Chiral MOP-phosphonite ligands: synthesis, characterisation and interconversion of \(\eta^1,\eta^6-(\sigma-P, \pi\text{-arene})\) chelated rhodium(i) complexes†

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The synthesis of rhodium(i) and iridium(i) complexes of chiral MOP-phosphonite ligands is reported. The full characterisation of \(\eta^1,\eta^6-(\sigma-P, \pi\text{-arene})\) chelated 18VE rhodium(i) complexes reveals hemilabile bonding on the arene which has been quantitatively analysed.

Monodentate phosphorus ligands based on the MOP architecture are proven as valuable ligands in asymmetric catalysis.\(^1\) It is widely recognised that these ligands can act as \(P,\pi\text{-arene}\) bidentate chelates to stabilise coordinatively unsaturated electron deficient metal centres.\(^2\) As such, hemilabile arene interactions are anticipated to be present, or indeed imperative, in catalytic processes. Whilst palladium\(^3\) and ruthenium\(^4\) complexes of this class have been investigated in detail, studies on rhodium-MOP complexes remain scarce, and some controversy persists about the exact nature of the ligand’s coordination via its aryl backbone, as no X-ray crystal structures have been reported.\(^5,\)\(^6\) This is despite the demonstrated catalytic ability of Rh-MOPs in a number of important asymmetric carbon–carbon bond forming reactions of biologically relevant targets,\(^7\) and the presence of an additional spectroscopic probe in the form of the NMR active rhodium nucleus \((^{103}\text{Rh}, I = 1/2)\),\(^8\) which better facilitates the study of these metal bonding modes.

As part of our on-going research on the stability and reactivity of MOP-type primary phosphines,\(^9\) we recently reported the synthesis of MOP-phosphonite ligands \(1a,b\) and \(2a,b\) (Fig. 1), and elucidated their coordination behaviour towards palladium by extensive NMR and X-ray crystallographic studies.\(^10\)

We have established that changing the stereochemistry of the binol fragment from \((S)\)- to \((R)\)-shuttles the position of the palladium from the front towards the back of the lower naphthyl ring in \([\text{PdCl}(\eta^1-C_4H_7)](1/2a,b)\) complexes. Coordination to the 1-aryl carbon was observed in the \([\text{Pd}(\eta^1-C_4H_7)](2a,b)\)]\(^*\) derivatives, indicating that these ligands were acting as an \(\eta^1,\eta^1\)-chelate. As a result we were able to probe the ramifications of this behaviour on the asymmetric hydrosilylation of styrene, a classic benchmark reaction for MOP ligands.\(^1,\)\(^11\)

Herein, we investigate rhodium(i) and iridium(i) complexes of MOP-phosphonites \(1a,b\) and \(2a,b\) and examine their metal-ligand bonding modes.

For an initial evaluation of their coordination behaviour, two equivalents of the respective ligands \(2a,b\) were reacted with \([\text{RhCl(\eta^1-cod)}]_2\). The resulting complexes \([\text{RhCl(2a)(\eta^1-cod)}]_3(2a)\) and \([\text{RhCl(2b)(\eta^1-cod)}]_3(3b)\) were both formed quantitatively; the \(^{31}\text{P}({^1}\text{H})\) NMR spectra show a doublet caused by coupling to the rhodium nucleus \((3a: 162.9\text{ ppm}, J_{\text{PRh}} = 223 \text{ Hz}; 3b: \delta = 161.5\text{ ppm}, J_{\text{PRh}} = 224 \text{ Hz}, \text{Fig. S1})\). In the case of \(3a\), single crystals suitable for X-ray analysis were obtained from slow diffusion of hexane into a dichloromethane solution (Fig. 2). Typical bond lengths are found within the coordination sphere of the metal. As expected, the Rh–P distance of this phosphonite donor \((2.2112(7)\text{ Å})\) is shorter than the bond lengths typically observed for aryl phosphine ligands \((2.308(2)-2.3607(14)\text{ Å})\)\(^12\) due to their stronger \(\pi\)-acceptor character.\(^10,\)\(^13\) The \(\eta^1\)-cod ligand shows the dominant \(trans\) effect of the phosphorus donar compared to the chloride; the alkenyl bond coordinated in the \(cis\) position is longer and closer to the

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**Fig. 1** MOP-phosphonite ligands utilised in this study with numbering.
rhodium compared to the alkene bound trans to the phosphorus atom.

In order to investigate the possibility of a hemilabile aryl coordination of the MOP-type ligand, an anion exchange from chloride to the non-coordinating tetrafluoroborate ion was carried out on 3a, b. Initial attempts produced large amounts of oxidation and no pure product could be isolated, however when another equivalent of the appropriate ligand 2a or 2b was added to the reaction mixture a clean, quantitative conversion was achieved to yield [Rh(2a)2]BF4 (4a) or [Rh(2b)2]BF4 (4b). The η6-cod ligand was thus replaced by a second phosphorus donor during the course of the reaction. Alternatively, the two compounds could also be obtained from the reaction of two equivalents of either 2a or 2b with [Rh(η4-cod)2]BF4, although in some cases oxidised by-products were formed.

Crystals of 4b suitable for crystallographic analysis were obtained from slow diffusion of diethyl ether into a dichloromethane solution (Fig. 3). The complex contains two phosphorus ligands, one of which is coordinated in the anticipated η1 binding mode via the phosphorus atom (Rh–P bond length: 2.2145(14) Å). The second ligand fills the coordination sphere of the rhodium metal by acting as an η1,η6 chelate; in addition to the η1-phosphorus donor (Rh–P bond length: 2.1882(14) Å), the lower naphthyl ring coordinates side-on via its π-system in an η6-fashion. Selected Rh–C bond lengths of the coordinated aryl group are given in Table 1. The plane of the η6-arene is only slightly distorted; the distance from its centre to the rhodium is 1.85 Å. To the best of our knowledge this is the first time that such a bonding motif of a MOP-type ligand has been unveiled in the solid-state.

NMR studies confirmed that the coordination environment retains these characteristics even in solution. The 31P{1H} NMR spectra show two doublets of doublets (4a: 181.3, 179.6 ppm; 4b: δ = 183.5, 178.4 ppm), caused by the two inequivalent phosphorus atoms coupling to each other (4a: JPP = 22.3 Hz; 4b: JPP = 23.5 Hz) and to the rhodium nucleus (4a: JPRh = 290 Hz, 300 Hz; 4b: JPRh = 277 Hz, 309 Hz, Fig. S1†). We attribute the smaller Rh–P coupling to the η1-bound ligand, based on 3H–31P correlations and 3H NOE contacts. In the 13C NMR spectra the η6-aryl binding situation of the coordinated carbon atoms is accompanied by a change in chemical shift to upper field relative to their counterparts in the η1-bound ligand, by a magnitude of 4.7 to 32.3 ppm in 4a (Table S1†) and 10.5 to 36.8 ppm in 4b (Table 1). Sections of the 13C–31H HSQC and HMBC spectra of 4b are shown in Fig. S2 and S3 respectively.†

Phosphorus NMR spectra show the expected 48 independent aromatic resonances, from which 24 originate from each ligand. At room temperature, exchange of all 24 pairs of signals is observed in the 1H-NOESY of 4a and 4b (Fig. 4); at −50 °C the NOESY spectrum of 4b showed strong positive NOE peaks without exchange (Fig. S4†). Combining the information from variable temperature NOESY experiments allowed for the unambiguous assignment of all 48 proton resonances in 4a, b. NOE contacts confirmed the solid-state structure of 4b in solution; the solution structure of 4a was also analysed, and the NOE signals in this case revealed a rotation of the η1-ligand about its C2–P bond in comparison to 4b (further details are given in Fig. S5†).

The dynamic behaviour in 4a, b is a result of the hemilabile binding of the aryl group; the side-on coordination of the η1,η6 chelating ligand is released, while in the same instance the η1-bound ligand coordinates as a chelate, ultimately reproducing the complex (Fig. S6†). Quantitative analysis of the 1H-NOESY spectra yielded exchange rate constants of k294K = 1.2 s⁻¹ and k273K = 0.12 s⁻¹ for 4b in CD2Cl2. The values only changed slightly when the experiments were carried out in CDCl3 (k294K

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Selected Rh–C bond lengths and 13C NMR resonances of 4b</th>
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<tbody>
<tr>
<td>Rh–C1</td>
<td>2.189(5)</td>
</tr>
<tr>
<td>Rh–C2</td>
<td>2.296(5)</td>
</tr>
<tr>
<td>Rh–C3</td>
<td>2.337(5)</td>
</tr>
<tr>
<td>Rh–C4</td>
<td>2.324(5)</td>
</tr>
<tr>
<td>C10</td>
<td>2.477(5)</td>
</tr>
<tr>
<td>C9</td>
<td>2.431(5)</td>
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</tbody>
</table>

*From X-ray data. b Solution NMR analysis (126 MHz, CD2Cl2, 21 °C)*.
Asymmetric addition of phenylboronic acid to 1-napthaldehyde, the aforementioned catalysis,\textsuperscript{7} with a conversion of 85% and an enantioselectivity of 34% (compared to MOP: conversion of 78%, enantioselectivity of 41%).\textsuperscript{7d}

To further understand the coordination behaviour of MOP ligands with the catalytically important group nine transition metals, we also reacted, in an analogous manner, MOP-phosphonites 2a,b with [IrCl(η\textsuperscript{4}-cod)], and were able to synthesise (to the best of our knowledge) the first iridium-MOP complexes [IrCl(2a)(η\textsuperscript{4}-cod)] (6a) and [IrCl(2b)(η\textsuperscript{4}-cod)] (6b); the \textsuperscript{31}P NMR spectra show a resonance at 140.4 (6a) or 139.6 ppm (6b). The crystal structure of 6a is depicted in Fig. 5; bond lengths and angles are very similar to the corresponding rhodium complex 3a (Ir-P distance: 2.2242(8) Å).

In contrast to the bonding situation found for rhodium, treatment of 6a with silver tetrafluoroborate and an additional equivalent of 2a gave [Ir(2a)(η\textsuperscript{4}-cod)]BF\textsubscript{4} (7a). The \textsuperscript{31}P NMR exhibits a single resonance at 156.3 ppm; rather than side-on coordination of the arene, the coordination sphere of the metal accommodates two equivalently bound η\textsuperscript{1}-phosphines and the η\textsuperscript{4}-cod ligand (Fig. S7). When a solution of complex 7a in CDCl\textsubscript{3} was reacted with hydrogen, we observed an immediate colour change from green to orange. The \textsuperscript{1}H NMR spectrum showed the disappearance of the cyclooctadiene resonances and the formation of a singlet at 1.53 ppm (indicative of cyclooctane formation) – an assignment of the aryl signals was not possible due to broadened and overlapping resonances. The \textsuperscript{31}P NMR spectrum revealed the formation of multiple products, with the starting material being completely consumed. Two major product peaks were observed as broadened singlets at 167.4 and 135.0 ppm, and the spectrum also showed a pair of doublets at 130.7 and 125.7 ppm with an associated coupling constant of 43.1 Hz (in addition to a number of other minor peaks between 155 and 142 ppm). These doublets indicate that two inequivalent phosphorus nuclei are coupled to each other, which might suggest the formation of an iridium analogue of the rhodium complex 4b. However, we were unable to isolate any of the products for the in-depth analysis which would be required to prove the existence of such a complex.

In summary, we have reported the first structural confirmation of a η\textsuperscript{1},η\textsuperscript{1}(σ-P, π-arene) chelated MOP-type ligand on rhodium(i) and the extent of the bonding has been analysed quantitatively by NOESY NMR. The fine tuning between metal-

\textsuperscript{1}H-NMR resonances are observed at 50.0 and 37.2 ppm (1H NMR and \textsuperscript{13}C NMR resonances were also found for 4a (in THF-d8: k\textsubscript{294K} = 0.9 s\textsuperscript{-1}). The free energies of activation of 4b in CD\textsubscript{2}Cl\textsubscript{2} were calculated from the appropriate rate constants and gave values of ΔG\textsubscript{294K} = 71.2 kJ mol\textsuperscript{-1} and ΔG\textsubscript{273K} = 71.5 kJ mol\textsuperscript{-1}. Related studies by Mirkin and co-workers gave free energies of activation of similar magnitude for their system.\textsuperscript{6} Mirkin and co-workers gave free energies of activation of 1.3 s\textsuperscript{-1} or THF-D\textsubscript{6} (k\textsubscript{294K} = 0.9 s\textsuperscript{-1}). Thus, we propose a concerted reaction mechanism as the rate of exchange showed no increase in coordinating solvent. Comparable exchange rate values were also found for 4a (in THF-d8: k\textsubscript{294K} = 0.9 s\textsuperscript{-1}). The free energies of activation of 4b in CD\textsubscript{2}Cl\textsubscript{2} were calculated from the appropriate rate constants and gave values of ΔG\textsubscript{294K} = 71.2 kJ mol\textsuperscript{-1} and ΔG\textsubscript{273K} = 71.5 kJ mol\textsuperscript{-1}. Related studies by Mirkin and co-workers gave free energies of activation of similar magnitude for their system.\textsuperscript{6f}

In order to clarify whether the phenomenon of η\textsuperscript{6} side-on coordination to rhodium is exclusive to our bulky MOP-phosphonite ligands 2a,b or is valid for complexes of other MOP type ligands too, we utilised Hayashi’s OMe-MOP ligand to synthesise the analogous [Rh(OMe-MOP)\textsubscript{2}]BF\textsubscript{4} (5) complex. Full characterisation by NMR spectroscopy revealed a similar (σ-P, π-arene)-binding situation as observed for 4a,b. Its two \textsuperscript{31}P NMR resonances are observed at 50.0 and 37.2 ppm (\textit{J}_\text{PP} = 217 Hz, 197 Hz; \textit{J}_{PP} = 32.1 Hz). The \textsuperscript{13}C NMR resonances of the six coordinated carbon atoms show the characteristic upfield shift (shifted by 8.4 to 38.4 ppm) which is slightly less pronounced for C9’ and C10’ (Table S1). In contrast to 4a,b we detected no dynamic exchange in the NOESY NMR spectrum at room temperature, suggesting the arene-coordination is stronger in this case. Reaction of [Rh(acac)(η\textsuperscript{5}-C\textsubscript{2}H\textsubscript{4})\textsubscript{2}] with two equivalents of OMe-MOP in CDCl\textsubscript{3} also gave characteristic upfield peaks in the \textsuperscript{13}C NMR spectrum indicative of some degree of π-arene bonding, which could have implications in the aforementioned catalysis,\textsuperscript{7b-d} however phosphine oxidation precluded a full characterisation.

Under adapted experimental conditions (to prevent hydrolysis of our phosphonites) we found 2a performed best in the asymmetric addition of phenylboronic acid to 1-napthaldehyde,
stabilisation and catalytic activity will be the focus of future research.

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Notes and references


