson camera, Xpert powder diffractometer and Parallel beamline diffractometer at ESRF Grenoble). The samples used for each technique contain crystals formed after a different drying history. For the Guinier-Johansson camera, the crystals were grown on a thin polymer film. After ca. 5 days of drying, the crystalline phase was completely yellow and suitable for measurement. In the case of the ‘Xpert powder diffractometer, the crystals were grown on a polymer disc. The yellow crystalline phase was already obtained after ca. 6 hours of drying. Finally, for the Parallel beamline diffractometer at ESRF, the sample was dried in a capillary. After 1-2 weeks of drying, the crystalline phase was yellow of colour.

**Guinier-Johansson camera**

After several trials (ca. 5 attempts) a diffraction diagram was recorded with good resolution (Figure 4.5). However, the occurrence of reflections of different profile widths indicates that the material possibly consists of a mixture of several phases. Attempts were made to eliminate a possible contamination by evacuation of the camera under reduced pressure, and by heating the specimen to moderate temperatures (up to 60 °C). After each attempt, a diffraction diagram was recorded. Since the diagrams remained essentially unchanged, it is likely that the diffraction diagram (as shown in Figure 4.5) represents one single phase.
Chapter 4

As mentioned earlier, using this technique, two different specimens were prepared as described above. From the first specimen, a diffraction diagram was recorded with very low intensities (Figure 4.6). It could be possible that only a small part of the material was in the solid crystalline state, while the larger part was in liquid crystalline state. After drying, another measurement of the very same sample gave a diffractogram very similar to the second specimen (Figure 4.7).
With respect to the line positions, the diagram of the second specimen (Figure 4.7) is similar to the Guinier-Johannson diagram (Figure 4.5). However, since their diffraction intensities are very much different, it can be assumed that either or both the Guinier-Johannson specimen and the 'Xpert specimen are textured.
Figure 4.7. X-ray powder diffraction diagram of second specimen of complex 2, recorded with an 'Xpert powder diffractometer.

Parallel beamline diffractometer at ESRF

It is likely that the specimen for the ESRF diffractometer was less textured than the Guinier-Johannson and the 'Xpert diffractomet specimens, since the latter two specimens consist of a flat thin layer, while the ESRF specimen is a glass capillary (diameter 1.0 mm) filled with material. During the measurement the capillary is rotated (spinned) along its axis. With respect to the reflection positions, the resulting diagram (Figure 4.8) was found to be very similar to the Guinier-Johannson and the 'Xpert diagrams. In contrast, their intensities are completely different, which indicates that texture states are different for the three cases. The resolution of the ESRF measurement is better than for the other two measurements, while texture might be smaller.
Determination of the unit cell and the spacegroup of complex 2.

The first attempts to derive the unit cell and the spacegroup from the powder diagram were carried out before the measurement on the ESRF diffractometer was available. For these attempts the Guinier-Johansson diagram was used. To assess the correctness of a possible unit cell De Wolff[58] proposed the use of a figure of merit $M_{20}(1)$. This figure of merit should be applied to those unit cells, which will index practically all observed reflections. Moreover, the accuracy of reflection positions derived from the diagram is essential. After many attempts, using the indexing program ITO,[59] the following orthorhombic unit cell could be derived from the Guinier-Johansson powder diagram using 49 reflections:

\[
\begin{align*}
\text{a} &= 50.90 \, \text{Å} \quad \alpha = 90, \\
\text{b} &= 16.64 \, \text{Å} \quad \beta = 90, \\
\text{c} &= 14.37 \, \text{Å} \quad \gamma = 90.
\end{align*}
\]

\[
\text{unit cell volume} = 12,171 \, \text{Å}^3.
\]
The spacegroup is most likely Pheca0, indicating an inversion of symmetry within the system like the complexes [RhCl$_2$(py)$_2$] and [RhCl$_2$(Carbonaryl)(py)$_2$] described in Chapter 2, and the $M_Z$ value for this solution is 12. A complication is the large volume of this unit cell. The accuracy of the reflection positions derived from the Guinier-Johnson diagram allows unit cells to be derived which are not larger than ca. 10 nm. This means that although all remaining conditions for correct indexing have been fulfilled, there still remains some doubt with respect to the correctness of the unit cell.

After the measurement at 1SRF, a powder diagram was available with an improved resolution, from which more accurate line positions could be derived with the program PROFIT. Using these reflection positions the orthorhombic unit cell could be refined to give the following values:

- $a = 50.78$ Å, $\alpha = 90^\circ$.
- $b = 16.599$ Å, $\beta = 90^\circ$.
- $c = 14.358$ Å, $\gamma = 90^\circ$.

The value of $M_Z$ increased to 35. The spacegroup is Pheca. From the chemical formula ($C_{47}H_{44}BrN_4RhSi_3$), it follows that this unit cell contains 8 molecules, which is also the multiplicity of the general position of this spacegroup.

**Positioning of the molecule in the unit cell using simulation data.** With the knowledge of the unit cell and spacegroup of complex 2, several attempts have been made to elucidate its crystal structure. For this, two possible models were built with Cerius2 $^{15}$ from C-H-Br-Cu-N, which were taken from the CSD. $^{16}$ The code CAIVO. $^{17}$ After changing Cu into Rh the rest of the molecule was added and energy minimization was performed. The resulting model was used for a grid-search procedure. For positioning the models in the asymmetric unit, 250 extracted intensities from the HPD were used in a grid-search technique (Chernyshev and Schenk, 1998). Unfortunately, all attempts to reach a satisfactory solution have failed. This is most likely due to the flexibility of the dendrimer moiety of the molecule.
Simulated structure of complex 2 by semi empirical calculations. To get some insight on the structural organisation of complex 2 within the lyotropic liquid crystalline phases, its structure is simulated with the Spartan program using the PM3 calculations (Figure 4.9a and 4.9b). It must be noted that PM3 is a very approximate method.

Since the rigid terpyridine ligand around the Rh atom is prone to π-stacking (Chapter 2), it is likely that complex 2 can form dimers as shown in Figure 4.9b. This dimer is depicted with an inversion symmetry, which is in accordance with the found space group Pbc a of the measured crystals of complex 2. This dimer has one axis (whose projection in the plane of the terpyridine ligands is parallel to the Rh-Br bond in this plane) that is likely to present nematic or smectic-like orientational order.

Figure 4.9a. Simulated structure of complex 2.

Figure 4.9b. Simulated dimer presentation of complex 2 with inversion of symmetry according to the determined spacegroup Pbc a. The (large) arrow, crossing the two monomers, shows approximately the axis of the dimer that most probably exhibits the orientational order responsible for the occurrence of the liquid crystalline state. The projection of this axis (small arrow) is shown in the RhBr-Tpy plane of the top monomer.
Discussion

Like the Rh(III)-terpyridine complexes described in Chapter 3, the syntheses of complexes 2-4 are very facile. Although G1 and G2 are prone to polymerisation, complexes 2 and 3 showed no polymerisation during the various measurements for their characterisation.

After purification/ work up of complex 2, the complex displayed lyotropic liquid crystalline behaviour in the presence of small amounts of CHCl₃ as observed under a polarised microscope. The observed mesogenic textures are typical for nematic and smectic C phases, which is further evidenced by the presence of Schlieren textures (Figures 4.2-3).

Another strong indication for the formation of a liquid crystalline phase has been observed while measuring a sample of 2 with the Xpert powder diffractometer. The recorded diffractogram (Figure 4.6) showed the presence of a significantly more ordered texture than a pure liquid phase, but far less ordered than a pure crystalline phase (Figure 4.7). It could be possible that this diffractogram (Figure 4.6) belongs to a liquid crystalline phase.

1H NMR studies of complex 2, at different concentrations, strongly indicate that only the aromatic protons interact with each other in solution. This could mean that the aromatic rings of the terpyridine ligands undergo stacking interactions (i.e. self-association), which supports the conformation of the simulated dimer depicted in Figure 4.9b. Unfortunately, from all the collected data concerned about the studied liquid crystalline phases of 2, it is impossible to conclude the statistical orientations of the discrete monomers in space without speculation. However, the structure shown in Figure 4.10 is in line with all data obtained. The fact that the molecules form a layered structure is reinforced by the shape of the single crystals obtained after drying (Figure 4.4): the plate shape is characteristic of the organisation in layers. The axis of the dimers is tilted with respect to the bilayer, which implies that the director (i.e., the mean orientation of the dimer axes) is also tilted, which corresponds to a smectic C phase.
Synthesis of lyotropic liquid crystals with Rh(I)-Tpy complex and dendrimer-wedge

Figure 4.10. Possible arrangement of dimers in a bilayer structure. The dendrimer-wedge groups of adjacent bilayers are probably interdigitated. Solvent molecules (CH$_2$Cl$_2$), necessary for the formation of the lyotropic liquid crystalline phase, are omitted.

It is unlikely that very small amounts of CH$_2$Cl$_2$ molecules (weight ratio complex 2:solvent > 1:2.5) can influence dramatically the organisation and orientation of complex 2 molecules, implying that the textures of the wet liquid crystalline and dry solid crystalline phases are very similar. Hence, the organisation and orientation of complex 2 in the liquid crystalline phase could be very similar to the organisation in single crystal plates (Figure 4.4) and to the simulated structures depicted in Figures 4.9 and 4.10.

The $^1$H NMR spectrum of the single crystals of complex 2, collected after several months standing at room temperature under air atmosphere, is exactly the same as for freshly synthesised powder of complex 2. This means that the studied structures are not affected by polymerisation processes.

Clearly, complex 3 showed no liquid crystalline behaviour. Based on the results, described in this chapter, for complex 4 it is not possible to conclude whether it has the capacities to display liquid crystalline behaviour, since relevant microscope observations were performed with impure samples of complex 4. However, based on similar $^1$H NMR signals and co-elution from SEC of complex 4 and compound A, it is highly likely that both products are chemically and physically similar to each other. From the fact that this mixture is an oil, it can be suggested that both compounds are an oil.
For the synthesis of chiroptropic liquid crystals, certain criteria must be met, as explained earlier. Concerning the relative size of the rigid and flexible parts needed for liquid crystal behavior, it is clear that G2 is suitable to form, together with complex 1, chiroptropic liquid crystals. In contrast, G1 and G3 did not show, together with complex 1, any liquid crystal behavior. Likely, G1 is too small and G3 too large to form a good combination with complex 1 to display liquid crystal behavior.

The approach presented in this chapter proves that the oxidative addition reactions can not only alter dramatically liquid crystalline phases, but can also be used to form mesogenic liquid crystalline phases directly from non-mesogenic precursors. The reaction described here is easy to perform and allows one to use a wide variety of precursors to generate different types of mesogens. Thus, it provides a useful alternative to the standard strategy of first preparing a mesogenic ligand and then coordinating it to a metal.

Acknowledgement

The authors would like to thank Drs. W. van Beek from BM 15 at the European Synchrotron Radiation Facility (ESRF) in Grenoble for his help during the measurements.

References


Chapter 5

Crystal Structure of the Novel Neutral Octahedral Complex \([\text{Rh}^{\text{III}}(\text{Br})(\text{Acetonyl})_2(4'-(4'-\text{Butylphenyl})-2,2':6',2''-\text{Terpyridine})]\).

Boke C. de Pater,' Hans-W. Frühauer,' Kees Goubitz,' Jan Fraanje,'
Peter H.M. Badzelaar,' Anton W. Gal,' Kees Vrieze.'

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Department of Inorganic Chemistry, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.
Abstract

In the previous chapters, we have described the syntheses, characterisation, properties, reactivity and an application of RhII-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 RhII-terpyridine complexes in different organic solvents, we encountered one such species. Upon standing at room temperature, a mixture of 4-i-butylphenyl-2,2',6,2''-terpyridine and [RhBr(COD)]$_2$ in acetone was found to deposit crystals of [Rh$^{III}$Br$_3$(acetonyl)$_3$]$_4$ (4-$i$-butylphenyl-2,2',6,2''-terpyridine). Here we report the synthesis and characterisation of this uncommon complex.
Introduction

We have synthesised several Rh(III)-terpyridine complexes in various organic solvents (ref. Chapter 2 and 3). Reaction of 4,4'-diethylphenyl-2,2':6,2''-terpyridine and [RhBr(COD)] in acetone, however, unexpectedly produced the Rh(III) complex [RhIII(Br-acetonyl)4-4'-diethylphenyl-2,2':6,2''-terpyridine](Br). Based on crystallographic studies, mass measurements (Fast Atom Bombardment and Field Desorption) and DFT calculations, we have a clear insight in its structure and composition. Each acetonyl group is σ-bonded to the Rh-metal of complex 1 in axial position relative to the plane of the Tpy^2 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'-diethylphenyl-2,2':6,2''-terpyridine (Tpy^2) 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 1 was formed in acetone under an inert atmosphere (purified argon), using standard Schlenk techniques. The formation of 1 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. Csl 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-MP902 HD/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 1 is done according to the following scheme:

\[
\text{[Rh}^{	ext{III}}\text{(Br)(acetonyl)}_2(4'-(4'-butylphenyl)-2,2';6',2''-terpyridine)]
\]

Acetone (40 ml) was added to 0.023 g [RhBr(COD)]_2 (0.039 mmol) and 0.029 g Tpy (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 1 (yield ~100%) was collected as a yellow powder.

FAB' MS: \( m/z \ 604.05 \) (M'). \( \text{FD}^{+} \text{MS}: m/z \ 611.08 \) (M').

Due to the insolubility of complex 1 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 1.**

A crystal with dimensions 0.15×0.20×0.05 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 \(-14 \leq h \leq 14, 0 \leq k \leq 28, 0 \leq l \leq 15\). Of
these, 2737 were above the significance level of 4σ (1.4) and were treated as observed. The range of (sin θ)/λ was 0.044–0.625 Å⁻¹ (3.960–7.460). Two reference reflections [1 0 3 1], [1 2 1 3] 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°<20<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 Ω scans of five reflections, with coefficients in the range 0.781–0.953. The structure was solved by the PATTY option of the DIRDIF-99 program system. The asymmetric unit contains half a molecule with Rh, Br, Ni(2), C(8), C(9), C(12), and C(13) on a special position (1 4 y 1). After isotropic refinement of 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(2Δ) and O(Δ) 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 = 0.065, (Aσ)obs = 0.02, S = 0.84. A weighting scheme w = [30 - 0.01σ²(Fobs)]⁻¹ - 0.01σ²(Fobs)] was used. The secondary isotropic extinction coefficient refined to 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 XFLS.7.7 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 1.

<table>
<thead>
<tr>
<th>Formula</th>
<th>C18H18N03Rh(CH3CO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mr</td>
<td>664.45</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
</tbody>
</table>
Table 5.1 | Crystallographic Data for Complex I

<table>
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</tr>
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</tr>
<tr>
<td>b, Å</td>
<td>22.679(2)</td>
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<tr>
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</tr>
<tr>
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<td>F(000)</td>
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<tr>
<td>D_cal., g/cm³</td>
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</tr>
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</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) [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 $^{[11,12]}$ using the BP86 functional $^{[13-18]}$ and an SV(P) basis set, a medium-sized integration grid and the RI approximation $^{[19]}$. 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.
Chapter 5

Results

Formation of $[\text{Rh}^{III}(\text{Br})(\text{acetonyl})_2(4'-(4\text{-butylphenyl})-2,2':6',2''\text{-terpyridine})]$ (1).

After stirring at room temperature $[\text{Rh}($Br$)(\text{COD})]_2$ (COD = 1.5-cyclooctadiene) and $4'-(4$-butylphenyl)-2,2':6',2''-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 $[\text{Rh}($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 $[\text{Rh}($Br$)(\text{Tp}^\ast)]$.

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

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

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>
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<td>2.543</td>
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<td>99.48°</td>
</tr>
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<td>2.054</td>
<td>2.064</td>
<td>Rh:Re N1</td>
<td>90.0°</td>
<td>99.8°</td>
</tr>
<tr>
<td>Rh-N1</td>
<td>1.032</td>
<td>1.036</td>
<td>N1-Re-N2</td>
<td>80.43°</td>
<td>80.68°</td>
</tr>
<tr>
<td>Rh-N1</td>
<td>2.054</td>
<td>2.064</td>
<td>Rh:Re: N1</td>
<td>80.85°</td>
<td>80.48°</td>
</tr>
<tr>
<td>Rh-C1</td>
<td>2.244</td>
<td>2.244</td>
<td>Rh:N1-C2</td>
<td>112.84°</td>
<td>113.47°</td>
</tr>
<tr>
<td>N1-C2</td>
<td>1.371</td>
<td>1.384</td>
<td>Rh:N1-C6</td>
<td>127.63°</td>
<td>124.02°</td>
</tr>
<tr>
<td>N3-C6</td>
<td>1.358</td>
<td>1.358</td>
<td>C2-N1-C6</td>
<td>119.96°</td>
<td>119.7°</td>
</tr>
<tr>
<td>N2-C2</td>
<td>1.406</td>
<td>1.407</td>
<td>Rh:N1-C2</td>
<td>129.32°</td>
<td>133.5°</td>
</tr>
<tr>
<td>N3-C9</td>
<td>1.350</td>
<td>1.357</td>
<td>Rh:N1-C6</td>
<td>134.94°</td>
<td>132.82°</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.126</td>
<td>1.126</td>
<td>C2-N1-C6</td>
<td>138.96°</td>
<td>128.37°</td>
</tr>
<tr>
<td>Rh-C13-C14</td>
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<td>2.358</td>
<td>Rh:Re-C13</td>
<td>85.69°</td>
<td>83.36°</td>
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<td>2.000</td>
<td>Rh:Re-C14</td>
<td>91.14°</td>
<td>89.70°</td>
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</table>

Crystallographic and DFT data show that the methylene carbon atom of each acetonyl group is σ-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 (Rh-Brodpy) in CCl₄ (or CH₂Cl₂), which is confirmed by UV–VIS spectroscopy. In contrast to the facile synthesis of 1, the mechanism for the isomeric formation of 1 from the intermediate (Rh-Brodpy) 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 (Rh-Brodpy) is soluble in acetone, while the Brodpy 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 DEI 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 acetylacetonate groups are attached to the Rh metal of complex 1. Both X-ray and DEI data show that bonding of the metal to oxygen atoms in the Rh metal can be excluded. Therefore, the acetylacetonate 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. 0.2 Å longer than the Rh C bond in comparable Rh-III tendentary nitrogen complexes described by Haarman et al. The difference in bond lengths in these related RhIII 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
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.

\[ \text{O} \quad \text{O} \]

So far, the reaction mechanism for the formation of complex 1 from [Rh'(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

Summary

This PhD thesis describes the synthesis and properties of neutral square planar Rh(II-κ²-terpyridine complexes. It continues and extends the long tradition of our laboratory in the coordination and organometallic chemistry with bi- and terdentate nitrogen donor ligands, and here in particular of Rh(II) complexes with κ¹-coordinated 2,6-diamino-pyridines, [RhCl₂(κ¹-R₂N=NR₂)](C₄H₆N). With a very nucleophilic rhodium centre and a very interesting reactivity. Particularly interesting was the pronounced activation of carbon-chloride bonds which resulted in fast and clean oxidative addition reactions, giving alkyl-Rh(III) compounds. Following the notion that a pyridine nitrogen is a stronger net donor than an imine nitrogen, it was expected that terpyridine ligands would increase the electron density at the central metal atom even more effectively than the 2,6-diamino-pyridine ligands, and render Rh(II-κ²-terpyridine complexes more nucleophilic than [RhCl₂(κ¹-R₂N=NR₂)](C₄H₆N).

Chapter 1 gives a general introduction, featuring selected examples from the coordination and organometallic chemistry of bidentate chelating α-dimine ligands, and collecting the earlier results with 2,6-diamino-pyridines. A short introduction to the syntheses of terpyridines and their coordination to metal centres is given, concluding with the aim and scope of this thesis.

In Chapter 2, the synthesis and characterisation of some highly air-sensitive Rh(II) terpyridine complexes are described in detail. Once proper conditions are applied, the yield of the relatively facile syntheses is nearly quantitative. A major drawback of the terpyridine complexes is their poor solubility in organic solvents, hampering full characterisation. As a result, NMR techniques were only of limited use. To improve solubility, we have tried to attach a bulky carboranyl group on the terpyridine ring. However, improvement was only minor. Despite the low solubility of the Rh(II)-terpyridine complexes, it was possible to collect single crystals of complexes [RhCl₂(κ²-O₂R₂N₂)](C₄H₆N) and [RhCl₂κ²-α-methyl-α-methyl-α-tolyl-carboranyl](κ²-O₂R₂N₂). Within the crystals, π-stacked structures and discrete dimers (for the former and latter complexes).
respectively) were observed, which is in line with their low solubility. Based on crystallographic data of [RhCl2(2,2'-6,2'-terpyridine), DFT/TDDFT calculations were performed. The main orbitals of the relevant complexes were analysed. It appears that the HOMO highest occupied molecular orbital of the Rh(III)-terpyridine complexes is located on the d-orbital of the Rh metal. The LUMO lowest unoccupied molecular orbital is predominantly located on the terpyridine ligand. Furthermore, from the DFT data, the dominant absorption bands in the UV/Vis spectra of the relevant Rh(III)-terpyridine complexes could be assigned. In the region of 250-400 nm, absorption bands are mainly intraligand charge transfers, while absorptions in the region 300-400 nm are dominated by metal to ligand and ligand to ligand charge transfers (MLCT and LLCT, respectively). The redox potentials of [RhCl₂2,2'-6,2'-terpyridine]- and [RhBr₂2,2'-6,2'-terpyridine]- were determined with cyclic voltammetry in DMF (dimethylformamide). The complex LUMO is located on the ligand and the HOMO on the metal, thus reduction takes place at the ligand while oxidation occurs at the metal centre. Since oxidative reactions of the Rh(III)-terpyridine complexes take place at the Rh metal centre, it was interesting to measure its oxidation potential. The first single electron oxidation step of [RhCl₂2,2'-6,2'-terpyridine] and [RhBr₂2,2'-6,2'-terpyridine] takes place at very low potentials of -0.84 V and 0.83 V vs Fe/Fe⁺ respectively. This indicates that the Rh-metal atoms have a relatively high electron density, explaining their relatively high reactivity towards carbon halide bonds. Unfortunately, these potentials had not been measured for the related 2,6-dimino-terpyridine complexes, so a comparison is not possible.

It is worth mentioning, that in the far infrared (FIR) spectra, the νRh-C and νRh-Br bands of RhCl₂2,2'-6,2'-terpyridine and [RhBr₂2,2'-6,2'-terpyridine] are facile to assign by simply comparing the FIR spectra of the two complexes.

In Chapter 5, the synthesis and characterisation of ca. twenty Rh(III)-terpyridine complexes are described. All of them are obtained in almost quantitative yields from the oxidative addition of complex [RhClBr₂2py]⁺ (2py = 4-(4-hexylphenyl)2,2'-6,2'-terpyridine) with bromo-hydrocarbons containing mainly terminal carbon-bromide bonds. The selection of bromo-hydrocarbons was such that at least a qualitative impression of their relative reactivities could be obtained. It appeared that sp²-C-Br bonds of the smallest alkyl bromides reacted the fastest, larger ones and vinyl bromides somewhat slower, and the sp³-C-Br bond of bromobenzene the slowest. Since neither the [RhBr₂2py]⁺ nor the [RhCl₂2py]⁺ complexes gave clean oxidative addition...
reactions with chloro-hydrocarbons, a direct comparison with the reactions of the related 2,6-dimino-pyridine complexes was unfortunately not possible. The obtained Rh(III)-terpyridine complexes are thermally and air-stable and well soluble in various organic solvents. Surprisingly, although the solubility of the Rh(III) complexes is significantly better than of the parent Rh(I) complexes, no single crystals could be grown. Therefore, the determination of the geometry of the Rh(III)-terpyridine complexes is entirely based on 'H, 'C, 'N and 2D NMR techniques.

The chemistry described in Chapter 3 turned out to be very useful for the synthesis of lyotropic liquid crystals, which is described in Chapter 4. For the synthesis of liquid crystals, it is essential to design material containing a rigid and a flexible part. The neutral square planar Rh(III)-terpyridine complexes are very rigid and reactive towards carbon-halide bonds. Oxidative addition of \([\text{Rh}^\text{III}(\text{Brn})_22.2':6'.2''\text{terpyridine}]\) with a bulky flexible dendrimer wedge containing a terminal C-Br bond proved to be useful for producing a suitable product for the formation of lyotropic liquid crystalline material in the presence of small amounts of CHCl₃. This is one of the first examples for the synthesis of a liquid crystalline material through simple oxidative addition of a metal complex to an organic reagent. The vast majority of liquid crystalline materials are still purely organic compounds.

In Chapter 5, the crystal structure of a very unusual Rh(III)-diacetonyl-terpyridine complex is described. During our research on Rh(I)-terpyridine chemistry, various organic solvents were used for different reasons. Soon it became clear, that many organic solvents were not suitable for the synthesis of the Rh(I) complexes, as uncharacterised products were formed. However, in an attempt to synthesise complex \([\text{Rh}^\text{III}(\text{Brn})_22.2':6'.2''\text{terpyridine}]\) in acetone as solvent, the formation of an unexpected thermally and air-stable complex, \([\text{Rh}^\text{III}(\text{diacetonyl})_2(\text{Brn})_22.2':6'.2''\text{terpyridine}]\) was observed. The crystal structure revealed a very intriguing property of the complex, namely that two acetonyl groups are trans situated and σ-bonded to the Rh metal. It should be noted, that the existence of neutral octahedral terdentate nitrogen metal complexes with two alkyl groups σ-bonded to the metal-centre has not been described in literature. The \textit{in situ} formation of \([\text{Rh}^\text{III}(\text{diacetonyl})_2(\text{Brn})_22.2':6'.2''\text{terpyridine}]\) underlines the interesting reactivity of the terdentate co-ordinated Rh(III)-terpyridine complexes.
Samenvatting

In dit proefschrift worden voor het eerst de synthese en karakterisering van neutrale vlakvierkante rhodium(1)-ket-terpyridine complexen beschreven. De lange traditie in onze groep van onderzoek naar de coördinatieve en organometalchemie van complexen met bi- en terdentate stikstofdonor liganden werd voorgezet en uitgebreid. Van bijzonder belang voor dit proefschrift zijn de eerder onderzochte Rh(I) complexen met ket-stikstofdonor liganden. De lang voor dit proefschrift zijn eerder onderzochte Rh(I) complexen met ket-stikstofdonor liganden, die een zeer nucleofiel rhodiumatom bevatten. Zij vertoonden onder meer een sterke activering van koolstof-chloor bindingen wat snelle en schone oxidatieve polymèreacties tot Rh(III)-alkyl verbindingen opleverde. Gebaseerd op een veronderstelde grotere donatie van elektronen door een pyridine stikstofatom t.o.v. een imine stikstofatom, werd verwacht dat de Rh(I)-terpyridine complexen mogelijk nog nucleofiel zouden zijn dan de Rh(I)-2,6-dimimopyridine complexen.

Hoofdstuk 1 bevat een algemene inleiding waarin enkele voorbeelden uit de coördinatieve en organometalchemie van bidentate chelierende θ-dimim liganden voorgesteld worden, gevolgd door de eerder verkregen resultaten met de terdentate 2,6-dimimopyridines. Vervolgens wordt de synthese van terpyridines en hun coördinatiedrag besproken, en afsluitend het doel en de onderdelen van dit proefschrift.

In Hoofdstuk 2 wordt de synthese en karakterisatie van thermisch stabiele, maar zeer luchtgevoelige, Rh(I)-terpyridine complexen uitvoerig beschreven. Na het vinden van de juiste reactiecondities werden de benodigde producten op relatief eenvoudige wijze gesynthetiseerd met zeer hoge opbrengsten. Hoewel de syntheses relatief eenvoudig zijn, is de karakterisering van de verkregen verbindingen vrij lastig. Dat komt vooral door de geringe oplosbaarheid van de Rh(I)-terpyridine complexen in organische oplosmiddelen. NMR spectroscopie kon dan ook maar zeer ten dele gebruikt worden voor de karakterisatie van de producten. De toepassing van een sterisch zeer grote carborylafgroep op de centrale pyridine ring verbeterde de oplosbaarheid helpt ook niet
door slaggevend. Ondanks de lage oplosbaarheden van de producten was het goedklijk mogelijk om de kristalstructuren van twee Rh-I-terpyridine complexen op te halteren, namelijk van 
[RhCl(C3H2N2)] (terpyridine) en [RhCl(2,2,6,2-butyldimethylsilyloxy-carbonanyl)2(2,6,2-terpyridine)]. Deze kristallografische studies maken duidelijk waarom de verbindingen slecht oplosbaar zijn, namelijk door het optreden van π-stacking-congestiveerde terpy en dimere vorming terpy met de sterkste grote carbonanyl substituent. Gebaseerd op de kristalstructuur van het complex [RhCl(2,6-py)] werden DFT-density functional theory berekeningen gedaan. De belangrijkste orbitalen van de relevante complexen werden geanalyseerd. Het bleek dat de HOMO (highest occupied molecular orbital) van de Rh-terpyridine complexen genee geïnliekeerd is op de d- orbitalen van het Rh-metaal. De HOMO dowerd nucare occupied molecular orbital von de bestudeerde complexen is voorafgaand geïnliekeerd op de terpyridine liganden. Tevens konden, m.b.v. TD DFT berekeningen, de dominante absorptionsbanden in het zichtbare gebied van de UV/Vis spectra van relevante complexen toegewezen worden aan specifieke ladingsoverdrachten binnen de complexen. Deze behoren tot de metal-to-ligand en ligand-to-ligand charge transfers (MLCT en LLCT, respectievelijk).

Een bewijs dat de Rh-terpyridine complexen zeer electronrijk zijn werd verkregen d.m.v. cyclovoltammetrie. De complexen [Rh(Cl)2(py)] en [Rh(Br)2(py)] worden in DME al bij een zeer negatief potentiaal E0 = -0.84 V en -0.83 vs FeCl3 definitief geïnliekeerd tot Rh(I) intermediaten. Het feit dat deze complexen zo eenvoudig oxideren is een sterke aanwijzing voor een grote electronenleiding op het metaalleen, omdat daar de HOMO geïnliekeerd is en als eerste electronen kwijt zal nemen in een oxidatieproces. Tevens kan de reactie zien ten opzichte van kwast-stof halogen bindingen verklaard worden door de grote electronenleiding op het metaalleen. Helaas zijn de gevonden redoxpotentiaal niet te vergelijken met die van de gerealiseerde 2,6-dimethylpyridine complexen omdat de overeenkomstige metingen toen niet zijn uitgevoerd.

Ten slotte is het vermeldenswaardig dat de Rh Cl en Rh Br bindingstellingen zichtbaar in het verre infrarood van de complexen [Rh(Cl)2(py)] en [Rh(Br)2(py)] relatief eenvoudig toe te kennen zijn door de twee spectra met elkaar te vergelijken.

In *Hoeftstuk 5* wordt de synthese van de zwakke Rh(I)-terpyridine verbindingen beschreven, welke verkregen zijn door oxidatieve decola van het complex [Rh(Br)2(py)2]+.
Samen vatting

rhynylphenyl-2,2'-6,2'-terpyridine met reagentia met veelal eindstandige C-Br bindingen. Bijna alle reacties verliepen kwantitatief. De keuze van de te添加en broomkoolwaterstoffen was dusdanig dat een tenminste kwalitatieve rangschikking van hun relative reactiviteit verkregen kon worden. Grotergere reageren kleine alkylbromides, met het broom op een sp³-koorstantoom, het snelst; grote alkylbromides en vinyl-broom bindingen iets langzamer en de sp²-C-Br binding van broombenzeen het langzaamst. Omdat noch het [RhCl(Tpy)] noch het [RhBr(Tpy)] complex schone reacties met chloroalkoolwaterstoffen opleverden, was het helaas onmogelijk om de reactiviteit met die van de overeenkomstige 2,6 dimmopyridine complexen te vergelijken.

De verkregen RhIII-terpyridine producten zijn evenals de RhIII-terpyridine complexen thermisch stabiel. Echter, de eerste verschillen van de laatstgenoemden in zoverre dat zij wel lachstableibel en rechrik tot zeer goed oplosbaar zijn. Ondanks de grotere oplosbaarheid van de RhIII verbindingen konden geen kristalstructuren worden opgedeeld. De bepaling van de geometrie van de RhIII-terpyridine complexen is dan ook geheel gebaseerd op H, C, N en 2D NMR technieken.

De chemie beschreven in hoofdstuk 5 bleek goed bruikbaar te kunnen worden voor de synthese van vloeibare kristallijne verbindingen (Hoofdstuk 4). Voor het maken van vloeibare kristallen, is het noodzakelijk om een molecuul te synthetiseren, dat uit een rigide en een flexibel deel is opgebouwd. De neutrale vlakvormige terdentate RhIII-terpyridine complexen zijn zeer rigide. Tevens reageren deze complexen goed met C-Br bindingen. Oxidatieve additie reactie tussen het complex [RhBr(Tpy)] en een bulky flexibele dendrimerswedge met een eindstandige C-Br binding zou dus in principe een product kunnen leveren dat geschikt zou kunnen zijn voor de vorming van vloeibare kristalachtig materiaal. Na de reactie tussen de twee relevante verbindingen bleek het gevormde product ondertussen hygroop vloeibaar kristallijn gedrag te vertonen in aanwezigheid van soortgelijke dichloorormaan. Dit is een van de eerste voorbeelden, waarbij een vloeibaar kristallijn materiaal wordt gevormd door een eenvoudige oxidatieve additie reactie tussen een metaalcomplex en een organisch reagens. Tot op heden ligt de nadruk bij het ontwikkelen van nieuwe vloeibaar kristallijn materialen op het synthetiseren van puur organische verbindingen.

In Hoofdstuk 5 wordt de kristalstructuur van een zeer interessant RhIII-diactonyl-terpyridine complex beschreven. Tijdens het in hoofdstuk 2 beschreven onderzoek naar de synthese en karakterisering van de RhIII-terpyridine complexen werden diverse organische oplosmiddelen
gebruikt. Vrij snel werd het duidelijk, dat er maar een klein aantal verschillende oplosmiddelen voor bepaalde complexen geschikt zijn. Echter, bij een poging het complex \([\text{Rh}^{III}\text{Br}_2\text{Tp'y}_2]\) te synthetiseren, werd de volledig onverwachte vorming van het thermisch en licht stabiele complex \([\text{Rh}^{III}(\text{acetonyl})\text{Br}_2\text{Tp'y}_2]\) ontdekt. Zeer interessant is het feit dat er, zoals uit een Röntgenstructuuranalyse duidelijk werd, twee acetonyl groepen \textit{trans} \(\sigma\)-gebonden zijn aan het metaal. Het bestaan van neutrale octaëdrische terdentate stikstof complexen met twee alkylen \(\sigma\)-gebonden aan het rhodium metaal zijn voor zover ons bekend nog niet eerder gepubliceerd. De \textit{in situ} vorming van het complex \([\text{Rh}^{III}(\text{acetonyl})\text{Br}_2\text{Tp'y}_2]\) onderstrept nogmaals de bijzondere reactiviteit van de terdentaat gecoordeerde \(\text{Rh}^{III}\)-terpyridine complexen.
Appendix

Full Colour Presentations:
Figures 4.1 – 4.4 and 4.9 – 4.10.

Figure 4.1. Formation of a liquid crystalline phase, based on complex 2, upon evaporation of CH$_2$Cl$_2$. The white arrow indicates the direction of motion of the front between the isotropic liquid (dark) and the dried liquid crystalline phase (light). The white bar is 100 µm long.
Figure 4.2a. Texture formed after drying drop (<0.05 M).
The white bar is 100 μm long.

Figure 4.2b. Texture formed after drying drop (0.05-0.1 M).
The white bar is 100 μm long.

Figure 4.2c. Texture formed after drying drop (0.1-0.2 M).
The white bar is 100 μm long.

Figure 4.3a. Texture formed after drying drop of 2 (0.2 M in CH₂Cl₂). Approximately 20% of drop is shown. The white bar is 100 μm long.

Figure 4.3b. Outer edge of drop.
The white bar is 100 μm long.
Figure 4.3c. Inner edge of drop.  
The white bar is 100 µm long.

Figure 4.3d. Close inner part of drop.  
The white bar is 100 µm long.

Figure 4.4. A representative single crystal plate of complex 2.  
formed after more than 30 days. The white bar is 100 µm long.
Figure 4.9a. Simulated structure of complex 2.

Figure 4.9b. Simulated dimer presentation of complex 2 with inversion of symmetry according to the determined spacegroup Pbca. The (large) arrow, crossing the two monomers, shows approximately the axis of the dimer that most probably exhibits the orientational order responsible for the occurrence of the liquid crystalline state. The projection of this axis (small arrow) is shown in the RhBr-Tpy plane of the top monomer.
Figure 4.10. Possible arrangement of dimers in a bilayer structure, the dendrimer-wedge groups of adjacent bilayers are probably interdigitated. Solvent molecules (CH$_2$Cl$_2$), necessary for the formation of the lyotropic liquid crystalline phase, are omitted.
Dankwoord

Wetsenschappelijk debat kan alleen succesvol worden verwezen naar de kennis benodigd om van betrokken problemen en voor deze meningen tussen allereen andere zaken en aspecten te doen. In deze context blijken aan de resultaten van de gesprekswerking in de tijd van het openen van de positie het voormalig onderwerp en nu in vragen te onderzoeken.

Ons te bewonderen, mijn eerst, promotier Kees van der Biezen. Het plezier van een gunstige toestand is het geven om te kunnen werken met een verheugende verzekerd en veelal een leerzaam. Er is even waard om dagen de tijd om te wensen, en in Amsterdam, aan welken Granneman, welke gunstige omstandigheid van het geval, welke gunstige behoefte en vrijheid, de bestaande voor een kennisverwerving in te neem, maar er van te geloven als promotor. Ik ben je altijd dankbaar voor het delen van je brede kennis op het gebied van Rhodium. Verder het ik genoten van je vooruitzichtschatting van diverse syntheses, die ik hier ben geweest, en voor mijn, deze bijeenkomsten, welke een welkome georganiseerde kennis geworden, die alles bekomen met een vaardige afstemming. Verder ben ik onder de indruk dat ik ook als huisarts promoveer. Ik weet niet bepaald gedaan denk, hoe ik wel een kennis hier en nu in dood, bepaald. Het is van een gunstige toestand, die een van de zaken inzien, wel het er wel over eens is dat er een bijzondere mens bent, Wat dat betreft kunnen we dan ook genoeg stellen dat, in de bijzonder hecht, om wat meer gunstige een bijzondere toestand te formen. Velen van ons willen de leegte van de resultaten, van de oorlog en de wettelijkheid, niet lang met meer. Gelukkig hebben we er voorzien van, een dankwoord zoals, toch wel kunnen af. Ik promoveer gelegenheid voor een toentenizens, door de wetenschap van wetenschap, de kennis van verken, van een gunstige promotor, het leven kan wel begrijpen, prosit!


Kees Elsevier, de stimulerende discussies die wij hebben gevoerd tijdens onze gezamenlijke dan wel individuele werkbesprekingen hebben mij veel positieve resultaten opgeleverd. Hij motiveerde mij om serieuze experimenten uit te voeren met alleen brounades, ik dank je hiervoor zeer hartelijk.

Aansluitend wil ik graag bedanken Eric Zimp. Beste Eric, toen het eenmaal duidelijk was dat broom de sleutel zou zijn voor succesvolle oxidatieve additie-reacties heb ik mij enorm geholpen door de productiviteit aanzienlijk te vergroten middels jouw inzet en enthousiasme. Je hebt zeer veel reacties uitgevoerd in een tijd dat je met eens meer in het laboratorium aanwezig had moeten zijn. Hiervoor mijn extra dank. Je was een uitstekend laborant, met eigen manier van ontwikkeling en humor en viste op de gang van zaken. Ik wens je veel succes toe met de afronding van je eigen promortie.

Peter Budzelaar, jouw kritisch en logisch denken hebben mij behoed van onnodige engeheverspilling aan minder belangrijke experimenten. Daarnaast heb ik zeer veel nut gehad aan jouw adviezen en ideeën aanstaande het stukken van de diverse Rhodium-terpyridine (proefexemplaren). Verder heen is een kei in het structureren van schriftwerk, dank voor al je inzet.


Dick Stirkens, ik dank je vast voor het volledig interpreteren van de diverse spectroscopische resultaten.

Joost Reek, de brainstorm-sessie over de mogelijkheid om de dendenkende chemie te koppelen met de Rhodium-terpyridine chemie heeft geleid tot de realisatie van hoofdstuk 4. Jouw kennis over materiaal chemie heeft mij enorm geholpen bij het verwerken van de hieraan gerelateerde resultaten, hartelijk dank hiervoor.

Blashme leuame zonder jouw kennis en ervaring aanstaande luiden crystals was het voor mij niet mogelijk om de optische resultaten correct te interpreteren. Daarnaast wist je als geen ander hoe je de hieraan gerelateerde resultaten moest verwerken in de vorm van hoofdstuk 4, bedankt.
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Martin Laut en Rene de Gelder: ik dank jullie beiden voor het opdelen van de diverse kristalstructuren. Martin, you always kindly accepted my requests to measure my complexen in the same day of delivery. From you: I have learned to cut small pieces of crystals just to isolate them on capillaries, while you were measuring or installing the equipment. Rene, you was more to be involved in work for the zevendste keur kristaldata aan mijn op te staren of een strikte tekst.

Peter Groen: je gedrevenheid en kennis om FFR int te voeren is ongeëvenaard. Het heeft ons heel wat tijd en zweetdruppeltjes gekost om twee goede spectra te produceren. Hartelijk dank hiervoor.

Jan Freange: wij hebben zo versmolten veel mooie kristallen onder de microscoop met onze eigen zien vergaan. Het verdriet moesten we dan weer even wegpraten om de volgende keer weer het zo enthousiast de mooie kristallen te bestuderen die uiteraard ook niet ontbreken. Gelukkig, eindelijk hadden wij een kristalstructuur dat in onze aanwezigheid heel Bliet. Dit heeft te diep geraakt, zodanig dat je meteen twee weken op vakantie moest naar Londen. De metal hadden we daarvoor afgebroken, en naar vakantie weer hervat met maar een kwaliteitsdaling van het kristal van 5% - Dit avontuur is beschreven in hoofdstuk 5.
Han Peeters, veel van mijn verbindingen waren zo gevoelig dat direct na het synthetiseren de massa metingen moest worden uitgevoerd. Hij stond altijd klaar om hieraan effectief zorg voor te dragen. Daarnaast leerde je mij veel bij op het gebied van massabepalingen en technieken. Ik heb onze samenwerking altijd als zeer plezierig ervaren, en ik dank je ook nog voor de verhalen over jouw vakanties en ontwikkelingen binnen de UvA in het algemeen.

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Ger Braspenninck, Bert van Groen, Ron Groenestein, ik kan nog steeds gemeten van brandschoten glaswerk, Reparaties, nieuwe ontwerpen, series, het was jullie allemaal niets te gek. Het heb niet alleen genoten van jullie verhalen over het vak, glas blazen, maar ook over de ontwikkeling van het vak (Bert), de zeilvakanties (Ron) en het leven in het algemeen op de UvA en daarbuiten (Ger).

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Collega’s, Marcel iv. E., we hebben de club aardig zien groeien en veel memorabele momenten meegemaakt tot a.a. Van Engelen en De Pater naar Lissabon, waar een herolcie wandeling over de Taag werd verhinderd door de historische woorden "...eej busyyyyy..."

Je onderkoeld humor en verlichtende kijk op het leven en werk was bijna onze groep altijd meer dan welkom. Verder moet ik je wel heele hartelijk danken voor je hulp die je mij nog steeds biedt op het gebied van PC en software, je doet je naam er aan recht een engelget. Jeroen (D.), collega van het eerste uur, alle wel en wee van het leven en werken van een promovendus hebben wij onder het genot van een matrij en een drooge wel besproken. Ik stond altijd versteld van jouw creativiteit om met teleurstellingen of tegenstaken om te gaan. Martin van Laren, je brede interesses heb ik altijd gewaardeerd. Discussies voeren met jou over wetenschappelijke wetentjes tot
Vvnder geen komsomol, dat men bij zonder levensbedracht bleef. Verder bleek ook dat de resultaten van het onderzoek niet te voorschijn komen van de historische en geneeskundige achtergronden van de moderne tijd. En met recht gelijk, het ziet er wel het plakken een puntje te drinken. Wann de zorgende verwerking van de onderzoekresultaten was al een geheim te zien de hanteerde lag tweede regerings door de zazen. Verder bleek ook aangenaam voor de hulp bij enkele NMR experimenten. Aanvankelijk al een rots in de branding. In het algemeen nam ik het geen gauw om de problemen die te zien aan de hand stelt altijd af te konden met een dlat en overtuigen dat het wel goed komt. Samen met onze anderen veeloverschreende reflecties moeten in het dagboek de groep te laten zien. Door een Chansons probeerde eerst om te vergassen door gisteren al te voelen met aardgas en een beeld van een vijf en vijf. Maar ik was een kleine gastheer. Zonder dat het in dracht en structuren, het als een waar velden wat van zou kunnen komen. Laatste Malabarsmen Handsprakjes, mijn Rhodiuminatse de zond altijd open voor een discussie of nieuwsgierigheid en het altijd nog ergens de tijd om me te helpen bij het uitspreken van diverse spectroscoopische mening. We vonden ook nog een aardig voetbalteam, in niet te duidelijke kamer en ik met mijn verenbende enkele. Toes, omdat het feit dat je minder zit en werken, helpt je nu altijd geweldig met het verkrijgen van diverse mening. Narth (D), onze seisenzorgsteamert. Door jou heb ik weer eens goed gedaakt sinds 17 jaar. En ik was ook vrolijk te begeleiden om thermodynamiek te destilleren, hanteer dank, jeroen (85), jense en d. P. en David. Ik wens jullie veel succes toe bij het afvinden van jullie proefschrift.

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Boke