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Asymmetric hydrogenation reactions using a practical in situ generation of chiral ruthenium–diphosphine catalysts from anhydrous $RuCl_3$

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Abstract—A very simple in situ preparation of chiral ruthenium–diphosphine catalysts from anhydrous $RuCl_3$ is reported. Prochiral C=O and C=C bonds have been reduced with high enantioselectivities via ruthenium-catalyzed hydrogenation.

1. Introduction

Transition metal-catalyzed enantioselective hydrogenation[1–9] of prochiral substrates represents one of the most efficient method for the preparation of chiral building blocks of biological interest. In this field, several groups have focused their research on the development of Ru-based hydrogenation catalysts. The utility of $RuCl_3 \cdot nH_2O$ as a starting material for multistep preparations of efficient ruthenium-chiral diphosphine[10] catalysts is shown in Scheme 1.[26] Ikariya et al.[11] have prepared a dinuclear complex formulated as $Ru_2Cl_4(BINAP)_2(NEt_3)$ (later elucidated as $[NH_2Et_2][\{RuCl(P*P)\}_2(\mu\text{-}Cl)_3]$ **1**[12] with P*P=(*R*)-*p*-MeO-BINAP) in a two-step sequence from $RuCl_3 \cdot nH_2O$ via the polymeric complex $[RuCl_2(COD)]_n$ (COD=cycloocta-1,5-diene) in 85% yield. The first mononuclear hexacoordinate ruthenium complex $Ru(O_2CR)_2(P*P)$ **2** bearing BINAP ligand has been reported by Noyori et al.[13,14] and prepared from Ikariya's complex **1**[11] by treatment with sodium acetate. An improved procedure[15] for the preparation of **2** has been described starting with $[RuCl_2(benzene)]_2$ (obtained from $RuCl_3 \cdot nH_2O$).

Ruthenium dicarboxylato complexes **2** $Ru(O_2CR)_2(P*P)$ (R=Me,CF_3,Ar) have also been prepared from Ru(COD)(η^3-methylallyl)$_2$, in 2–4 steps.[16,17] Treatment of $[RuX_2(arene)]_2$ with 1 equiv. of (*S*)-BINAP in a 8:1 mixture of ethanol and benzene afforded the cationic complexes **3**.[18] In situ preparation of $Ru(acac)_2$[(*S*)-BINAP)] **4**[19] from $Ru(acac)_3$ and synthesis of air stable BINAP-ruthenium complexes **5** Ru(RCp)(Binap)Cl (R=H, CH_3)[20] from $Ru(RCp)(PPh_3)_2Cl$ have been reported. The Ru-based precursors to the complexes **2**, **3**, **4** and **5**, respectively, Ru(COD)(η^3-methylallyl)$_2$, $[RuX_2(arene)]_2$, $Ru(acac)_3$ and $Ru(RCp)(PPh_3)_2Cl$ are all prepared from $RuCl_3 \cdot nH_2O$. Our contribution to this field has been the development of general synthetic methods for the preparation of chiral ruthenium(II)-catalysts bearing various chiral diphosphines. These preparations include the direct use of the polymeric complex $[RuCl_2(COD)]_n$[21] as well as the chiral catalysts Ru(P*P)(η^3-methylallyl)$_2$ **6**[22,23] used for the preparation of ruthenium complexes **7** defined by the empirical formula $Ru(P*P)X_2$.[23] These catalysts have been also prepared from ruthenium dicarboxylato complexes **2** by treatment with HX or $(CH_3)_3SiI$.[24] In situ-generated catalysts **7** have been more conveniently synthesized from a 1:1 mixture of Ru(COD)(η^3-methylallyl)$_2$ and the appropriate chiral diphosphine by treatment with 1.5–2.2 equiv. of HX (X=Cl, Br).[23] More recently, a new cationic monohydride ruthenium complex **8** [Ru((*R,R*)-Me-DuPHOS)(H)(η^6-1,3,5-cyclooctatriene)](BF_4) has been discovered and efficiently used for the industrial hydrogenation of tetrasubstituted olefins.[25]

As demonstrated above, $RuCl_3 \cdot nH_2O$ is the readily available source for most of the multisteps preparations of chiral diphosphine ruthenium complexes. Our continuing interest in the practical preparations of chiral Ru(II)-based catalysts prompted us to look for a more convenient way to obtain these complexes directly from anhydrous $RuCl_3$ avoiding, therefore, the synthesis and handling of **1**–**7**. To our knowledge, only one example of the use of $RuCl_3 \cdot nH_2O$ has been described in the asymmetric hydrogenation of the amine salt of 2-(4-isobutylphenyl)propenoic acid with fair enantioselectivity.[19] We report herein, the direct use of

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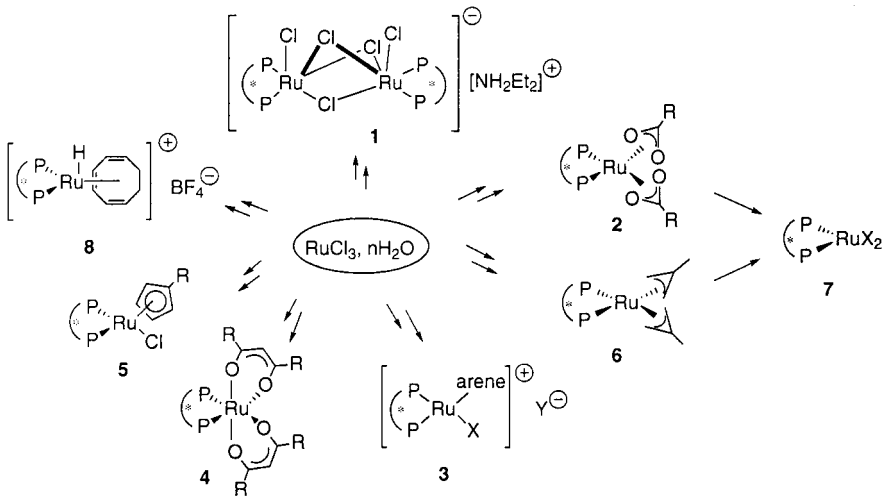


1: P*P = *p*-MeO-BINAP[12]
2: R = Me; P*P = BINAP;[13] R = Me, CF_3; P*P = MeO-BIPHEP, BIPHEMP, *p*-Tol-BINAP, BINAP[16]; R = CF_3, Ar; P*P = BINAP[17]
3: P*P = BINAP; arene = C_6H_6, *p*-$MeC_6H_4CHMe_2$; X = Cl, Br, I; Y = Cl, Br, I, BF_4, BPh_4[18]
4: R = CH_3, CF_3; P*P = BINAP, SKEWPHOS, DIOP[19]
5: R = H, CH_3; P*P = BINAP[20]
6: P*P = BINAP, MeO-BIPHEP, BIPHEMP, Me-DuPHOS, SKEWPHOS, CHIRAPHOS, DIPAMP, DIOP, PROPHOS, DEGPHOS, NORPHOS[22,23]
7: P*P = BINAP, BIPHEMP, CHIRAPHOS, DIOP, CBD;[23] BINAP;[24] Me-CnrPHOS[26]
8: P*P = Me-DuPHOS, JOSIPHOS[25]

Scheme 1.

anhydrous $RuCl_3$ as a source of in situ-generated chiral ruthenium complexes for the asymmetric hydrogenation of prochiral ketones and olefins.

2. Results and discussion

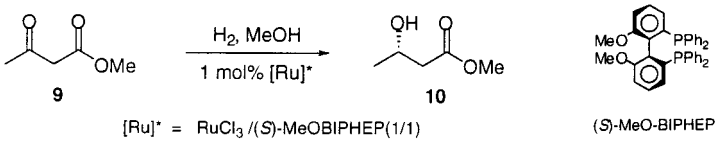
A preliminary evaluation of the best experimental conditions has been studied in the hydrogenation of methyl acetoacetate **9** as standard substrate (Table 1). Hydrogenation of **9** has been first conducted at 50 bar and 50°C for 17 h using 1 mol% of anhydrous $RuCl_3$ and (*S*)-MeO-BIPHEP as ligand. Under these conditions (*S*)-methyl 3-hydroxybutyrate **10** was obtained in quantitative yield and excellent enantiomeric excess (entry 1). Further studies involving this catalytic system revealed that complete conversion could be achieved in only 4 h and at 4 bar to yield (*S*)-**10** in 99% e.e. (entry 3) (Scheme 2).

In contrast to our method, which involves directly Ru(III)-precatalyst, most of the enantioselective ruthenium-mediated hydrogenation reactions proceed from Ru(II)-precatalysts. It is reasonable to expect that Ru(III) is reduced to Ru(II) species under the reaction conditions by either hydrogen or the chiral phosphine. Tentative elucidations for the identification of the catalytic species by ^{31}P NMR were unsuccessful since many signals were detected whose assigment proved to be difficult. Hydrogenation reactions of a variety of β-keto esters were then conducted under 4 bar and 50°C in methanol or ethanol using 1 mol% of the chiral ruthenium catalyst and on a 1 mmol scale. As can be seen, very high enantioselectivities and complete conversions have been achieved under these reaction conditions

Table 1. Ru-catalyzed hydrogenation of methyl acetoacetate **9** using $RuCl_3$+(*S*)-MeO-BIPHEP

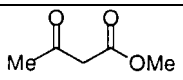
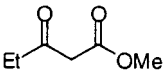
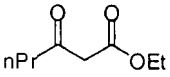
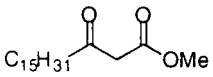
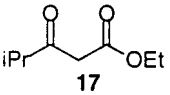
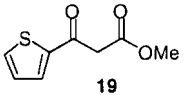
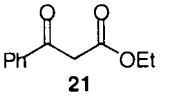
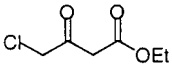
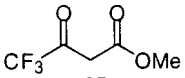
Entry	Catalyst	Conditions			Conv. (%)	e.e.[a] (conf.)
		P (bar)	*T* (°C)	*t* (h)		
1	$RuCl_3$+(*S*)-MeO-BIPHEP	50	50	17	100	99 (*S*)
2	$RuCl_3$+(*S*)-MeO-BIPHEP	4	50	17	100	99 (*S*)
3	$RuCl_3$+(*S*)-MeO-BIPHEP	4	50	4	100	99 (*S*)

[a] Enantiomeric excesses were determined by chiral GC analysis (Lipodex A column).



Scheme 2.

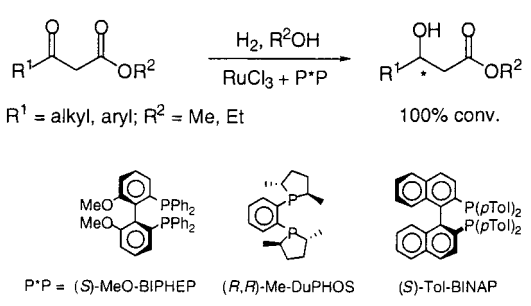
Table 2. Ruthenium-catalyzed hydrogenation of β-keto esters using $RuCl_3$ and chiral diphosphine

Entry	Substrate	Ligand P*P	Conditions[a,b]			e.e.[c] (%)	Conf.
			P (bar)	*T* (°C)	*T* (h)		
1	 **9**	(*S*)-Tol-BINAP	4	50	24	99	(*S*)-**10**
2		(*R*,*R*)-Me-DuPHOS	50	80	72	85	(*R*)-**10**
3	 **11**	(*S*)-MeO-BIPHEP	4	50	24	99	(*S*)-**12**
4	 **13**	(*S*)-MeO-BIPHEP	4	50	24	99[d]	(*S*)-**14**
5	 **15**	(*R*)-MeO-BIPHEP	4	50	24	98[e]	(*R*)-**16**
6	 **17**	(*S*)-MeO-BIPHEP	4	50	24	99	(*R*)-**18**
7		(*R*,*R*)-Me-DuPHOS	50	80	72	89	(*S*)-**18**
8	 **19**	(*S*)-MeO-BIPHEP	10	30	40	76	(*R*)-**20**
9	 **21**	(*S*)-MeO-BIPHEP	4	50	24	88	(*R*)-**22**
10		(*S*)-MeO-BIPHEP	4	80	24	95	
11	 **23**	(*S*)-MeO-BIPHEP	4	50	24	57	(*R*)-**24**
12		(*S*)-MeO-BIPHEP	4	80	24	76	
13		(*S*)-MeO-BIPHEP	4	120	6	92	
14	 **25**	(*S*)-MeO-BIPHEP	10	120	6	50	(*R*)-**26**

[a] 1 mol% of chiral Ru-catalyst was used.
[b] Reaction times are not optimized.
[c] Enantiomeric excesses were determined by chiral GC analysis (Lipodex A column) except for **14** and **16**.
[d] Enantiomeric excess was determined on the benzoyl derivative by chiral HPLC (Daicel Chiralcel OJ column).
[e] Enantiomeric excess was determined on the (*S*)-2-acetoxypropionyl derivative by GC analysis (DB 1701 column).

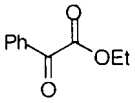
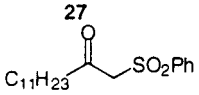
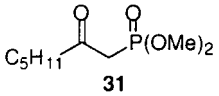
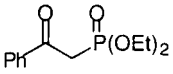
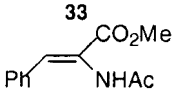
(Table 2). The test substrate methyl acetoacetate was reduced in 99% e.e. using (*S*)-Tol-BINAP (entry 1) while a lower enantiomeric excess was obtained with (*R*,*R*)-Me-DuPHOS and the reaction required higher pressure, temperature and reaction time for complete conversion (85% e.e., entry 2) (Scheme 3).

The standard set of reaction conditions (4 bar of hydrogen, 50°C, 24 h) was applied to β-keto esters bearing linear alkyl chains such as methyl 3-oxo-pentanoate **11**, ethyl 3-oxo-hexanoate **13** and methyl 3-oxo-octadecanoate **15** to afford, respectively, the corresponding β-hydroxy esters (*S*)-**12**, (*S*)-**14** and (*R*)-**16** with high levels of enantioselectivity (entries 3–5). Hydrogenation of a branched alkyl-substituted β-keto ester such as ethyl isobutyrylacetate **17** yielded (*R*)-ethyl 3-hydroxy-4-methylpentanoate **18** in 99% e.e. using (*S*)-MeO-BIPHEP (entry 6) and in lower enantiomeric excess with (*R*,*R*)-Me-DuPHOS (89% e.e., entry 7). Methyl 3-oxo 3-(2-thiophenyl) propanoate **19** has been reduced to the corresponding β-keto ester (*R*)-**20** at 10 bar and 30°C in 76% e.e. (entry 8). Hydrogenation of ethyl benzoylacetate **21** catalyzed by (*S*)-MeO-BIPHEP/$RuCl_3$ under the standard conditions yielded (*R*)-**22** in 88% e.e. (entry 9), while the reaction at 80°C afforded the desired alcohol with higher enantioselectivity (95% e.e., entry 10). This temperature effect was also observed in the reduction of ethyl 4-chloro-acetoacetate **23** to (*R*)-**24** since increase of the temperature from 50 to 120°C allowed a much better level of enantioselectivity (57–92% e.e., entries 11–13). Finally, reduction



Scheme 3.

Table 3. Ru-catalyzed hydrogenation of prochiral C=O and C=C bonds using $RuCl_3$+(*S*)-MeOBIPHEP

Entry	Substrate	Ligand P*P	Conditions			e.e. (%)	Conf.
			P (bar)	*T* (°C)	*t* (h)		
1		(*S*)-MeO-BIPHEP	4	50	17	69	(*S*)-**28**
2		(*S*)-MeO-BIPHEP	4	80	17	80	
3	**27**	(*S*)-MeO-BIPHEP	4	99	17	88[a]	
4	 **29**	(*S*)-MeO-BIPHEP [b]	4	50	48	94[c]	(*S*)-**30**
5	 **31**	(*S*)-MeO-BIPHEP	4	r.t.	17	99[d]	(*S*)-**32**
6	 **33**	(*S*)-MeO-BIPHEP	5	50	65	98[e]	(*R*)-**34**
7	 **35**	(*S*)-MeO-BIPHEP	4	50	17	79[f]	(*S*)-**36**

[a] Enantiomeric excess was determined by chiral GC analysis (Lipodex A column).
[b] 2 mol% of chiral Ru-catalyst
[c] Enantiomeric excess was determined by ^1H NMR (400 MHz) with $Eu(tfc)_3$
[d] Enantiomeric excess was determined by chiral GC analysis (Chiralsil Val-2 column).
[e] Enantiomeric excess was determined by chiral GC analysis (Megadex 5 column).
[f] Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD-H column).

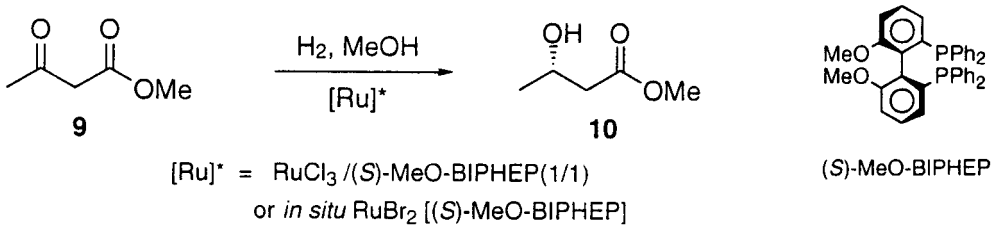
of ethyl 4,4,4-trifluoro-3-oxo butanoate **25** at 120°C afforded (*R*)-**26** in 50% e.e., a value which compares favorably with those previously reported.[27,28] The above results are comparable with those obtained using the chiral Ru(II)-catalysts prepared in situ.[23,29,30]

Expansion of these studies to other substrates revealed that the (*S*)-MeO-BIPHEP/$RuCl_3$ catalyst provides a general, enantioselective method for the reduction of functionalized ketones and alkenes (Table 3). Hydrogenation of methyl phenylglyoxylate **27** was carried out under the usual conditions and afforded (*S*)-mandelate **28** in a moderate 69% e.e. (entry 1). However, when conducted at 99°C, the hydrogenation reaction yielded quantitatively (S)-**28** in 88% e.e. (entry 3). This (*S*)-MeO-BIPHEP/$RuCl_3$ system was also found to serve as an excellent catalyst for the hydrogenation of β-keto sulfones. Thus, (*S*)-1-(phenylsulfonyl)tridecan-2-ol **30** has been prepared with high enantioselectivity (94% e.e., entry 4). Excellent enantiofacial discrimination was also achieved for the ruthenium-mediated hydrogenation of β-keto phosphonates such as dimethyl 2-oxoheptylphosphonate **31** and diethyl 2-oxo 2-phenylphosphonate **33** leading, respectively, to (*S*)-**32** (99% e.e. at room temperature, entry 5) and (*R*)-**34** (98% e.e., entry 6). Comparable yields and enantioselectivities were observed using the in situ generated Ru(II)-complexes in the hydrogenation of compounds **29**[31] and **31**.[32] Finally, (*Z*)-methyl α-acetamidocinnamate **35** was hydrogenated to the corresponding (*S*)-*N*-acetylphenyl alanine methyl ester **36** in 79% e.e. (entry 7).

We have previously reported that in situ ruthenium-complexes prepared from Ru(COD)(η^3-methylallyl)$_2$ were efficient catalysts at 1 atm pressure of hydrogen[29] and it was therefore of interest to study the efficiency of the $RuCl_3$/(*S*)-MeO-BIPHEP system under these very mild conditions. As shown in Table 4, we found that the above catalytic system appears less reactive at atmospheric pressure and 50°C

Table 4. Comparative study between $RuCl_3$+(*S*)-MeO-BIPHEP and in situ $RuBr_2$[(*S*)-MeO-BIPHEP]

Entry	Catalyst	Conditions			Conv. (%)	e.e. (conf.)
		P (bar)	*T* (°C)	*t* (h)		
1	2 mol% $RuBr_2$[(*S*)-MeO-BIPHEP]	1	50	48	100	99(*S*)
2	2 mol% [$RuCl_3$+(*S*)-MeO-BIPHEP]	1	50	48	0	–
3	2 mol% [$RuCl_3$+(*S*)-MeO-BIPHEP]	4	Rt	48	100	98(*S*)
4	0.1 mol% [$RuCl_3$+(*S*)-MeO-BIPHEP]	4	50	48	85	99(*S*)
5	0.1 mol% $RuBr_2$[(*S*)-MeO-BIPHEP]	4	50	48	100	99(*S*)
6	0.03 mol% $RuBr_2$[(*S*)-MeO-BIPHEP]	4	50	24	100	99(*S*)
7	0.1 mol% [$RuCl_3$+(*S*)-MeO-BIPHEP]	50	50	48	100	99(*S*)



Scheme 4.

compared to the in situ generated Ru(II)-catalysts. (*S*)-methyl 3-hydroxybutyrate **10** was quantitatively obtained in enantiomerically pure form using $RuBr_2$[(*S*)-MeO-BIPHEP] (entry 1) while no conversion was observed under these conditions with the present catalytic system (entry 2). However, at higher pressure of hydrogen (4 bar), $RuCl_3$/(*S*)-MeO-BIPHEP furnished quantitatively (*S*)-**10** at room temperature in 98% e.e. (entry 3). These asymmetric hydrogenations are of potential industrial importance for the production of chiral compounds as demonstrated by Noyori[9] and us.[25,33–35] Thus it was of interest to carry out these reactions with low catalyst loading. The $RuCl_3$/(*S*)-MeO-BIPHEP system was found to display lower activity than the corresponding homogeneous species prepared in situ. The reaction using (*S*)-MeO-BIPHEP/$RuCl_3$ with a catalyst/substrate ratio of 1:1000 at 4 bar and 50°C furnished (*S*)-methyl 3-hydroxybutyrate **10** in only 85% yield (entry 4) while complete conversion and 99% e.e. were obtained with the in situ $RuBr_2$[(*S*)-MeO-BIPHEP] complex under the same conditions (entry 5) or with a lower catalyst/substrate ratio of 1:3000 (entry 6).[36] However, when the reaction was performed at higher pressure of hydrogen (50 bar) the former system furnished quantitatively (*S*)-**10** in 99% e.e. (entry 7) (Scheme 4).

3. Conclusion

In conclusion, $RuCl_3$/chiral diphosphine is an efficient system in asymmetric hydrogenation of a wide range of functionalized ketones leading to high levels of enantioselectivity. Furthermore, anhydrous $RuCl_3$ is the most available and inexpensive ruthenium precursor to chiral Ru-catalysts reported to date. In addition, this preparation does not require multistep reactions or isolation of intermediates and is easy to perform. Our method will allow a particularly rapid screening of new chiral diphosphines and may offer new opportunities for industrial synthetic applications. Further studies aimed at investigating the scope of this simple preparation are continuing.

4. Experimental

4.1. Typical procedure for the asymmetric hydrogenation of prochiral ketones and alkenes

(*S*)-MeO-BIPHEP (5.8 mg, 0.01 mmol) and anhydrous $RuCl_3$ (2.1 mg, 0.01 mmol, purchased from Aldrich chemicals) were placed in a Schlenk tube and degassed by three cycles of vacuum/argon at room temperature. Degassed methanol (2 mL) and the prochiral ketone (1 mmol) were added. The resulting mixture was placed under the desired hydrogen pressure and temperature until complete conversion. All reactions were run on a 1 mmol scale and led to the corresponding functionalized alcohols in quantitative yields except when specified.

Acknowledgements

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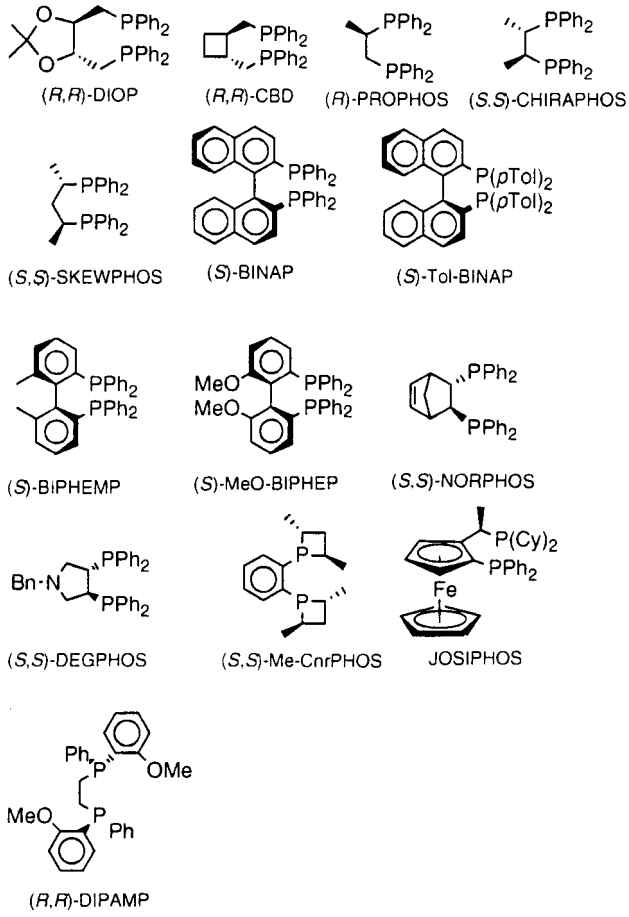
10. Chiral diphosphines structures:



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