Rhodium, iridium and nickel complexes with a 1,3,5-triphenylbenzene tris-MIC ligand. Study of the electronic properties and catalytic activity

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Abstract
The coordination versatility of a 1,3,5-triphenylbenzene-tri-mesoionic carbene is illustrated by the preparation of complexes with three different metals: rhodium, iridium and nickel. The rhodium and iridium complexes contained the [MCl(COD)] fragments, while the nickel compound contained [NiCpCl]. The preparation of the tris-MIC complex with three [IrCl(CO)₂] fragments, allowed the estimation of the Tolman Electronic Parameter (TEP) for the ligand, which was compared with the TEP value for a related 1,3,5-triphenylbenzene-tris-NHC ligand. The electronic properties of the tris-MIC ligand were also studied by cyclic voltammetry measurements. In all cases, the tris-MIC ligand showed a stronger electron-donating character than related NHC-based ligands. The catalytic properties of the tri-rhodium complex were tested in the addition of arylboronic acids to α,β-unsaturated ketones, were it proved to be less active than its tris-NHC analogue.
Introduction

Highly symmetrical poly-NHCs are a very interesting type of ligands, because they allow the preparation of a variety of supramolecular assemblies that include molecular squares and triangles,[1-6] cylinder-like structures,[7-13] organometallic polymers[14-22] and even organometallic mesoporous materials.[21],[22] Another interesting feature of this special type of poly-NHCs, is that they can form multimetallic catalysts whose catalytic performances can be compared with analogous monometallic NHC complexes,[23-25] and in many occasions their activity has proven higher than the activities shown by their monometallic counterparts.[23, 26] In the last few years we became interested in the design of several types of $C_{3v}$-symmetry tris-NHCs, both for the preparation of self-assembly molecular cages,[12-13, 27] and for the design of discrete trimetallic molecules whose catalytic performances were explored.[23, 25, 28-29] Among these types of ligands, we found that those featuring a nanoscale distance between the metals were especially interesting,[13, 27] because for these systems catalytic cooperativity between the active metal sites should not be expected, and therefore all catalytic improvements should be assigned to reasons dealing with supramolecular interactions,[30] or with the higher nanolocal concentration of metal sites in the multimetallic catalyst.[31] In this context, we obtained the 1,3,5-triphenylbenzene-based $C_3$-symmetry tris-NHC \textbf{A} (Scheme 1), which we coordinated to rhodium and iridium.[25] The catalytic activity of the trirhodium complex was tested in the addition of arylboronic acids to 2-cyclohexen-1-one, where it showed good activity. The same ligand was used for the preparation of nanometer-sized cylinder-like structures of Cu, Ag and Au.[13] Because mesoionic carbenes (MICs) are known to provide stronger electron donor properties compared to NHCs,[32-36]and also because poly-MIC ligands are less explored,[37-46] we very recently obtained the related tris-diarylated-(1,2,3-triazol-5-ylidene)-1,3,5-triphenylbenzene-based ligand (\textbf{B}), which afforded trisilver and trigold cages with very interesting rearranging properties when mixed with the related 1,3,5-triphenylbenzene-based tris-NHC Ag cages.[27] Soon after, Sarkar and co-workers used a dialkylated-(1,2,3-triazol-5-ylidene)-1,3,5-triphenylbenzene-based ligand for the preparation of the corresponding tris-Ir(III) and Pd(II) complexes, for which their catalytic activities were preliminary explored.[47]
Based on these previous findings, we now report the preparation of the tri-metallic complexes of Rh(I), Ir(I) and Ni(II) with the tris-MIC ligand B. The preparation of these complexes gives us an excellent opportunity to compare the electronic properties of this tris-MIC ligand with the properties shown by its tris-NHC analogue, A. The catalytic activity of the tris-MIC-trirhodium complex was tested in the addition of arylboronic acids to 2-cyclohexen-1-one, so that we could compare its activity with the one shown by its tris-NHC analogue.

**Results and discussion**

The in situ deprotonation of the tris-triazolium salt 1 with potassium bis(trimethyl)silyl amide (KHMDS) in the presence of [RhCl(COD)]₂ in THF at -78°C, allowed the formation of the tris-MIC-trirhodium (I) complex 2, which was isolated in 84% yield, after purification by column chromatography. For the preparation of the related iridium (I) complex, we found more convenient to use a preparative method inspired by a recent work by Plenio and co-workers,[48] which involves the reflux of a mixture of 1 with [IrCl(COD)]₂, in the presence of K₂CO₃ in acetone for 24h. The triiridium (I) complex 3 was obtained in 60% yield after purification. Complexes 2 and 3 were characterized by NMR and mass spectrometry. Both, the ¹H and the ¹³C NMR spectra of the complexes were consistent with the threefold symmetry of the molecules, as exemplified by appearance of one only signal due to the carbene carbons, at 173.4 (¹J₉-H₉ = 41.5 Hz) and 172.1 ppm, for 2 and 3, respectively.
Scheme 2: Synthesis of rhodium (I), iridium (I), and nickel (II) complexes of ligand B

In order to explore whether we could widen the coordination scope of the tris-MIC ligand B, we obtained its related Ni(II) complex. The reaction of 1 with [NiCp₂] in the presence of NEt₄Cl in refluxing dioxane, afforded the tris-MIC complex of Ni(II) 4, as a red solid in 40% yield after purification. The threefold symmetry of this complex was also confirmed by its NMR spectra, which revealed a singlet due to the equivalent 15 protons at the three cyclopentadienyl rings in the ¹H NMR spectrum. The ¹³C NMR spectrum showed the distinctive signal due to the metallated carbene carbon at 151.4 ppm, which is in the region of the previously reported [NiCpCl(MIC)] complex (148 ppm).[49] The trimetallic nature of the complex was confirmed by mass spectrometry, which revealed a peak at a m/z value of 810.7, assigned to [M-2Cl]²⁺. This compound is very interesting, because despite the fact that many [NiCpX(NHC)] complexes have already been reported,[49-53] to our knowledge, this is the first tris-MIC-trinickel complex described so far.

In order to evaluate the electron-donating character of the tris-MIC ligand B, the iridium hexacarbonyl complex 5 was obtained by bubbling carbon monoxide into a solution of 3 in CH₂Cl₂. The resulting yellow solid was obtained
in 93 % yield. The IR spectrum of a CH$_2$Cl$_2$ solution of 5 showed the characteristic CO stretching bands at 2057 and 1972 cm$^{-1}$, from which we could estimate a Tolman Electronic Parameter (TEP) of 2042 cm$^{-1}$, by using the well accepted correlations.[54-56] This TEP value is slightly lower than the one shown by the tri-NHC analogue A, for which the reported Tolman Electronic Parameter was 2045 cm$^{-1}$, therefore suggesting that the tris-MIC ligand B is a stronger electron-donor than A. However, this comparison must be taken with care, because the tris-carbene ligands A and B, not only differ in the nature of their carbenes (MIC vs NHC), but also in the substituents at the carbene rings, which may also be affecting the electronic nature of the ligands.

In order to gain some insight into the electronic properties of the tris-MIC ligand B, we performed the cyclic voltammetry studies of 2 and 3 (Figure 1) and 4 (Figure 2). The rhodium complex 2 showed an irreversible wave at $E_{1/2} = 0.56$ mV, while the iridium complex 3, showed a pseudo-reversible wave at a half-wave potential of $E_{1/2} = 0.63$ mV. Compared to the cyclic voltammetry data for the analogue complexes of rhodium and iridium with the tris-NHC ligand A ($E_{1/2} = 0.67$ mV, for both complexes),[25] the lower $E_{1/2}$ value for 2 and 3 is consistent with a higher degree of electron-donating character of the tris-MIC ligand B. The appearance of only one redox wave for both complexes, 2 and 3, is consistent with the electronic disconnection of the three metals in both trimetallic complexes.

![Figure 1. CV plots of complexes 2 (a), and 3 (b). Experiments carried out using 1mM solutions of the complexes in dry CH$_2$Cl$_2$ with 0.1M [NBu$_4$][PF$_6$] as the supporting electrolyte, 100 mVs$^{-1}$ scan rate, Fc$^+$/Fc used as internal standard with $E_{1/2} (Fc/Fc^+) = 0.44$ V vs. SCE.](image-url)
the same reaction, in order to have some comparative data, which could give us information about the effects of the ligand in the monometallic NHC complex 
contains three nickel fragments that are essentially decoupled.

Figure 2. CV plot (c) and relevant DPV section (d) of complex 4. Experiments carried out using 1 mM solution of the complex in dry CH₂Cl₂ with 0.1 M [NBu₄][PF₆] as the supporting electrolyte, 100 mVs⁻¹ scan rate, Fc⁺/Fc used as internal standard with E₁/₂ (Fc/Fc⁺) = 0.44 V vs SCE.

The cyclic voltammetry diagram of the tri-Ni(II) complex 4 is shown in Figure 2, together with the Differential Pulse Voltammetry (DPV) plot. The complex showed a quasi-reversible wave at a half-wave potential of E₁/₂ = 0.64 mV, which is significantly lower than the half-wave potential shown by the monometallic NHC-based complex [NiCpCl(IMes)][50] (IMes = 1,3-mesityl-imidazolylidene), which showed a half-wave potential of E₁/₂ = 0.72 mV, therefore in agreement with the higher degree of electron-donating character for the ligand in 4 compared to IMes. From the Differential Pulse Voltammetry (DPV) analysis generated for 4 it can be established that there is only one redox event taking place, and thus it becomes evident that the tri-metallic complex 4 contains three nickel fragments that are essentially decoupled.

Since we previously evaluated the catalytic properties of the tris-NHC Rh(I) complex 6 (Scheme 3) in the rhodium catalysed addition of arylboronic acids to \( \alpha,\beta \)-unsaturated ketones,[25] we decided to study the activity of complex 2 in the same reaction, in order to have some comparative data, which could give us information about the effects of changing the nature of the carbene ligand while maintaining a similar structural environment on the catalyst. The catalytic addition of arylboronic acids to \( \alpha,\beta \)-unsaturated ketones,[57-61] is a process for
which several Rh(I)-NHC complexes have afforded excellent activities and chemoselectivities.[57, 62-63]

Scheme 3: Schematic representation of complex 6.

**Table 1.** 1,4-Addition of arylboronic acids to 2-cyclohex-1-one

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>R</th>
<th>Conv/Yield (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>H</td>
<td>*100 (91)</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>H</td>
<td>*66 (43)</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>Me</td>
<td>*85 (69)</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>Me</td>
<td>*63 (34)</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>OMe</td>
<td>*48 (16)</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>OMe</td>
<td>*52 (15)</td>
</tr>
</tbody>
</table>

Reaction conditions: Catalyst (0.066 mol %), 2-cyclohex-1-one (0.5 mmol), KOH (0.09 mmol), ArB(OH)2 (0.6 mmol), dry toluene (3 mL). Conversions determined by gas chromatography (GC), using *anisol or *b2,4,6-trimethylphenol as internal standards. Yields are given in parenthesis. The results given for the use of complex 6 were taken from ref. [25]

For our catalytic experiments, we studied the arylation of 2-cyclohexen-1-one with several aryl boronic acids, and compared the activity of 2 and 6, using a catalyst loading 0.066 mol%. As can be observed from the data given in Table 1, the activity of complex 2 is lower than that shown by complex 6, both in terms of conversion and selectivity. For all the reactions carried out with 2, we observed a side reaction involving the deborylation of the aryl boronic acid, and
this justifies the differences found between conversions and yields for all of the reactions that we studied. This observation is more relevant for the case of the use of 4-methoxy-phenylboronic acid, for which the formation of anisole is the dominant process (entries 5 and 6).

Conclusions
In summary, with this work we illustrated the high coordination versatility of a nano-sized tris-MIC ligand, by obtaining a series of complexes of Rh(I), Ir(I) and Ni(II). Interestingly, the tris-MIC complex of Ni is the first trimetallic Ni complex with a tris-carbene ligand. The electron-donating properties of the ligand were assessed by cyclic voltammetry studies, and by IR spectroscopy of the corresponding carbonylated tris-Ir(I) complex. Both techniques indicate that the ligand is a stronger electron-donor than its related tris-NHC analogue. The catalytic properties of the tri-rhodium complex were tested in the addition of arylboronic acids to \(\alpha,\beta\)-unsaturated ketones, were it proved to be less active than its tris-NHC analogue.

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References

