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Biarylphosphonites: a class of monodentate phosphorus(III) ligands that outperform their chelating analogues in asymmetric hydrogenation catalysis

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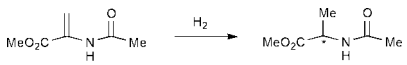
Rhodium(I) complexes of monodentate phosphonites derived from 2,2′-binaphthol and 9,9′-biphenanthrol are compared with diphosphonite chelate analogues as catalysts for asymmetric hydrogenation; the high ee's (up to 92%) obtained with the monodentate systems and the observation that they are sometimes superior to the chelate analogues are discussed.

The enantioselective hydrogenation of prochiral alkenes is perhaps the most important application of asymmetric catalysis with synthetic catalysts and is decidedly the most studied and best understood. In 1972 Kagan *et al.*[1] were the first to show that a diphosphine was more efficient as an ancillary ligand for asymmetric hydrogenation than corresponding monophosphines. Since then, it has been found[2] that complexes of bidentate ligands consistently give higher asymmetric inductions in hydrogenation. This has been rationalised in terms of the chirality of the phosphorus substituents whose retention is enforced by the chelate ring. We report here, hydrogenation catalysis that challenges this received wisdom in that monodentate phosphonite species show, in some cases, higher enantioselectivity than the analogous bidentate phosphonites.

The resolved monodentate biarylphosphonites **1a–c** and **2a–c** and the related diphosphonites **3** and **4** are afforded by the routes shown in Scheme 1. The corresponding rhodium(I)–monophosphonite complexes **5a–f** and rhodium(I)–diphosphonite complexes **6a**,**b** have been isolated and characterised by a combination of elemental analysis, ^{31}P, ^{1}H and ^{13}C NMR spectroscopy; the monophosphonite **2b** has been previously reported[3] and while this work was in progress[4] Reetz *et al.*,[5] reported the preparation of **3**.

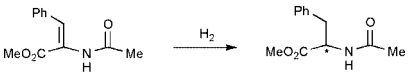
The results for the asymmetric hydrogenation of methyl-2-acetamido acrylate [eqn. (1)] catalysed by our rhodium



(1)

phosphonite complexes are given in Table 1. The monophosphonite complexes give remarkably high enantioselectivities, up to 92% ee with **5c** (entry 3). Furthermore the monophosphonite complexes **5e** and **5f**, derived from biphenanthrol are much more selective than the corresponding diphosphonite **6b**.

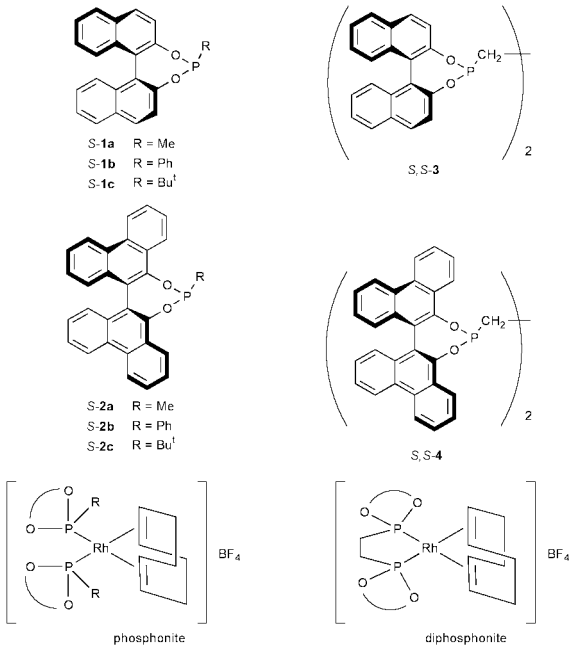
The results for the asymmetric hydrogenation of methyl-2-acetamido cinnamate [eqn. (2)] are also given in Table 1. For



(2)

this reaction, the diphosphonite complexes **6a** and **6b** both give poor (< 20% ee) enantioselectivities (entries 15 and 16) and in several cases (see entries 9, 10, 13 and 14) the monophosphonite analogues give superior enantioselectivities (ee up to 80%).

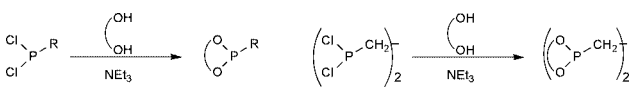
The phosphonite ligands reported here are therefore an apparent exception to the rule in enantioselective hydrogenation that catalysts based on bidentate phosphorus(III) ligands are



superior to their monodentate analogues. This dogma is based on the idea that the conformational control in metallochelates provides efficient stereocontrol that is not possible with monodentate ligands because of a low energy barrier to M–P bond rotation in the latter case. The most effective monophosphine for asymmetric hydrogenation to date (up to 90% ee) is PMePh(C_6H_4OMe-2);[6] however this ligand may form a hemilabile chelate *via* coordination of the *o*-methoxy group and moreover the bidentate analogue (dipamp) gives a much more enantioselective hydrogenation catalyst.[7]

The solution ^{31}P NMR behaviour of the rhodium complexes **5b** and **5e** was unexceptional. In each case a single sharp doublet was observed at +25 °C which remained essentially unaltered down to −90 °C. This is consistent with rapid M–P bond rotation and/or the presence of predominantly one rotamer.

We have been unable to obtain crystals of salts of the rhodium(I) complexes suitable for X-ray crystallography but the crystal structures of [$PtCl_2$(*R*-**2b**)$_2$] *R*,*R*-**7** (an analogue of the enantiomer of **5e**) and [$PtCl_2$(*S*,*S*-**4**)$_2$] *S*,*S*-**8** (an analogue of **6b**)



Scheme 1

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Table 1 Asymmetric hydrogenations of methyl-2-acetamido acrylate and cinnamate[a]

	Acrylate				Cinnamate		
Entry	Catalyst	Conv.	%ee	Entry	Catalyst	Conv.	%ee
1	**5a**	76	78(*R*)	9	**5a**	100	80(*R*)
2	**5b**	100	73(*R*)	10	**5b**	100	63(*R*)
3	**5c**	73	92(*R*)	11	**5c**	100	10(*R*)
4	**5d**	100	29(*R*)	12	**5d**	97	14(*S*)
5	**5e**	100	78(*R*)	13	**5e**	100	59(*S*)
6	**5f**	30	70(*R*)	14	**5f**	100	49(*R*)
7	**6a**	100	90(*R*)[b]	15[c]	**6a**	81	19(*R*)
8	**6b**	99	23(*R*)	16	**6b**	100	14(*R*)

[a] Reaction conditions: methyl-2-acetamido acrylate or cinnamate (3.5 mmol), catalyst (0.0073 mmol) and CH_2Cl_2 (7.5 cm^3) were placed in a stainless steel autoclave, which was then pressurised to 1.5 atm with hydrogen and the reaction mixture was stirred at 25 °C for 3 h (acrylate) or 20 h (cinnamate). Conversions and ee's were determined by GC using a Hewlett-Packard 5800 A with a L-Chirasil-Val column. [b] This ee agrees with the literature report[5] but we unambiguously assign the opposite configuration to the major enantiomer.[c] In MeOH.

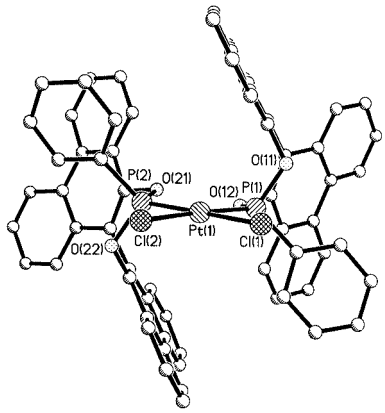


Fig. 1 Molecular structure of *S*,*S*-**7**. Important bond lengths (Å) and angles (°) include: Pt(1)–P(1) 2.201(2), Pt(1)–P(2) 2.199(2), Pt(1)–Cl(1) 2.346(2), Pt(1)–Cl(2) 2.344(2); P(1)–Pt(1)–P(2) 100.84(8). Hydrogen atoms have been omitted for clarity.

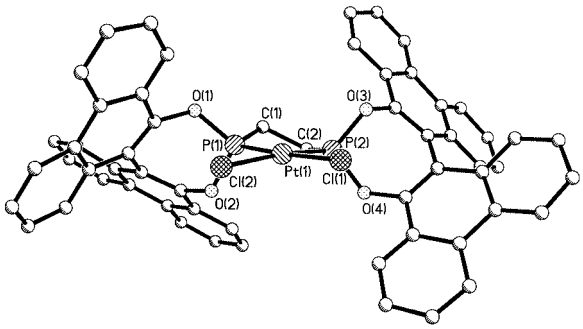
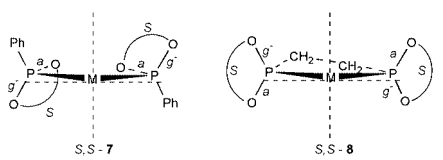


Fig. 2 Molecular structure of *S*,*S*-**8**. Important bond lengths (Å) and angles (°) include: Pt(1)–P(1) 2.189(2), Pt(1)–P(2) 2.183(3), Pt(1)–Cl(1) 2.351(2), Pt(1)–Cl(2) 2.337(3); P(1)–Pt(1)–P(2) 85.93(9). Hydrogen atoms have been omitted for clarity.



Scheme 2

as solvates† have been obtained. The structures of the *mirror image* of *R*,*R*-**7,** *i.e*. *S*,*S*-**7** (for ease of comparison) and *S*,*S*-**8** are shown in Figs. 1 and 2. In both cases the conformation about the P–O bonds is of note. In *S*,*S*-**7**, both P(1) and P(2) show *a* and g^- Pt–P–O–C conformations [*i.e*. *anti* (*a*, Pt–P–O–C torsion angle *ca*. 180°) and *gauche* negative (g^-, Pt–P–O–C torsion angle *ca*. −80°)] at the P–O bonds as counted clockwise from the P–C bond, viewed down the M–P bond, see Scheme 2. Identical behaviour is observed for *S*,*S*-**8** and a range of > 20 phosphonites and phosphites in which the phosphorus is incorporated in a seven-membered POC_4O ring containing a biaryl unit.[8] The implication of this observation is that the absolute stereochemistry of the biaryl unit controls the conformations of the P–O bonds at the phosphorus in such species (enforcing ag^- conformations for *S* and g^+a for *R* biaryls).

The *anti* arm of the phosphonites in **7** and **8** has the attached phenanthryl group far from the metal and the *gauche* arm phenanthryl closer to it. This arrangement provides a highly asymmetric ligand profile. Models suggest that as a result, rotation about the M–P bond in **7** is not possible and that the observed conformation (with the two *anti* arm oxygens essentially in the coordination plane, see Fig. 1 and Scheme 2) is the only likely rotamer. Similar conclusions seem likely to hold for other cases where the carbon substituent is significantly more bulky than the *anti* arm of the phosphonite (and less bulky than the *gauche* arm). Quadrant diagrams for *S*,*S*-**7** and *S*,*S*-**8** based on this analysis are shown in Scheme 2. It is notable that in the chelate species, **8**, the quadrant occupied by the *gauche* arm of the phosphonite is altered as compared with **7**. Hence, in this instance, it seems the primary effect of chelation is to *change* the preferred rotamer rather than to stop rotation about the M–P bond. Furthermore the rotamer favoured in the chelate form (as in **8** or **6b**) has the *gauche* arm phenanthryl group essentially face-on to the coordination plane whereas the rotamer favoured in the monodentate case (as in **7** or **5e**) has the *gauche* arm phenanthryl edge-on (see Figs. 1 and 2). The implication of the higher ee's observed for **5e** as compared with **6b** is that the edge-on phenanthryl in the former causes greater asymmetric induction.

In conclusion, the asymmetric ligand profile caused by the biaryl backbone in these phosphonites has three consequences: (i) rotation about the M–P bond in monodentate phosphonites is prevented; (ii) a different rotamer from that in the chelate analogues is favoured; (iii) the favoured rotamer causes more effective chiral induction in the hydogenation catalyses. The results presented here challenge the view that chelating ligands are essential for high stereocontrol and open the possibility that chiral monodentate phosphorus ligands may be designed that can equal or better their bidentate analogues for hydrogenation.

Notes and references

† *Crystal data*: *R*,*R*-**7**·thf·0.76$CHCl_3$): $C_{72.76}H_{50.76}Cl_{4.27}O_5P_2Pt$, M = 1413.38, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 13.3036(19), b = 19.602(4), c = 23.287(4) Å, U = 6072.9(18) $Å^3$, Z = 4, μ = 2.605 mm^{-1}, T = 173 K, 10674 unique data, $R1$ = 0.0445. *S*,*S*-**8**·3thf·2$CHCl_3$: $C_{72}H_{50}Cl_8O_7P_2Pt$, M = 1555.65, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 14.8155(16), b = 19.132(3), c = 23.690(2) Å, U = 6714.8(14) $Å^3$, Z = 4, μ = 2.510 mm^{-1}, T = 173 K, 10534 unique data, R1 = 0.0498. CCDC 182/1604. See http://www.rsc.org/suppdata/cc/b0/b001638i/ for crystallographic files in .cif format.

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