First Metal Complexes of 6,6’-Dihydroxy-2,2’-bipyridine: From Molecular Wires to Applications in Carboylation Catalysis

Christopher M. Conifer, Russell A. Taylor, David J. Law, Glenn J. Sunley, Andrew J. P. White and George J. P. Britovsek

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The first square planar rhodium(I) complexes containing the 6,6’-dihydroxy-2,2’-bipyridine ligand have been prepared. The
complexes form molecular wires in the solid state and are active catalysts for the carboylation of methyl acetate.

2,2’-Bipyridine, known as bipy, is one of the ligands that has acquired legendary status in coordination chemistry and catalysis. Metal complexes with bipy ligands have been prepared, probably of all metals known, and numerous variations on the basic ligand framework have been made. However, one remarkably simple derivative that has been elusive so far is 6,6’-dihydroxy-2,2’-bipyridine (1). A few metal complexes of bipy ligands with hydroxy substituents at other positions have been reported, for example 3,3’- and 4,4’-dihydroxy-2,2’-bipyridine and also 6-hydroxy-2,2’-bipyridine has been coordinated to a metal centre but, to the best of our knowledge, no reports have appeared on the synthesis of a metal complex containing the 6,6’-dihydroxy-2,2’-bipyridine ligand. For some time now, we have been interested in the application of ligands with proximate H-bonding substituents in catalysis and we therefore set out to prepare metal complexes containing the 6,6’-dihydroxy-2,2’-bipyridine ligand and investigate their application in carboylation catalysis.

6,6’-Dihydroxy-2,2’-bipyridine normally exists as its tautomer, 2,2’-bipyridone (see Figure 1), which in this form is not able to coordinate to a metal centre in a bidentate fashion. The 2,2’-bipyridone tautomer was therefore converted to 6,6’-bis(terbutyl-dimethylsilyloxy)-2,2’-bipyridine, which is subsequently hydrolysed after coordination to the metal centre.

The reaction of the protected 6,6’-dihydroxy-bipyridine with [RhI(cod)Cl] in wet acetone results in complex [RhI(cod)SBF6]. Subsequent reaction with CO forms the dicarbonyl complex [RhI(CO)2]SBF6 (Figure 1), which was isolated as a metallic looking purple solid in 81 % yield. The OH signal is observed at 12.9 ppm in the ‘H NMR spectrum in d6-acetone and at 3324 cm1 in the IR spectrum. The carbonyl ligands are observed at 2108 and 2052 cm−1 and at 184.3 ppm (Jc,o = 70.9 Hz) in the 13C(1H) NMR spectrum.

The solid state structure of [RhI(CO)2]SBF6 was found to contain five crystallographically independent molecules A-E in the asymmetric unit; complex [RhI(CO)2]SBF6-A is shown in Figure 2 (complexes B-E can be found in the ESI). Each complex is nearly planar with the angles between the {N(1),C(6),C(7),N(12)} and {N(1),N(12),Rh} planes being ca. 2, 0, 0 and 2° for complexes A to E respectively. The complexes stack in an alternating E…A…B…C…D…E…A fashion along the crystallographic a axis direction with the repeat being a unit cell translation along a (see Figure 3). The most notable feature of these chains are the close Rh…Rh separations of between 3.28 and 3.33 Å; the associated Rh…Rh angles are between 172 and 178°. Within these chains there are significant π-π interactions between the pyridyl rings of adjacent complexes and in each case the rings are inclined by less than 2°.
Square planar d⁸ Rh(I) complexes are known to form Rh(I)-Rh(I) interactions in the solid state resulting in one-dimensional molecular chains. The metal-metal interactions, together with π-π interactions between the ligands, give rise to unusual optical and electrical properties, which make these materials of interest for example as molecular wires. The Rh–Rh interaction explains the metallic lustre of complex [Rh(I)(CO)₃]SbF₆ and the dichroic behaviour by changing from purple in the solid state to green in solution.

Figure 3. Part of one of the chains of complexes along the crystallographic a axis direction present in the crystals of [Rh(I)(CO)₃]SbF₆. The Rh–Rh separations (Å) are (a) 3.33, (b) 3.33, (c) 3.28, (d) 3.33 and (e) 3.28. The π-π interactions (f, g, h, i and j) have centroid–centroid and mean interplanar separations (Å) of (f) 3.85, 3.31, (g) 3.62, 3.30, (h) 3.45, 3.30, (i) 3.62, 3.33 and (j) 3.64, 3.31.

The addition of one equivalent of a base such as 2,6-di(tert-butyl)pyridine or KOH to a green solution of [Rh(I)(CO)₃]SbF₆ in methanol results in the immediate precipitation of a purple solid, which is very insoluble in common solvents. Elemental analysis is consistent with the formulation of this material as the neutral complex [Rh(I⁺)(CO)₃], where I⁺ is the mono-deprotonated ligand I (see Fig. 4). The IR spectrum of complex [Rh(I⁺)(CO)₃] shows two carbonyl bands at ν(CO) = 2072 and 2002 cm⁻¹ (cf. 2108 and 2052 cm⁻¹ for complex [Rh(I)(CO)₃]SbF₆), consistent with an increased electron density at the metal centre. Addition of two equivalents of KOH to complex [Rh(I)(CO)₃]SbF₆ results in a red complex K[Rh(I⁺⁺)(CO)₃], where I⁺⁺ is the doubly deprotonated ligand I. The IR spectrum for this anionic complex shows two carbonyl bands at even lower wavenumbers (ν(CO) = 2047 and 1966 cm⁻¹) and the ¹H NMR spectrum in d₆-DMSO consists of three signals, which are shifted significantly upfield (6.1-7.1 ppm) compared to [Rh(I)(CO)₃]SbF₆ due to the loss of aromaticity.

In the ¹³C{¹H} NMR spectrum, five resonances are assigned to the ring system and the carbonyl ligands are observed as a doublet at 188.5 ppm (J_{C–H} = 68.1 Hz). The lack of solubility of [Rh(I⁺⁺)(CO)₃] has hampered the determination of the pKₐ values for the OH groups in [Rh(I)(CO)₃]SbF₆.

However, previous reports on 6-hydroxy-2,2′-bipyridine ruthenium(II) complexes have established a pKₐ value of ca. 3.5 (in H₂O at 25°C), which is considerably more acidic than, for example, phenol (pKₐ = 9.95). The addition of an excess of the weak acid CD₃COOD to a red suspension of K[Rh(I⁺⁺)(CO)₃] in d₆-acetone leads to the immediate formation of the purple neutral complex [Rh(I⁺⁺)(CO)₃]. The addition of DCI results in double protonation to give the cationic complex [Rh(I⁺⁺)(CO)₃]⁺, confirming the reversible nature of the equilibria shown in Figure 4.

Figure 4. Acid-base behaviour of complex [Rh(I)(CO)₃]SbF₆.

We were interested whether these acid-functionalised rhodium complexes could be used as catalysts in carboxylation catalysis. The reaction of methanol with CO to acetic acid is of great industrial importance and is typically catalysed by rhodium- or iridium-based catalysts in combination with iodide promoters. Solid acids such as zeolites, heteropolyacids and superacids are known activators in the carboxylation of methanol. These strong acids presumably protonate methanol, which upon elimination of H₂O generates carbenium cations CH₃⁺. Although strong acids can carboxylate methanol without the presence of a transition metal, the selectivities are generally lower due to the formation of significant amounts of dimethylether.

Several rhodium complexes with nitrogen-based ligands such as diimines and pyridine ligands have been previously investigated as catalysts in carboxylation catalysis, including monodentate pyridine ligands with carboxylic acid functions.

Preliminary carboxylation experiments have shown that complex [Rh(I)(CO)₃]SbF₆ catalyses the carboxylation of methyl acetate to acetic acid. In methanol carbonylation, methyl acetate is formed under the reaction conditions, which is carboxylated to acetic anhydride and subsequently hydrolysed to acetic acid, according to the overall equation 1.

All carboxylation reactions were carried out in a mixture of acetic acid/water as the solvent at 130 °C and 30 bar CO pressure, using MeI as the promoter and methyl acetate as the substrate. The results are collected in Table 1.
Table 1. Results for the carboloylation of methyl acetate.

<table>
<thead>
<tr>
<th>Run</th>
<th>Complex</th>
<th>Rh (mol)</th>
<th>Mel (mol)</th>
<th>Conv. (%)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Rh(CO)Cl]₂</td>
<td>24</td>
<td>80</td>
<td>48</td>
<td>250</td>
</tr>
<tr>
<td>2</td>
<td>[Rh(bipy)(CO)]₂SbF₆</td>
<td>24</td>
<td>80</td>
<td>41</td>
<td>220</td>
</tr>
<tr>
<td>3</td>
<td>[Rh(I)(CO)]₂SbF₆</td>
<td>24</td>
<td>80</td>
<td>35</td>
<td>180</td>
</tr>
</tbody>
</table>

Conditions: Solvent: Acetic acid (720 mmol) and H₂O (500 mmol); Substrate: MeOAc (200 mmol); P(CO): 30 bar; T = 130 °C; t = 16 h. a) Conv. = conversion of methyl acetate determined by ¹H NMR analysis. b) TOF = mol MeOAc/mol cat⁻¹ h⁻¹.

The conversion of methacrylate was determined by ¹H NMR spectroscopy (see ESI) and the only product observed was acetic acid. As can be seen from run 3 in Table 1, complex [Rh(I)(CO)]₂SbF₆ catalyzes the carboloylation reaction with a turnover frequency (TOF) of 180 mol methyl acetate per mol catalyst per hour. Comparative experiments using an unfunctionalized 2,2’-bipyridine ligand gave similar results (run 2) and both ligand-substituted catalysts are slightly less active compared to the industrially used Monsanto catalyst (run 1). So far, these initial experiments do not indicate any special effects due to the acid-functionalized 6,6’-dihydroxy-2,2’-bipyrididine ligand 1 under the reaction conditions used. However, given the current interest in metal-ligand cooperativity in homogeneous catalysis, in particular reactions involving proton transfer, we are currently investigating catalytic applications of other metal complexes containing this fascinating new ligand.

In summary, we have presented here the synthesis and characterization of the first metal complexes containing 6,6’-dihydroxy-2,2’-bipyridine as the ligand. The rhodium(I) complex [Rh(I)(CO)]₂SbF₆ forms Rh⋯Rh interactions in the solid state, resulting in the formation of molecular wires. The complex effectively catalyzes the carboloylation of methyl acetate to acetic acid.

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Notes and references

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Rhodium(I) complexes containing 6,6'-dihydroxy-2,2'-bipyridine form molecular wires in the solid state and are active catalysts for methyl acetate carbonylation.

\[
\text{AcO} + \text{CO} + \text{H}_2\text{O} \rightarrow 2 \text{AcOH}
\]