

Chiral MOP-phosphonite ligands: synthesis, characterisation and interconversion of η^1, η^6 -(σ -P, π -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 η^1, η^6 -(σ -P, π -arene) chelated 18VE rhodium(i) complexes reveals hemilabile binding 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,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 palladium³ and ruthenium⁴ 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 (¹⁰³Rh, $I = 1/2$),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 [PdCl(η^3 -C₄H₇)(**1/2a,b**)] complexes. Coordination to the 1'-aryl carbon was observed in the [Pd(η^3 -C₄H₇)(**2a,b**)]⁺ derivatives, indicating that these ligands were acting as an η^1, η^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 binding modes.

For an initial evaluation of their coordination behaviour, two equivalents of the respective ligands **2a,b** were reacted with [RhCl(η^4 -cod)]₂. The resulting complexes [RhCl(**2a**)(η^4 -cod)] (**3a**) and [RhCl(**2b**)(η^4 -cod)] (**3b**) were both formed quantitatively; the ³¹P{¹H} NMR spectra show a doublet caused by coupling to the rhodium nucleus (**3a**: 162.9 ppm, ¹J_{PRh} = 223 Hz; **3b**: δ = 161.5 ppm, ¹J_{PRh} = 224 Hz, 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) Å) is shorter than the bond lengths typically observed for aryl phosphine ligands (2.308(2)–2.3607(14) Å)¹² due to their stronger π -acceptor character.^{10,13} The η^4 -cod ligand shows the dominant *trans* effect of the phosphorus donor compared to the chloride; the alkene bond coordinated in the *cis* position is longer and closer to the

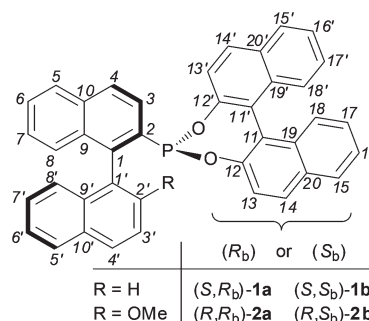


Fig. 1 MOP-phosphonite ligands utilised in this study with numbering.

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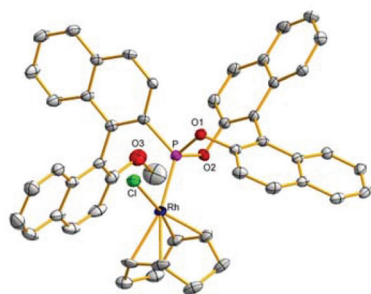


Fig. 2 View of the molecular structure of $[\text{RhCl}(\mathbf{2a})(\eta^4\text{-cod})]$ (**3a**) (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

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 $[\text{Rh}(\mathbf{2a})_2]\text{BF}_4$ (**4a**) or $[\text{Rh}(\mathbf{2b})_2]\text{BF}_4$ (**4b**). The $\eta^4\text{-cod}$ 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 $[\text{Rh}(\eta^4\text{-cod})_2]\text{BF}_4$, 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 η^1 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 η^1, η^6 chelate; in addition to the η^1 -phosphorus donor (Rh–P bond length: 2.1882(14) Å),

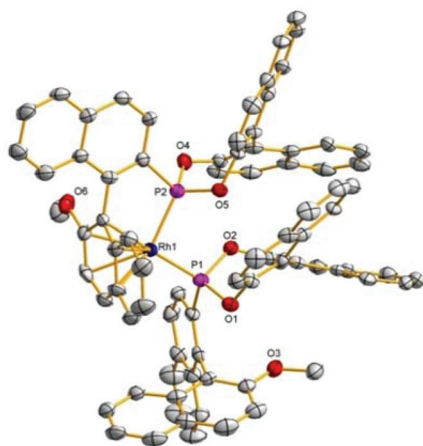


Fig. 3 View of the molecular structure of $[\text{Rh}(\mathbf{2b})_2]\text{BF}_4$ (**4b**) (50% probability thermal ellipsoids). Hydrogen atoms, the BF_4^- anion and co-crystallised solvent are omitted for clarity.

Table 1 Selected Rh–C bond lengths and ^{13}C NMR resonances of **4b**

	Rh–C ^a [Å]	$^{13}\text{C}(\eta^1, \eta^6)^b$ [ppm]	$^{13}\text{C}(\eta^1)^b$ [ppm]
C1'	2.189(5)	101.6	118.8
C2'	2.296(5)	145.3	155.8
C3'	2.337(5)	90.1	112.3
C4'	2.324(5)	93.1	129.9
C10'	2.477(5)	114.0	129.1
C9'	2.431(5)	122.0	133.8

^a From X-ray data. ^b Solution NMR analysis (126 MHz, CD_2Cl_2 , 21 °C).

the lower naphthyl ring coordinates side-on *via* its π -system in an η^6 -fashion. Selected Rh–C bond lengths of the coordinated aryl group are given in Table 1. The plane of the η^6 -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 $^{31}\text{P}\{^1\text{H}\}$ 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**: $^2J_{\text{PP}}$ = 22.3 Hz; **4b**: $^2J_{\text{PP}}$ = 23.5 Hz) and to the rhodium nucleus (**4a**: $^1J_{\text{PRh}}$ = 290 Hz, 300 Hz; **4b**: $^1J_{\text{PRh}}$ = 277 Hz, 309 Hz, Fig. S1†). We attribute the smaller Rh–P coupling to the η^1 -bound ligand, based on ^1H – ^{31}P correlations and ^1H NOE contacts. In the ^{13}C NMR spectra the η^6 -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 η^1 -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 ^{13}C – ^1H HSQC and HMBC spectra of **4b** are shown in Fig. S2 and S3 respectively.†

The proton 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 η^1 -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 η^1, η^6 chelating ligand is released, while in the same instance the η^1 -bound ligand coordinates as a chelate, ultimately reproducing the complex (Fig. S6†). Quantitative analysis of the ^1H -NOESY spectra yielded exchange rate constants of $k_{294\text{K}} = 1.2 \text{ s}^{-1}$ and $k_{273\text{K}} = 0.12 \text{ s}^{-1}$ for **4b** in CD_2Cl_2 . The values only changed slightly when the experiments were carried out in CDCl_3 ($k_{294\text{K}}$

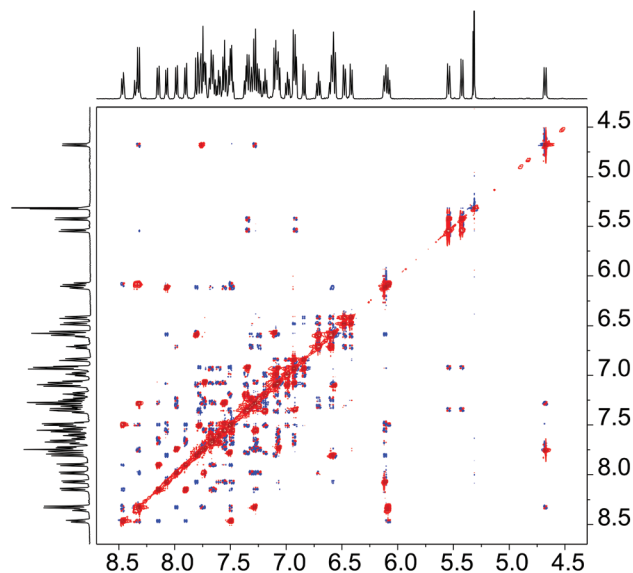


Fig. 4 Aromatic resonances of **4b** in the ^1H -NOESY spectrum (mixing time of 500 ms) in CD_2Cl_2 at 21°C . Negative NOE correlations are shown in blue, positive exchange correlations are shown in red.

$= 1.3\text{ s}^{-1}$) or THF-D_8 ($k_{294\text{K}} = 0.9\text{ s}^{-1}$). 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-d_8 : $k_{294\text{K}} = 0.9\text{ s}^{-1}$). The free energies of activation of **4b** in CD_2Cl_2 were calculated from the appropriate rate constants and gave values of $\Delta G_{294\text{K}}^\ddagger = 71.2\text{ kJ mol}^{-1}$ and $\Delta G_{273\text{K}}^\ddagger = 71.5\text{ kJ mol}^{-1}$. Related studies by Mirkin and co-workers gave free energies of activation of similar magnitude for their system.^{6f}

In order to clarify whether the phenomenon of η^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 $[\text{Rh}(\text{OMe-MOP})_2]\text{BF}_4$ (**5**) complex. Full characterisation by NMR spectroscopy revealed a similar ($\sigma\text{-P}$, $\pi\text{-arene}$)-binding situation as observed for **4a,b**. Its two ^{31}P NMR resonances are observed at 50.0 and 37.2 ppm ($^1J_{\text{PRh}} = 217\text{ Hz}$, $^{197}\text{ Hz}$; $^2J_{\text{PP}} = 32.1\text{ Hz}$). The ^{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 $[\text{Rh}(\text{acac})(\eta^2\text{-C}_2\text{H}_4)_2]$ with two equivalents of OMe-MOP in CDCl_3 also gave characteristic upfield peaks in the ^{13}C NMR spectrum indicative of some degree of $\pi\text{-arene}$ bonding, which could have implications in the aforementioned catalysis,^{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-naphthaldehyde,

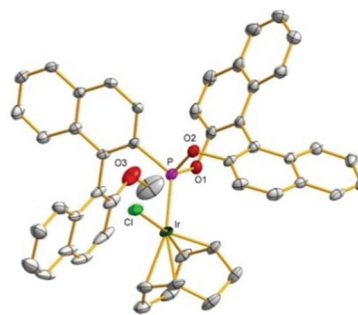


Fig. 5 View of the molecular structure of $[\text{IrCl}(\mathbf{2a})(\eta^4\text{-cod})]$ (**6a**) (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

with a conversion of 85% and an enantioselectivity of 34% (compared to MOP: conversion of 78%, enantioselectivity of 41%).^{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 $[\text{IrCl}(\eta^4\text{-cod})_2]$ and were able to synthesise (to the best of our knowledge) the first iridium-MOP complexes $[\text{IrCl}(\mathbf{2a})(\eta^4\text{-cod})]$ (**6a**) and $[\text{IrCl}(\mathbf{2b})(\eta^4\text{-cod})]$ (**6b**); the ^{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 $[\text{Ir}(\mathbf{2a})_2(\eta^4\text{-cod})]\text{BF}_4$ (**7a**). The ^{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^1 -phosphines and the $\eta^4\text{-cod}$ ligand (Fig. S7†). When a solution of complex **7a** in CDCl_3 was reacted with hydrogen, we observed an immediate colour change from green to orange. The ^1H 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 ^{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^1, η^6 -($\sigma\text{-P}$, $\pi\text{-arene}$) 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-

stabilisation and catalytic activity will be the focus of future research.

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Notes and references

- (a) J. W. Han and T. Hayashi, *Tetrahedron: Asymmetry*, 2010, **21**, 2193; (b) T. Hayashi, *Acc. Chem. Res.*, 2000, **33**, 354.
- (a) Y. Canac and R. Chauvin, *Eur. J. Inorg. Chem.*, 2010, 2325; (b) P. S. Pregosin, *Chem. Commun.*, 2008, 4875; (c) P. S. Pregosin, *Coord. Chem. Rev.*, 2008, **252**, 2156.
- See for example: (a) T.-K. Zhang, D.-L. Mo, L.-X. Dai and X.-L. Hou, *Org. Lett.*, 2008, **10**, 3689; (b) P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati and S. Rizzato, *Organometallics*, 2004, **23**, 4247.
- (a) T. J. Geldbach, P. S. Pregosin, S. Rizzato and A. Albinati, *Inorg. Chim. Acta*, 2006, **359**, 962; (b) T. J. Geldbach, F. Breher, V. Gramlich, P. G. A. Kumar and P. S. Pregosin, *Inorg. Chem.*, 2004, **43**, 1920; (c) T. J. Geldbach, P. S. Pregosin and A. Albinati, *Organometallics*, 2003, **22**, 1443; (d) T. J. Geldbach, D. Drago and P. S. Pregosin, *J. Organomet. Chem.*, 2002, **643–644**, 214; (e) T. J. Geldbach, P. S. Pregosin, A. Albinati and F. Rominger, *Organometallics*, 2001, **20**, 1932; (f) T. J. Geldbach, D. Drago and P. S. Pregosin, *Chem. Commun.*, 2000, 1629.
- (a) E. F. Clarke, E. Rafter, H. Müller-Bunz, L. J. Higham and D. G. Gilheany, *J. Organomet. Chem.*, 2011, **696**, 3608; (b) M. Soleilhavoup, L. Viau, G. Commenges, C. Lepetit and R. Chauvin, *Eur. J. Inorg. Chem.*, 2003, 207.
- Selected examples of other phosphorus-alkene ligands on rhodium(i): (a) R. Shintani, R. Narui, Y. Tsutsumi, S. Hayashi and T. Hayashi, *Chem. Commun.*, 2011, **47**, 6123; (b) A. R. O'Connor, W. Kaminsky, D. M. Heinekey and K. I. Goldberg, *Organometallics*, 2011, **30**, 2105; (c) Z. Liu, H. Yamamichi, S. T. Madrahimov and J. F. Hartwig, *J. Am. Chem. Soc.*, 2011, **133**, 2772; (d) M. Montag, G. Leitus, L. J. W. Shimon, Y. Ben-David and D. Milstein, *Chem.–Eur. J.*, 2007, **13**, 9043; (e) H. Werner, *Dalton Trans.*, 2003, 3829; (f) E. T. Singewald, C. A. Mirkin, A. D. Levy and C. L. Stern, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2473.
- (a) R. Shintani, M. Inoue and T. Hayashi, *Angew. Chem., Int. Ed.*, 2006, **45**, 3353; (b) T. Hayashi and M. Ishigedani, *Tetrahedron*, 2001, **57**, 2589; (c) T. Hayashi and M. Ishigedani, *J. Am. Chem. Soc.*, 2000, **122**, 976; (d) M. Sakai, M. Ueda and N. Miyaura, *Angew. Chem., Int. Ed.*, 1998, **37**, 3279.
- (a) L. Carlton, *Annu. Rep. NMR Spectrosc.*, 2008, **63**, 49; (b) J. M. Ernsting, S. Gaemers and C. J. Elsevier, *Magn. Reson. Chem.*, 2004, **42**, 721.
- (a) A. Ficks, C. Sibbald, S. Ojo, R. W. Harrington, W. Clegg and L. J. Higham, *Synthesis*, 2013, **45**, 265; (b) B. Stewart, A. Harriman and L. J. Higham, *Organometallics*, 2011, **30**, 5338; (c) A. Ficks, I. Martinez-Botella, B. Stewart, R. W. Harrington, W. Clegg and L. J. Higham, *Chem. Commun.*, 2011, **47**, 8274; (d) R. M. Hiney, L. J. Higham, H. Müller-Bunz and D. G. Gilheany, *Angew. Chem., Int. Ed.*, 2006, **45**, 7248.
- A. Ficks, R. M. Hiney, R. W. Harrington, D. G. Gilheany and L. J. Higham, *Dalton Trans.*, 2012, **41**, 3515.
- (a) T. Hayashi, S. Hirate, K. Kitayama, H. Tsuji, A. Torii and Y. Uozumi, *J. Org. Chem.*, 2001, **66**, 1441; (b) T. Hayashi, *Acta Chem. Scand.*, 1996, **50**, 259.
- (a) J. Tiburcio, S. Bernès and H. Torrens, *Polyhedron*, 2006, **25**, 1549; (b) Q. L. Horn, D. S. Jones, R. N. Evans, C. A. Ogle and T. C. Masterman, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2002, **58**, m51.
- D. Selent, W. Baumann, R. Kempe, A. Spannenberg, D. Röttger, K.-D. Wiese and A. Börner, *Organometallics*, 2003, **22**, 4265.