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P-Stereogenic diphosphines in the ruthenium-catalysed asymmetric hydrogenation of C=C and C=O double bonds

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Abstract—Bis(acetato) and dichloro complexes of ruthenium(II) containing *P*-stereogenic ligands have been prepared and tested in the asymmetric catalytic hydrogenation of functionalised olefins and keto esters. The best performance (52.6% ee) has been obtained in the hydrogenation of ethyl acetoacetate with [RuCl(PPh_3)((*S*,*S*)-1,1′-bis(1-naphthylphenylphosphino)ferrocene)] **4**.
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1. Introduction

After Knowles' seminal work with dipamp,[1] synthetic problems have long hampered the development of *P*-stereogenic ligands.[2] In recent years, however, the development of new synthetic strategies has made a vast number of *P*-stereogenic diphosphines (P–P*) available for catalytic asymmetric reactions.[3–8] Most efforts have been directed to the rhodium-catalysed hydrogenation of olefins, where Imamoto's systems have shown very high efficiency.[3] A lesser effort has been directed to the application of P–P* to other catalytic reactions, such as rhodium-catalysed hydrosilylation[9] and palladium-catalysed allylic alkylation.[10] As *P*-stereogenic diphosphines have been rarely used in connection with ruthenium,[11–13] we decided to extend the scope of such ligands in the ruthenium-catalysed hydrogenation of C=C and C=O double bonds.

It is a well established fact that dichloro complexes of the general formula '[$RuCl_2$(P–P)]$_n$' are ideally suited for the hydrogenation of carbonyl functionalities (ketones and keto esters), whereas acetato complexes of the type [Ru$(RCOO)_2$(P–P)] are most effective for the hydrogenation of olefins.[14] However, the access to suitable catalyst precursors of ruthenium is not always straightforward, as even subtle changes in the steric and electronic properties of the diphosphine ligands can dramatically affect the outcome of standard synthetic procedures. One of us has previously shown that dichloro ruthenium complexes of the type [$RuCl_2$(PPh_3)(P–P)] (**A**; P–P = chiral diphosphine; Chart 1) are easily prepared from [$RuCl_2(PPh_3)_3$] and are suitable catalyst precursors for the hydrogenation of 1,3-diketones.[15] The acetato complexes [Ru(η^2-$O_2CCX_3)_2$(P–P)] (**B**) have been developed in Nagoya[16] and at Roche[17] and Ciba.[18] The bis(2-methylallyl) complexes **C**, prepared with the methodology developed by Genêt,[19] are also versatile precatalysts, as they give ready access to both classes of compounds mentioned above.

Our investigation was directed to complementing sparse data concerning the ruthenium-catalysed hydrogenation with *P*-stereogenic ligands, such as dipamp **2b** and its analogue $Me_2Si(CH_2P(\textit{o}\text{-An})Ph)_2$ **3b** (*o*-An = *o*-anisyl) (Chart 2).[11] In the 1-naphthyl series, we have previously prepared (*S*,*S*)-Ph(1-Np)PCH_2CH_2P(1-Np)Ph[13] **2a** (1-

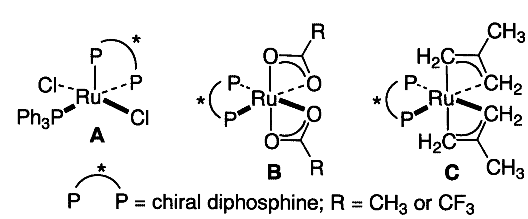

Chart 1.

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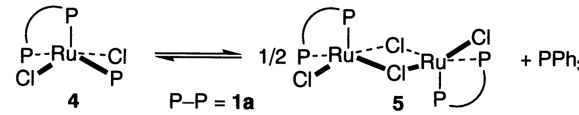
Np = 1-naphthyl) and (*S*,*S*)-$Me_2Si(CH_2P(1\text{-}Np)Ph)_2$ **3a**.[15c] Its ruthenium complex [$RuCl_2(PPh_3)$(**3a**)] has been tested in the catalytic hydrogenation of 1,3-diketones.[15c] Ligand **2a** has been used in the rhodium-catalysed hydrogenation of acrylic acid[20] and in the ruthenium-catalysed cyclopropanation of olefins.[13] Thus, we have addressed the synthesis of ruthenium(II) complexes of the general type [$RuX_2(L)_n$(P–P)] (X = anionic ligand) containing one of the diphosphine ligands (*S*,*S*)-**1a**, (*S*,*S*)-**1b**, (*S*,*S*)-**2a**, and (*R*,*R*)-**3b** depicted in Chart 2 and either two chloro ligands and a neutral ligand L (such as **A**), or two acetato ligands (such as **B**). The *P*-stereogenic ligands chosen span a wide range of steric requirements in view of the different diphosphine bridge (ethane-1,2-diyl, 2,2-dimethyl-2-sila-propane-1,3-diyl, or ferrocene-1,1′-diyl). The dppf-analogues **1a** and **1b** have been recently prepared and tested in connection with rhodium[21] and palladium.[10] The synthesis and application of these new complexes in the hydrogenation of prostereogenic keto esters and olefins are described below.

2. Results and discussion

2.1. Dichloro complexes

The reaction of [$RuCl_2(PPh_3)_3$] with the ligand (*S*,*S*)-**1a** (1 equiv.) in CH_2Cl_2 at room temperature gave the dark-red 16-electron complex [$RuCl_2(PPh_3)$((*S*,*S*)-**1a**)] **4**, whose formula was confirmed by elemental analysis and mass spectrometry (FAB$^+$)). The room-temperature ^{31}P NMR spectrum of **4** in CD_2Cl_2 shows a broadened ABX system analogous to that observed for related [$RuCl_2(PPh_3)$(P–P)] complexes,[15,22,23] which possess a square-pyramidal structure (Scheme 1).[23] The low-temperature ^{31}P NMR spectra recorded down to −80°C did not display a well-resolved ABX system, probably due to the slowing down of conformational equilibria related to the 1-naphthyl groups.[15c,21a] One PPh_3 ligand partially dissociates from **4** in CD_2Cl_2 solution at room temperature, as indicated by the broadened singlet at δ −6 ($w_{1/2}$ = 30 Hz) in the ^{31}P NMR spectrum, which is attributed to free PPh_3 in chemical exchange with **4** (Scheme 1). Broad signals at δ 41 and 29 are assigned to the dinuclear species [(**1a**)ClRu(μ-Cl)$_2$RuCl(**1a**)] **5**. Approximately 25% of **4** dissociates to give the dinuclear complex **5**. Analogous dissociation equilibria have been described for [$RuCl_2(PPh_3)_3$][24] and [$RuCl_2(PPh_3)$-(P–P)].[15,22,23]



Scheme 1.

Instead of a five-coordinate complex, the reaction of [$RuCl_2(PPh_3)_3$] with **1b** afforded the six-coordinate, orange complex [$RuCl_2$((*S*,*S*)-**1b**)] **6**. In agreement with this formula, **6** is a non-electrolyte in CH_2Cl_2 and displays an MS (FAB$^+$) molecular peak at 786. Vapour-pressure osmometric measurements gave a molecular weight of 783 g/mol. The diphosphine **1b** acts as a tetradentate ligand by means of coordination of the two methoxy groups to ruthenium. Several examples of *o*-anisyl-substituted phosphines that coordinate ruthenium as a bidentate P–O ligand have been reported.[25,26] The coordination of both methoxy groups is indicated by the shifts of the ^1H NMR signals of the methoxy protons (δ 3.28 and 4.86) as compared to the free ligand (δ 3.67), with a pattern analogous to that observed for [$RuCl_2$(CO)(P–O-κ^1*P*)(P–O-κ^2*P*,*O*)] (P–O = P(*o*-An)Ph_2).[26] The low-field shift (δ 4.86) is typical of coordinated methoxy groups, whereas the high-field shift (δ 3.28) of one C*H*$_3$O-signal can be explained by the close proximity of the corresponding methoxy group to the face of one aryl group (see below, Fig. 1).[26]

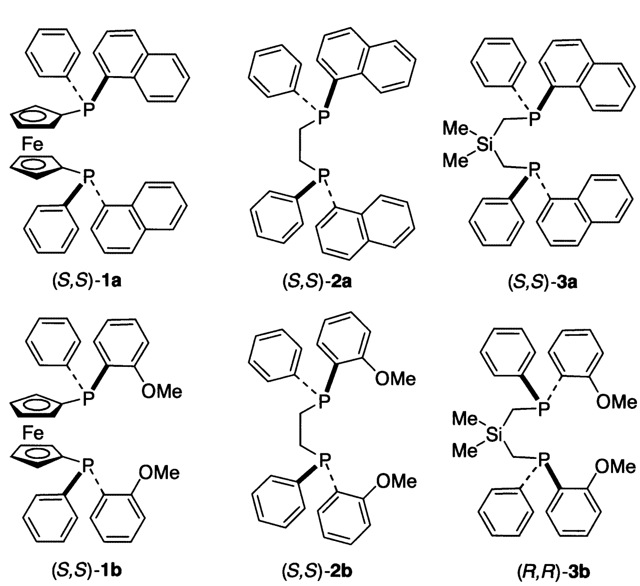


Chart 2.

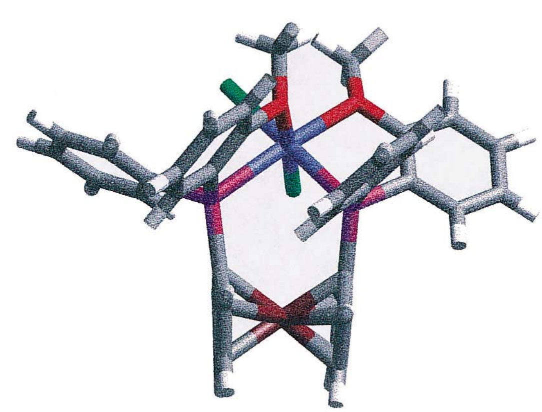
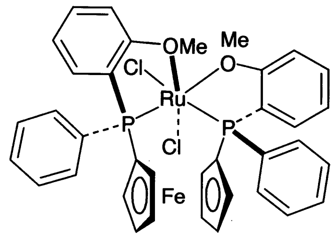


Figure 1.



6

Complex **6** is formed in the reaction as a single diastereoisomer, as indicated by its ^{31}P NMR spectrum, which consists of an AB system ($\delta_A = 75.8$, $\delta_B = 66.7$, $J_{AB} = 39.4$ Hz). The non-equivalence of the two P atoms is indicative of C_1-symmetry, and the presence of two bands at 232.1 and 241.3 cm^{-1} in the IR spectrum supports a *cis* arrangement of the chloro ligands. As we were unable to grow crystals for X-ray and the determination of the absolute configuration at ruthenium, we performed molecular modelling calculations (Cerius^2)[27] to assess the energy of the possible diastereomeric structures. The only structure compatible with the features discussed above that refined to a reasonable energy value is shown in Fig. 1. Interestingly, the methoxy group *trans* to chloride is close to the face of one phenyl group, which accounts for the high-field shift of one MeO-signal discussed above.

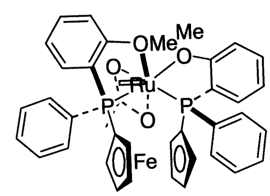
2.2. Bis(2-methallyl) complexes

The reaction of the bis(2-methylallyl) complex [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(COD)] **7a**[28] with ligand (*R*,*R*)-**3b** in pentane at room temperature gave [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(**3b**)] **8b** in moderate yield. As ligand **2a** did not react with **7a** at room temperature, [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(**2a**)] **8a** was prepared by heating a hexane solution of (*S*,*S*)-**2a** and **7a** (1 equiv.) at 70°C for 5 h. The ^{31}P NMR spectrum of **8a** consists of a singlet at δ 83.0. Ligands **1a** and **1b** did not react with [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(COD)] even when heated at 70°C for 72 h. As higher temperatures are likely to cause epimerisation at the stereogenic phosphorus atoms, an alternative approach was devised that started from the bis(acetato) complexes.

2.3. Bis(acetato) complexes

The bis(trifluoroacetato) dinuclear complex [Ru$_2$(η^2-O$_2$CCF$_3$)$_4$(OH$_2$)(COD)$_2$] **7b**[29] reacted with ligand **1a** giving a complex that decomposed upon attempted isolation, probably owing to the lability of the trifluoroacetato ligand. As acetato is a less labile ligand than trifluoroacetato is, we tested [Ru(η^2-O$_2$CCH$_3$)$_2$(COD)] **7c** as precursor.[17] Indeed, the reaction of **7c** with ligand **1a** yielded the stable complex [Ru(η^2-O$_2$CCH$_3$)$_2$(**1a**)] **9** that was isolated and characterised by elemental analysis and mass spectrometry (FAB$^+$). The ^{31}P NMR spectrum consisted of an AX system with two doublets centred at δ 64.40 and 78.39, respectively, and with $J_{PP'} = 42$ Hz. The presence of two inequivalent P atoms indicates that the complex has a lower symmetry than C_2 in solution. This can be explained either by a distortion due to steric crowding or by the existence of an aqua complex in solution. In agreement with the latter interpretation, a signal at δ 1.82 in the ^{1}H NMR spectrum of **9** can be attributed to a coordinated water molecule, which is accommodated by the change of hapticity of one acetato ligand from η^2 to η^1. In fact, bis(acetato) complexes of ruthenium containing bulky phosphine ligands have been reported to react with water even if present in traces.[30] In the analogous [Ru(η^2-O$_2$CCF$_3$)$_2$(P–P)], the trifluoroacetato ligands are monodentate, and 2 mol of the alcohol solvent are coordinated to ruthenium.[18]

The reaction of [Ru(η^2-O$_2$CCF$_3$)$_2$(COD)] **7b** with **1b** in MeOH gave a stable complex that was isolated as an orange powder and was formulated as [Ru(η^2-O$_2$CCF$_3$)(**1b**)]O$_2$CCF$_3$ **10**. In the mass spectrum of **10**, the signal of the [Ru(η^2-O$_2$CCF$_3$)(**1b**)]$^+$ fragment is very weak, which confirms that CF$_3$COO$^-$ is a more labile ligand than CH$_3$COO$^-$. In agreement with the easy dissociation of one CF$_3$COO$^-$ ligand, **10** is a 1:1 electrolyte in CH$_2$Cl$_2$ solution ($\Lambda_M = 16.2$ Ω^{-1} cm^2 mol^{-1}, 10^{-3} M solution). The ^{31}P NMR spectrum consists of an AB system with the signals of P_A and P_B centred at δ 73.3 and 71.8, respectively ($J_{PP'} = 42.6$ Hz), which indicates the presence of two non-equivalent P atoms in *cis* position. The ^{19}F NMR spectrum revealed the presence of two non-equivalent CF$_3$ groups at δ −75.5 and −76.1. One of the methoxy signals in ^{1}H NMR spectrum is shifted to lower field (δ 4.3 and 3.7) as compared to free ligand **1b** (δ 3.67), in a similar pattern as observed for the dichloro species **6**. The spectroscopic and conductivity data suggest that **10** features an η^2-bound trifluoroacetato ligand as shown below. The configuration at ruthenium is arbitrarily drawn, but corresponds to the energy-minimised structure of **6**.



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2.4. Ru-catalysed hydrogenation of keto esters

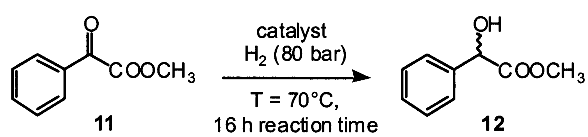
The complexes [RuCl$_2$(PPh$_3$)(**1a**)] **4**, [RuCl$_2$(**1b**)] **6**, [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(**2a**)] **8a**, and [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(**3b**)] **8b** were tested in the asymmetric hydrogenation of keto esters. Complex **6** catalysed the hydrogenation of methyl benzoylformate **11** to methyl (*R*)-mandelate (*R*)-**12** with moderate enantioselectivity (43.9% ee) (Table 1, entry 2). Complex **4**, containing the naphthyl analogue **1a**, is less efficient (9.6% ee, entry 1). The bis(2-methylallyl) complexes **8a** and **8b** show the same trend of the enantioselectivity, which increases on changing from 1-naphthyl (**8a**, 16.6% ee) to *o*-anisyl (**8b**, 26.7% ee) as *P*-substituents. However, this trend does not apply for other substrates.

Indeed, ethyl acetoacetate **13** is hydrogenated to ethyl (*R*)-3-hydroxybutyrate (*R*)-**14** with higher enantioselectivity in the case of the naphthyl-substituted ligand **1a** in complex **4** (52.6% ee, Table 2, entry 1) than with the *o*-anisyl derivative **1b**, whose derivative **6** gave racemic product (entry 3). The enantioselectivity found for the hydrogenation of ethyl acetoacetate with **1a** is comparable to that obtained in the hydrogenation of acetylacetone with the related complex [$RuCl_2(PPh_3)$((*S*,*S*)-**3a**)], which gave (*S*,*S*)-pentane-2,4-diol with 56% ee.[15c] Precatalyst **4** also hydrogenated methyl 3-oxopentanoate **15** to methyl (*R*)-3-hydroxypentanoate (**16**) in CH_2Cl_2 with 28% yield and 23% ee (Table 2, entry 2). As observed with substrate **11**, complex **8a** shows the least activity, as it failed to hydrogenate **13** even at high pressure of H_2 and high temperature ($P(H_2) = 80$ bar in the presence of HCl (entry 4). In the hydrogenation of methyl 3-oxopentanoate **15**, complex **8b** is more active and enantioselective (51% ee, entry 5) than **4** (28% ee, entry 2). For comparison, some results concerning the related ligands $R(Me)PCH_2CH_2P(Me)R$ (BisP*; R = bulky alkyl group)[12] and some atropisomeric ligands.[31] are given in Table 1 (entries 5, 6) and Table 2 (entries 6, 7).

2.5. Ru-catalysed hydrogenation of olefins

Functionalised olefins such as (*E*)-2-methylcinnamic acid **17**, methyl *Z*-α-*N*-methyl-acetamidocinnamate **19**, and dimethyl itaconate **21** were chosen as standard substrates. Complexes **4**, **6**, **8a**, **8b**, and **10** were scarcely effective in the hydrogenation of **17** to 2-methylhydrocinnamic acid **18** (Table 3). Only **4** gave a quantitative yield of **18**, but at high H_2 pressure and with low enantioselectivity (21.6% ee, entry 1). The enantioselectivity was slightly higher with ligand **1b**, either in complex **6**, (32.0% ee, entry 2), or in **10** (35.7% ee, entry 3), but the chemical yield was low at 20 bar H_2 pressure. The bis(2-methylallyl) derivatives **8a** and **8b** were inactive towards **17** (<2% yield under comparable conditions) (entries 4 and 5). In contrast, [$Ru(\eta^3$-$(CH)_2CHCH_3)_2$(P–P*)] (P–P = **2b** or **3b** (**8b**)) hydrogenate tiglic acid quantitatively with 15 and 25% ee, respectively.[11b] For comparison, (*E*)-2-methylcinnamic acid is hydrogenated with up to 89% ee by [$Ru(\eta^2$-$O_2CCH_3)_2(H_8$-binap)] (H_8-binap = 2,2′-bis-(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl) (entry 6).[32]

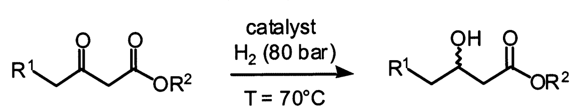
Table 1. Hydrogenation of methyl benzoylformate **11** to methyl (*R*)-mandelate **12**



Entry	Ligand	Cat.	S/C	Yield (%)	Ee (%)	Conf.
1	**1a**	**4**	200	99	9.6	*S*
2	**1b**	**6**	200	99	43.9	*R*
3	**2a**	**8a**	100	<50	16.6	*R*
4	**3b**	**8b**	200	95	26.7	*R*
5	(*S*)-BisP*	[a]	200	90	70	*R*
6	(*R*)-Bichep	[b]	100	>99	>99	*S*

[a] From Ref. 12, '$RuBr_2$(BisP*)' as catalyst (BisP* = $Me(Bu^t)PCH_2CH_2P(Bu^t)Me$).
[b] From Ref. 31a, [$RuI(\eta^6$-*p*-cymene)(bichep)] as catalyst under transfer-hydrogenation conditions (bichep = 2,2′-bis(dicyclohexylphosphino)-6,6′-dimethyl-1,1′-biphenyl).

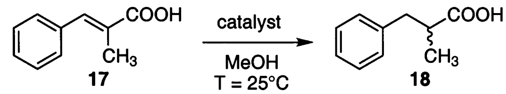
Table 2. Hydrogenation of β-keto esters **13** and **15** to β-hydroxyesters **14** and **16**[a]



Entry	Subst.	R_1	R_2	Ligand	Cat.	S/C	Solvent	*t* (h)	Yield (%)	Ee (%)	Conf.
1	**13**	H	Et	**1a**	**4**	1000	EtOH	16	>99	52.6	*R*
2	**15**	Me	Me	**1a**	**4**	1000	CH_2Cl_2	18	28	23	*R*
3	**13**	H	Et	**1b**	**6**	200	EtOH	16	66	rac.	–
4	**13**	H	Et	**2a**	**8a**	200	EtOH	24	<1	–	–
5[b]	**15**	Me	Me	**3b**	**8b**	100	MeOH	16	66	51	*R*
6	**15**	Me	Me	BisP*	[c]	800	MeOH/H_2O	10	96	98	*R*
7	**15**	Me	Me	(*R*)-binap	[d]	2000	MeOH	36	99	>99	*R*

[a] Other reaction conditions: A 1N HCl solution (50–120 μL) was added to the reaction solution.
[b] $T = 80°C$, $p(H_2) = 100$ bar.
[c] From Ref. 12, see Table 1, footnote a.
[d] From Ref. 31b, the catalyst was '$RuCl_2$((*R*)-binap)', $P(H_2) = 100$ atm, $T = 23°C$.

Table 3. Hydrogenation of (*E*)-2-methylcinnamic acid **17** to 2-methylhydrocinnamic acid **18**

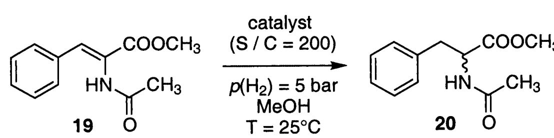


Entry	Ligand	Cat.	S/C	Additive (equiv./Ru)	$p(H_2)$ (bar)	*t* (h)	Yield (%)	Ee (%)	Conf.
1[a]	**1a**	**4**	200	$^iPr_2NEt_2$ (4)	80	19	>99	21.6	*R*
2	**1b**	**6**	200	NEt_3 (6)	20	16	12	32.0	*R*
3	**1b**	**10**	200	NEt_3 (6)	20	18	16	35.7	*R*
4	**2a**	**8a**	100	CF_3COOH (2)	5	16	<1	n.d.	n.d.
5	**3b**	**8b**	200	CF_3COOH (4)	20	17	<2	n.d.	n.d.
6	(*S*)-H_8-Binap	[b]	200	–	1.5	48	87	89	*S*

[a] 2-Propyl alcohol was used in place of MeOH.
[b] From Ref. 32, the catalyst was $[Ru(\eta^2-O_2CCH_3)_2(H_8\text{-binap})]$ (H_8-binap = 2,2′-bis(diphenylphosphino)-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl).

The hydrogenation of **19** to *N*-acetylphenylalanine methyl ester **20** is quantitative with **4**, but the enantioselectivity is low (18.2% ee, Table 4, entry 1). Changing the solvent from methanol to dichloromethane improves the enantioselectivity (42.2% ee, entry 2) at the expense of the chemical yield. The catalyst precursors containing ligand **1b** give racemic product (entries 3 and 4). The bis(2-methylallyl) complexes **8a** and **8b** are nearly inactive (entries 5 and 6). For comparison, $[RuH(MeCN)_3(binap)]$ catalyses the hydrogenation of **19** giving **20** with up to 94% ee (entry 7).[33] Dimethyl itaconate **21** was the last olefin tested. Complex **4** quantitatively hydrogenated **21** to dimethyl methylsuccinate **22** with 17.1% ee (Table 5, entry 1), whereas **6** and **8a** gave racemic **22** (entries 2 and 3). Indeed, the analogue substrate itaconic acid was hydrogenated with up to 98% ee by binap or biphemp complexes of ruthenium (entry 4).[11b]

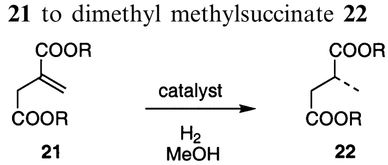
Table 4. Hydrogenation of methyl (*Z*)-α-acetamidocinnamate **19** to *N*-acetylphenylalanine methyl ester **20**



Entry	Ligand	Catalyst	*t* (h)	Yield (%)	Ee (%)	Conf.
1	**1a**	**4**	19	>99	18.2	*S*
2[a]	**1a**	**4**	16	11	42.2	*S*
3	**1b**	**6**	17	25	Racemic	–
4	**1b**	**10**	24	98	4.5	*R*
5[b]	**2a**	**8a**	16	18	9.4	*S*
6[b]	**3b**	**8b**	16	17	Racemic	–
7	(*R*)-Binap	[c]	[c]	>99	94	*R*

[a] The solvent was CH_2Cl_2.
[b] The precatalyst was activated with CF_3COOH (2 and 4 equiv. versus Ru for **8a** and **8b**, respectively).
[c] From Ref. 33, the catalyst was $[RuH(solv)_3((R)\text{-binap})]$ (solv = MeCN or acetone).

Table 5. Hydrogenation of dimethyl itaconate **21** to dimethyl methylsuccinate **22**



Entry	R	Ligand	Cat.	S/C	$P(H_2)$ (bar)	*T* (°C)	*t* (h)	Yield (%)	Ee (%)	Conf.
1	Me	**1a**	**4**	200	5	25	16	>99	17	*R*
2	Me	**1b**	**6**	200	5	25	16	89	Racemic	–
3	Me	**2a**	**8a**	100	40	40	16	>99	3	*R*
4	H	(*R*)-Binap	[a]	100	3	50	[a]	>99	98	*S*

[a] From Ref. 11b, '$RuBr_2((R)\text{-binap})$' as catalyst in THF solvent.

3. Final remarks

The present work is, to the best of our knowledge, the first systematic investigation directed to prepare ruthenium complexes containing *P*-stereogenic ligands with different frameworks and aryl substituents at the phosphorus atoms. Overall, the P–P* ligands screened, which feature two aryl substituents at the stereogenic phosphorus atom, are less efficient than the related ligands R(Me)PCH$_2$CH$_2$P(Me)R (BisP*; R = bulky alkyl group) and cannot compete with the atropisomeric ligands of the binap family, at least in the asymmetric hydrogenation of C=C and C=O functionalities. The ferrocene-based ligands **1a** and **1b** give the highest activity and enantioselectivity, confirming that bulky ligands are best suited for ruthenium-based hydrogenation catalysts. A remarkable feature of the above systems is the ability of **1b** to act as a tetradentate *O*,*P*,*P*,*O*-ligand with ruthenium. This feature is beneficial in the hydrogenation of methyl methyl benzoylformate. Together with Imamoto's results with a ruthenium/BisP* system, this study suggests that a further exploration of ruthenium complexes containing *P*-stereogenic ligands with *bulky alkyl groups* may prove fruitful.

4. Experimental

4.1. General

Reactions with air- or moisture-sensitive materials were carried out under an argon atmosphere using Schlenk techniques or in a glove box under purified nitrogen. Solvents were purified by standard procedures. The ^{1}H, ^{31}P, and ^{11}B NMR and mass spectra, HPLC, GC, melting points, specific rotations, and elemental analyses were measured as described before.[21a] The compounds (*S*,*S*)-**1a**,[21a] (*S*,*S*)-**1b**,[21a] (*S*,*S*)-**2a**,[13] [Ru(η^3-(CH)$_2$CHCH$_3$)$_2$(COD)] **7a**,[28] [Ru$_2$(η^2-O$_2$CCF$_3$)$_4$(OH$_2$)-(COD)] **7b**,[29] and [Ru(η^2-O$_2$CCH$_3$)(COD)] **7c**[17] were prepared according to literature procedures. The use of ligand **3b** has been reported,[11] but its synthesis has not been described, thus we report the preparation of (*R*,*R*)-**3b**.

4.2. (*R*,*R*)-Si(Me)$_2$(CH$_2$P(*o*-An)(Ph)(BH$_3$))$_2$, 3

sec-BuLi (1.24 M hexane solution, 4.4 mL, 1 equiv.) was added dropwise over 10 min to a solution of (*R*)-P(BH$_3$)(Ph)(*o*-An)(Me) (1.43 g, 5.85 mmol) in THF (20 mL) at a constant temperature of −78°C. After stirring for 2 h, Cl$_2$SiMe$_2$ (0.35 mL, 3.0 mmol) was rapidly added by syringe. The solution was left to reach rt overnight. The reaction was quenched with 1 M HCl (18 mL). The THF was evaporated, and the aqueous phase was extracted with CH$_2$Cl$_2$ and dried over MgSO$_4$. The solvent was evaporated, and the crude product was recrystallised from hot hexane. Yield: 1.204 g (75.5%). ^{31}P NMR (CDCl$_3$): δ 12.4 (br q, 2P). ^{1}H NMR (CDCl$_3$): δ 8.1–7.9 (m, 2H, Ar*H*), 7.7-7.19 (m, 12H, Ar*H*), 7.2-7.0 (m, 2H, Ar*H*), 6.9–6.75 (m, 2H, Ar*H*), 3.62 (s, 6H, OC*H*$_3$), 2.3–2.1 (dd, 2H, SiC*H*$_2$), 1.7–1.45 (dd, 2H, SiC*H*$_2$), −0.175 (s, 6H, SiC*H*$_3$). MS (FAB$^+$): *m*/*z* 543 (M$^+$, 46), 529 (M$^+$−BH$_3$, 100), 517 (M$^+$−2BH$_3$, 23).

4.3. (*R*,*R*)-Si(Me)$_2$(CH$_2$P(*o*-An)Ph)$_2$, 3b

The diborane adduct (*R*,*R*)-Si(Me)$_2$[(CH$_2$P(*o*-An)(Ph)(BH$_3$)]$_2$ (1.09 g, 2.01 mmol) was dissolved in morpholine (100 mL) at room temperature. After 3 days, morpholine was evaporated under vacuum, and the yellowish product was purified by flash chromatography (silica gel, toluene, R_f 0.23) to remove the amine borane complex. Evaporation of the solvent under vacuum gave a colourless oil. Yield: 0.217 g (21%). $[\alpha]_D^{20}$ = 156 (*c* 1, CHCl$_3$). ^{31}P NMR (CDCl$_3$): δ −31.7 (s, 2P), ^{1}H NMR (CDCl$_3$): δ 7.95–6.8 (m, 18H, Ar*H*), 3.8 (s, 6H, OC*H*$_3$), 1.6 (d, 6H, SiC*H*$_3$). MS (FAB$^+$): *m*/*z* 517 (M$^+$, 62). Anal. calcd for C$_{30}$H$_{34}$O$_2$P$_2$Si 0.77C$_7$H$_8$: C, 72.14; H, 6.87. Found: C, 72.22; H, 6.89%.

4.4. [RuCl$_2$(PPh$_3$)((*S*,*S*)-1a)], 4

[RuCl$_2$(PPh$_3$)$_3$] (213 mg, 0.222 mmol) and (*S*,*S*)-**1a** (144 mg, 0.222 mmol) were dissolved in CH$_2$Cl$_2$ (5 mL). After stirring for 2 h at room temperature, 2-PrOH (5 mL) was slowly added. After evaporation of the solvent, the dark-brown precipitate was filtered off, washed with 2-PrOH, and dried under vacuum (198 mg, 82%). ^{31}P NMR (CD$_2$Cl$_2$): ^{31}P NMR (CD$_2$Cl$_2$): **4**: broad ABX system, δ 58.3 (P_X, 1P), 35.8 (P_B, 1P), 31.7 (P_A, 1P). **5**: δ 40.8 (br, 2P), 29.3 (br, 2P). Free PPh$_3$: δ −6 (br s, *P*Ph$_3$, $w_{1/2}$ = 30 Hz). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.87–6.89 (m, 39H, Ar*H*), 4.85, 4.53, 4.37, 4.13 (4 s, 8H, 2Cp*H*). MS (FAB$^+$): *m*/*z* 1017 (M$^+$−2Cl, 27%), 755 (M$^+$−2Cl−PPh$_3$, 72%). Anal. calcd for C$_{60}$H$_{47}$Cl$_2$FeP$_3$Ru: C, 66.19; H, 4.35. Found: C, 66.18; H, 4.55%.

4.5. [RuCl$_2$((*S*,*S*)-1b)], 6

[RuCl$_2$(PPh$_3$)$_3$] (244 mg, 0.254 mmol) and (*S*,*S*)-**1b** (156 mg, 0.254 mmol) were dissolved in CH$_2$Cl$_2$ (5 mL). After stirring for 3 h at room temperature, 2-PrOH (5 mL) was added as a layer over the CH$_2$Cl$_2$ solution. Crystals of **6** were formed overnight by diffusion of 2-PrOH into the CH$_2$Cl$_2$ solution, and the orange solid was filtered off and dried under vacuum (136 mg, 68%). $[\alpha]_{20}^{D}$ = +81.2 (*c* 0.25, CHCl$_3$). Mp 206°C (dec.). Λ_M (0.001 M in CH$_2$Cl$_2$): 0.0 Ω^{-1} cm^2 mol^{-1}. ^{31}P NMR (CDCl$_3$): δ 75.8 (d, 1P, $J_{PP'}$ = 39.4 Hz), 66.7 (d, 1P, $J_{PP'}$ = 39.4 Hz). ^{1}H NMR (CDCl$_3$): δ 8.14-8.07 (m, 3H, Ar*H*), 7.57–6.91 (m, 14H, Ar*H*), 6.42–6.37 (m, 1H, Ar*H*), 5.72, 5.07, 4.79, 4.44, 4.36, 4.32, 4.28, 4.11 (8 s, 8H, 2Cp*H*), 4.86, 3.28 (2 s, 6H, 2 OC*H*$_3$). IR (CsI): 232, 241 cm^{-1} (ν(RuCl$_2$)). MS (FAB$^+$): *m*/*z* 786 (M$^+$, 100%), 751 (M$^+$−Cl, 93%), 660 (M$^+$−Cl−PhO+H, 11%), 583 (M$^+$−Cl−PhO+H−Ph, 8%). Molecular mass (vapour-pressure osmometry): 783 g/mol. Anal. calcd for C$_{36}$H$_{32}$Cl$_2$FeO$_2$P$_2$Ru: C, 54.98; H, 4.10. Found: C, 54.69; H, 4.25%.

Table 6. Analytical details of ee determination

Product	Method	Column	T (°C)	Carrier	P (kPa)	R_t (R) (s)	R_t (S) (s)
12	GC	Lipodex A	125	H_2	150	9.05	9.25
14	GC	Lipodex E	85	He	150	5.4	6.9
16	GC	Lipodex E	85	He	150	6.75	7.9
18	HPLC	Chiralcel OB	rt	[a]		58.9[b]	64.4[b]
20	GC	L-Chirasil-Val	170	He	120	17.52	17.70
22	GC	Lipodex E	85	He	150	11.5	11.0

[a] Eluent:hexane/^{i}PrOH (97:3), flow 0.1 mL min^{-1}.

[b] The attribution is arbitrary. Absolute configuration not determined.

4.6. [Ru(η^2-O_2CCH_3)$_2$((*S*,*S*)-1a)], 9

A CH_2Cl_2 solution (2 mL) of **7c** (11 mg, 0.034 mmol) was added to a CH_2Cl_2 solution (3 mL) of (*S*,*S*)-**1a** (22 mg, 0.034 mmol). The reaction solution was stirred in a glove box at room temperature for 24 h, after which the solvent was removed under vacuum, and the product was isolated as an orange powder (18 mg, 61%). Λ_M (0.001 M in CH_2Cl_2): 0.0 Ω^{-1} cm^2 mol^{-1}. ^{31}P NMR (CD_2Cl_2): (AX system) δ 64.40 (d, 1P, P_A, $J(P_A, P_B)=$ 42 Hz), 78.39 (d, 1P, P_B, $J(P_{AB})=42$ Hz). ^{1}H NMR (CD_2Cl_2): δ 7.94-6.59 (m, 39H, Ar*H*), 4.71, 4.52, 4.33, 4.18, 4.09, 4.00, 3.97, 3.72 (8 s, 8H, 2Cp*H*), 1.91 (d, 6H, 2CH_3, $J_{PH}=6.1$ Hz), 1.82 (s, 2H, H_2O). MS (FAB$^+$): *m*/*z* 873 (M^+, 5%), 814 (M^+–O_2CCH_3, 16%), 755 (M^+–2O_2CCH_3–**1a**, 35%). Anal. calcd for $C_{46}H_{38}FeO_4P_2Ru$: C, 63.24; H, 4.38. Found: C, 63.32; H, 4.61%.

4.7. [Ru(η^3-$(CH)_2CHCH_3$)$_2$((*S*,*S*)-2a)], 8a

Complex **7a** (96 mg, 0.3 mmol) and (*S*,*S*)-**2a** (149 mg, 0.3 mmol) were dissolved in hexane (6 mL). After stirring for 5 h at 70°C, the solution was concentrated under vacuum (1 mL). The resulting yellow precipitate was filtered off, washed with hexane, and dried under vacuum (128 mg, 61%). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 82.6 (s, 2P). ^{1}H NMR ($CDCl_3$): δ 8.73 (m, 2H, Np*H*), 7.97–6.84 (m, 22H, Ar*H*), 4.90, 3.75 (2 s br, 4H, 4 =C*H*), 3.94–3.32 (m, 4H, 2CH_2), 1.81 (s, 6H, 2CH_3). MS (FAB$^+$): *m*/*z* 709 (M^+, 24), 598 (M^+–2 (η^3-$(CH)_2CHCH_3$), 64). Anal. calcd for $C_{42}H_{42}P_2Ru$: C, 71.07; H, 5.96. Found: C, 71.10; H, 6.02%.

4.8. [Ru(η^3-$(CH)_2CHCH_3$)$_2$((*R*,*R*)-2b)], 8b

A pentane solution (1 mL) of (*R*,*R*)-**2b** (0.217 g, 0.42 mmol) was added to **7a** (0.134 g, 0.42 mmol) in pentane (3 mL). After stirring for 2 days at room temperature, evaporation of the solvent yielded a yellow–green precipitate, which was filtered off under argon and dried under vacuum (0.160 g, 52%). ^{31}P NMR (CD_2Cl_2): δ 34 (*s*, 2P). ^{1}H NMR (CD_2Cl_2): δ 7.8–6.3 (m, 18H, Ar*H*), 3.2 (s, 6H, OCH_3), 2.2 (s, 6H, Si(CH_3)$_2$). MS (FAB$^+$): *m*/*z* 672 (M^+–(η^3-$(CH)_2CHCH_3$), 10), 617 (M^+–2 (η^3-$(CH)_2CHCH_3$), 6), 442 (M^+–2 (η^3-$(CH)_2CHCH_3$)–Ru–Ph+3H, 100). Anal. calcd for $C_{38}H_{48}O_2P_2SiRu\cdot 0.5C_5H_{12}$: C, 63.67; H, 7.12. Found: C, 63.87; H, 6.95%.

4.9. [Ru(η^2-O_2CCF_3)((*S*,*S*)-1b)]O_2CCF_3, 10

A solution of **8b** (72.3 mg, 0.0814 mmol) in methanol (2 mL) was added to a CD_2Cl_2 solution (0.3 mL) of (*S*,*S*)-**1b** (100 mg, 0.1627 mmol). The reaction mixture was stirred in a glove box for 2 days under purified N_2 at room temperature. The solvent was removed under vacuum, and the solid was dissolved in Et_2O. Partial evaporation of Et_2O gave the pure product as an orange powder (62 mg, 81%). Λ_M (0.001 M in CH_2Cl_2): 16.2 Ω^{-1} cm^2 mol^{-1}. ^{31}P NMR (CD_2Cl_2): δ 73.3 (d, 1P, $J_{PP'}=42.6$), 71.8 (d, 1P, $J_{PP'}=42.6$). ^{1}H NMR (CD_2Cl_2): δ 7.7–6.8 (m, 28H, Ar*H*), 4.7–4.1 (m, 8H, Cp*H*), 4.3 (br s, 3H, OCH_3), 3.7 (br s, 3H, OCH_3). ^{19}F NMR δ −75.5, −76.1 (2 s, 6F, 2CF_3). MS (FAB$^+$): *m*/*z* 829 (M^+–$OCOCF_3$, 100). Anal. calcd for $C_{40}H_{32}Cl_2F_6FeO_6P_2Ru$: C, 51.03; H, 3.42. Found: C, 50.75; H, 4.03%.

4.10. Catalytic hydrogenation

The standard procedure was as follows: the substrate and the catalyst (3 µmol) (and, when appropriate, the additive) were dissolved in the solvent (10 mL) under argon. The solution was stirred for 15 min, and then transferred via steel capillary into a 180 mL thermostatically controlled glass reactor or a 50 mL stainless steel autoclave. The inert gas was then replaced with hydrogen (three cycles), and the pressure was set. After completion of the reaction, the conversion was determined by gas chromatography, and the product was recovered after filtration of the reaction solution on a plug of silica to remove the catalyst. Analytical details concerning the determination of the enantiomeric excess of the products are given in Table 6.

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