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NOVEL, GENERAL SYNTHESIS OF THE CHIRAL CATALYSTS DIPHOSPHINE-RUTHENIUM (II) DIALLYL COMPLEXES AND A NEW PRACTICAL *IN SITU* PREPARATION OF CHIRAL RUTHENIUM (II) CATALYSTS

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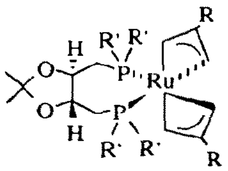
Abstract : A general and new synthesis of hexacoordinate chiral 1-[2-methylallyl]Ru^{II} 2 complexes is presented. This synthesis uses the very accessible CODRu(2-methylallyl)$_2$ complex as starting material. These complexes (P*P)Ru(η^3-(CH$_2$)$_2$CCH$_3$)$_2$ (e.g. P*P=DIOP, CBD, DEGUPHOS, BINAP, BIPHEMP, CHIRAPHOS, PROPHOS, DIMPC, BPPM, BDPP, DIPAMP, DIPAMPSi, β-PO-OP) have been characterized spectroscopically. X-Ray structures were obtained for (S,S)-DIOP and (S,S)-CHIRAPHOS. They are suitable for the preparation of chiral dihalide ruthenium (II) catalysts. In addition, we have found that it was possible to prepare these same catalysts directly ***in situ*** from (COD)Ru(η^3-(CH$_2$)$_2$CCH$_3$)$_2$ by adding 1-1.3 equiv. of the appropriate chiral ligand in the presence of HX in acetone at room temperature.

Introduction

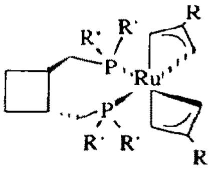
In the field of asymmetric hydrogenation, spectacular achievements have been made by using homogeneous catalysts. A great number of chiral diphosphines have been prepared and used with rhodium complexes[2]. They are easily available from dimeric rhodium species [RhCl(olefin)$_2$]$_2$[1]. The first chiral Ru^{II} catalyst RuDiop$_3$Cl$_4$ was discovered by James in 1975[2]. Several other halogen containing Ru^{II} complexes bearing chiral diphosphines have been also proposed[2]. More recently asymmetric hydrogenation using the BinapRu(η^2-O$_2$CCH$_3$)$_2$ and BinapRu(arene)Cl have been introduced by Noyori and Takaya[3] and [BinapRuCl$_2$]$_2$NEt$_3$ by Ikariya and Saburi[4]. These catalysts have found wide application in asymmetric hydrogenation with outstanding performances[5]. We have also introduced a new class of mononuclear chiral Ru^{II} catalysts, (P*P)Ru(η^3-(CH$_2$)$_2$CCH$_3$)$_2$[6]. Our synthetic general method allows the production of ruthenium complexes from a wide variety of diphosphines : Diop, Chiraphos, atropisomeric diphosphines and diphosphines having chirality at the phosphorus atom such as Dipamp [7]. Heiser has found a synthetically useful method for the first *in situ* preparation of atropisomeric diphosphines Ru^{II} bisacetate complexes including Binap, Biphemp and MeO-Biphep[8]. Brown has also described a facile preparation of a new chiral

P * P Ru(II)(2-methylallyl)$_2$ complexes ; P*P Ru(II)L$_2$

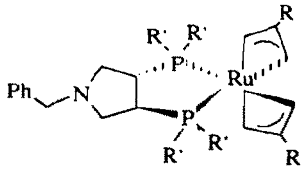
(L_2 =(2-methylallyl)$_2$, R=Me, R'=Ph)



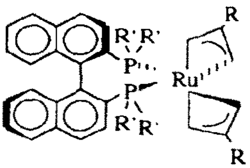
(R,R)-(-)-DIOPRu(II)L_2
71%



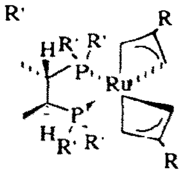
(R,R)-(+)-CBDRu(II)L_2
65%



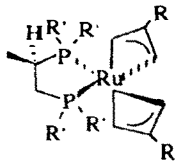
(S,S)-DEGUPHOSRu(II)L_2
58%



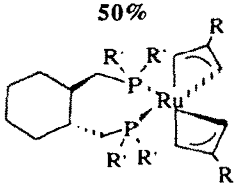
(R)-(+)-BINAPRu(II)L_2
50%



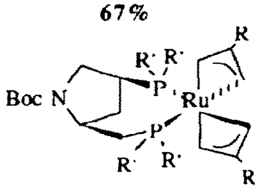
(S,S)-(-)-CHIRAPHOSRu(II)L_2
67%



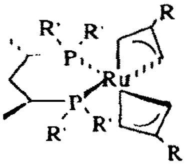
(R)-PROPHOSRu(II)L_2
75%



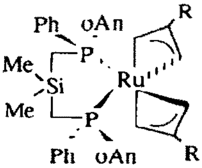
(R,R)-(-)-DIMPCRu(II)L_2
74%



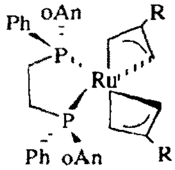
(S,S)-(-)-BPPMRu(II)L_2
60%



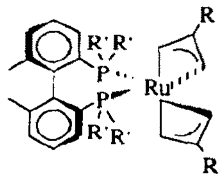
(S,S)-(-)-BDPPRu(II)L_2
70%



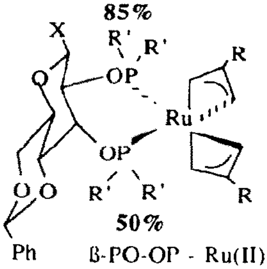
(R,R)-DIPAMPSiRu(II)L_2
50%



(R,R)-DIPAMPRu(II)L_2
85%



(S)-(+)-BIPHEMPRu(II)L_2
50%



50%

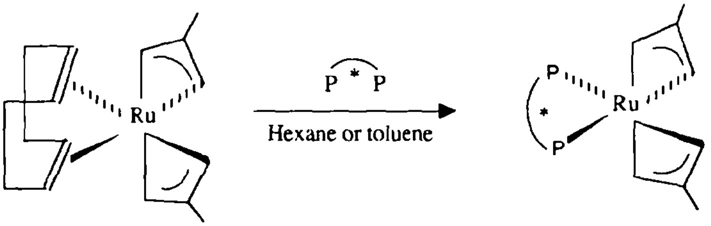
ß-PO-OP - Ru(II)L_2
X = OPh

Table 1

complex (P*P)Ru(allyl)(η^3-O_2hexafluoroacetylacetonate)[9]. These conditions were suitable for the preparation of several catalysts from various diphosphines. Very recently, several other groups have described new improvements[10] for the synthesis of Binap Ru catalysts including the Ikariya and Saburi complex[4]. We report here the synthesis of a novel family of mononuclear Ru^{II} complexes containing chelating phosphines.

Results and Discussion

In the preparation of P*P bidendate chiral Ru^{II} complexes (2-methylallyl)[11], the starting point of this study was the readily accessible $(COD)Ru^{II}(\eta^3\text{-}(CH_2)_2CCH_3)_2$ **1** [12] as starting material easily prepared in quantitative yield from the polymeric material $(RuCl_2COD)_n$ [13].The complexes were isolated after heating $(COD)Ru^{II}(\eta^3\text{-}(CH_2)_2CCH_3)_2$ in hexane or toluene in the presence of the appropriate chiral ligand (e.g. : DIOP, CBD, DEGUPHOS, CHIRAPHOS, DIMPC, BPPM, BDPP, β PO-OP). After displacement of 1,5 cyclooctadiene (COD), the hexacoordinate Ru^{II} catalysts **2** were isolated in 50-85% yield as shown in table 1.



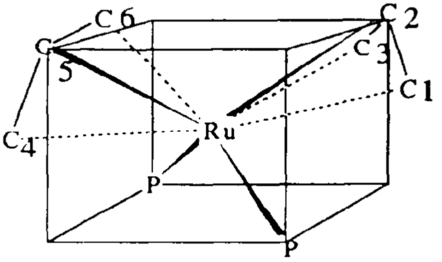
1 **2**

Scheme 1

We have developed an efficient method for the preparation of diphosphines with two stereogenic phosphorus atoms (R,R)-DIPAMP [15] and modified (R,R)-DIPAMPSi [16]. The COD ligand exchange reaction of **1** (scheme 1) with these chelating diphosphines, afforded in 50 to 85% yields respectively the desired Ru-complexes **2**. The method described above was also applied to Binap and Biphemp [17]. However the displacement of COD in **1** required higher temperatures (100-110°C, in toluene) for 5h to get an acceptable conversion. For these corresponding catalysts (Binap or Biphemp)Ru^{II}, it was not possible to characterize unambiguously their structures by ^1H or ^{13}C NMR. However, the ^{31}P NMR showed in both cases a common singlet at δ 27 ppm.

The structures of this full set of chiral catalysts are summarized in table 1. Most of these new chiral ruthenium (II) hexacoordinate complexes were isolated in an analytically pure state (except Binap and BiphempRu^{II}) and have been characterized by ^1H, ^{13}C, ^{31}P, IR, mass spectrum and elemental analysis. The ^{31}P NMR spectra observed for the 5-membered ring ruthenium (II) complexes with chelating 1.2 diphosphines exhibited phosphorus resonance at δ 91-97 ppm range except for Deguphos (δ 64 ppm) whereas the ^{31}P NMR spectra of the 7-membered ring Ru complexes with ligands such as Bppm, Diop, Cbd, Binap showed resonances at higher field (δ 56-21ppm). This observation has already been reported for related complexes $(Ph_2P(CH_2)_nPPh_2RuOAc)BF_4$ [18]. Interestingly, the ^{13}C NMR of all of these Ru^{II} complexes exhibited for the central carbon of the allyl moiety signals at δ 94-97 ppm range except for Bppm and Prophos which revealed two signals at δ 95.5 and 94.4 ppm and δ 96.4 and 96.7 ppm respectively.

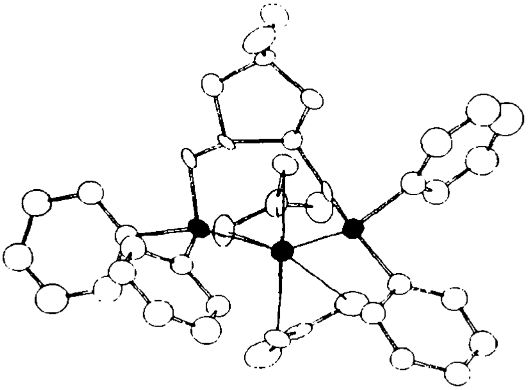
The structure of two of these complexes has been confirmed by X-ray crystallography. Figure 1 shows the structure of the mononuclear unit of (S,S)-DIOPRu^{II}(η^3-$(CH_2)_2CCH_3)_2$ and (S,S)-CHIRAPHOS Ru^{II}(η^3-$(CH_2)_2CCH_3)_2$.



Scheme 2

The ruthenium atom is η3 coordinated to the approximately planar allyl ligand as depicted in scheme 2. The ruthenium atom has distorted octahedral geometry defined by the two phosphorus atoms and the two η^3 allyl ligands. The Ru-P bond distances for these two complexes fall within the range reported for related $(allyl)_2Ru(PPh_3)_2$ complexes [19]. In contrast, P-Ru-P angles (table 2 and 3) are smaller (96.8° for Diop and 84.9° for Chiraphos) than those reported with triphenyl phosphine. However, these values fall within the range reported for diphosphine Ru^{II} catalysts[3a, 9, 2d].

The ruthenium - C_2 (Ru-C_2) carbon bond is shorter than the Ru-C_1 and Ru-C_3 bonds. The lengths as well as the angles for the η3-allyl moiety of (S,S)-DiopRu^{II}(η^3-$(CH_2)_2CCH_3)_2$ and (S,S)-ChiraphosRu^{II}(η^3-$(CH_2)_2CCH_3)_2$ are summarized in table 2 and 3.



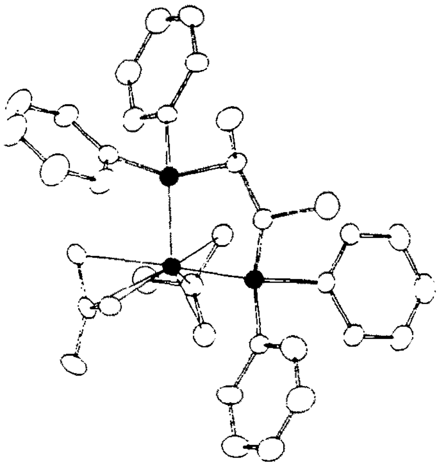
(S,S)-DIOPRu(2-methylallyl)$_2$

	Bond lengths (Å)	
d(Ru-P)	2.325 2.342	
d(Ru-C_2)	2.17	
d(Ru-C_5)	2.19	
d(C_2-C_1) ; d(C_2-C_3)	1.40	1.45
d(C_5-C_4) ; d(C_5-C_6)	1.38	1.38
d(Ru-CH_2)	2.24	2.25
(C_1, C_3, C_4, C_6)	2.25	2.29

	Bond angles (°)	
α (P-Ru-P)	96.8	
α (P-Ru-C_2)	119.5	122.6
α (P-Ru-C_5)	110.1	108.4

Table 2

Perspective views of (S,S)-DIOP Ru^{II}(η^3-$(CH_2)_2CCH_3)_2$



(S,S)-CHIRAPHOSRu(2-methylallyl)$_2$

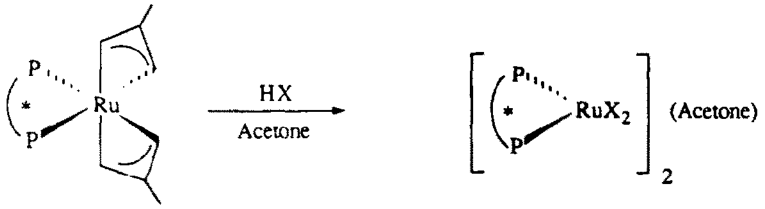
	Bond lengths (Å)	
d(Ru-P)	2.292 2.299	
d(Ru-C_2)	2.187	
d(Ru-C_5)	2.189	
d(C_2-C_1) ; d(C_2-C_3)	1.386	1.403
d(C_5-C_4) ; d(C_5-C_6)	1.41	1.39
d(Ru-CH_2) (C_1, C_3, C_4, C_6)	2.224 2.233	2.243 2.244
	Bond angles (°)	
α (P-Ru-P)	84.96	
α (P-Ru-C_2)	125.9	129.2
α (P-Ru-C_5)	110.1	109.2

Table 3

Perspective views of (S,S)-CHIRAPHOS $Ru^{II}(\eta^3\text{-}(CH_2)_2CCH_3)_2$.

This efficient and reliable synthesis of hexacoordinate mononuclear ruthenium complexes $(P^*P)Ru^{II}(\eta^3\text{-}(CH_2)_2CCH_3)_2$ allowed a general and easy preparation of halogen-containing complexes of the type $P^*P\ Ru^{II}\ X_2]_2$(acetone) **3** by mixing the chiral diphosphineRu(2-methylallyl)$_2$ and HX (X = Cl or Br) in a 1 : 2 ratio[20]. These catalysts were not isolated but used without any purification for asymmetric hydrogenation.

In the case of Ru^{II} catalysts containing chloride, these latter complexes were presumably dimeric species: $[P^*PRuCl_2]_2$(acetone) confirmed by ^{31}P NMR spectra observed in the case of Diop as ligand (2 AB patterns, δ=45.0ppm, J=47.5Hz and δ=51.5ppm J=43.7Hz) and in agreement with previous results reported by several authors[4a, 2f, 10h].

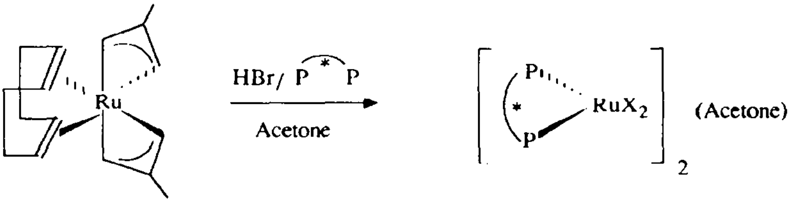


2 **3**

Scheme 3

Interestingly, in addition to the previous method of protonation of chiral catalyst $(P^*P)Ru^{II}(\eta^3\text{-}(CH_2)_2CCH_3)_2$ (scheme 3), we were pleased to find a new and short method of preparation of chiral ruthenium (II) dibromide complexes :$[X_2Ru\ P^*P]_2$(acetone). These chiral catalysts were also prepared directly *in situ* under one set of conditions (scheme 4) from (COD)$Ru(\eta^3\text{-}(CH_2)_2CCH_3)_2$ by adding at room temperature in acetone 1.2 equiv. of the appropriate chiral ligand in the presence of HX. After stirring 30 min and removal of the solvent, some of these resulting complexes preformed (scheme 3) or prepared *in situ* (scheme 4) were examined by ^{31}P NMR.

The ^{31}P NMR(100MHz) spectra of [CbdRuBr$_2$]$_2$(acetone), [ChiraphosRuBr$_2$]$_2$(acetone) and [BinapRuBr$_2$]$_2$(acetone) preformed (scheme 3) and prepared *in situ* (scheme 4) were studied in order to compare the different species present for each chiral catalyst : the ^{31}P NMR spectra indicated clearly a single common species between the catalyst preformed and prepared *in situ* in the case of [CbdRuBr$_2$]$_2$(acetone) (AB pattern, δ 55.4 ppm, J=39.4Hz). However, for Chiraphos and Binap, in addition to the common species observed for [ChiraphosRuBr$_2$]$_2$(acetone) (singlet, δ 40.5 ppm) and [BinapRuBr$_2$]$_2$(acetone) (singlet, δ 40.1 ppm), we noticed the presence of additional species not clearly identified.



1 **3**

Scheme 4

Conclusion

Firstly, the present paper describes a new synthesis of chiral ruthenium(II) hexacoordinate complexes starting with (COD)Ru(η^3-(CH$_2$)$_2$CCH$_3$)$_2$[12], which consists of a generally mild exchange between cyclooctadiene (COD) and a wide range of optically active ligands including Diop, Chiraphos, Prophos, Cbd, Binap, Biphemp etc as well as chiral ligands having the phosphorus atom (Dipamp) as stereogenic center. Secondly, the application of this study as well as the new *in situ* generation of a whole set of new chiral catalysts presented in the following paper demonstrates the general character of our method.Thirdly, our method allows the rapid screening of a large set of new chiral diphosphines with preformed or prepared *in situ* ruthenium (II) complexes in asymmetric hydrogenation as demonstrated in the following paper.

Our new method of *in situ* preparation of dihalogeno chiral ruthenium (II) complexes offers some advantages compared to methods previously described[19] in the literature : very mild reaction conditions, availability of the stable (COD)Ru(η^3-(CH$_2$)$_2$CCH$_3$)$_2$[12] and finally compatibility with various new chiral diphosphines.

Acknowledgments · We appreciate Elf Aquitaine for providing generous financial support and grants to S. Mallart, C. Pinel and X. Pfister as well as CNP$_q$ (Brazil) for a fellowship to M.C. Cano De Andrade. We thank Dr B. Heiser (Hoffman La Roche) for a gift of (+)-(S)-Biphemp and Dr C. Mercier (Rhône-Poulenc) for providing us with a sample of (+) and ( ) CBD. We also thank Dr. H. Frauenrath (Institut organische chemie der technische Hochschule) for a sample of β-PO OP. We are also very gratefull to Dr J. Waisserman

(Laboratoire Chimie des métaux de transitions, Université P. & M. Curie) for the determination of X-ray structures.

Experimental

General Methods

$RuCl_3, 3H_2O$, Binap, Diop are commercially available from Janssen Chimica. Chiraphos, Prophos, Bppm, Dimpc are commercially available from Aldrich. Bnpe, Dipamp and DipampSi were prepared according to the published procedure[15, 16]. The following solvents were freshly distilled and stored under argon prior to use : hexane and toluene from calcium hydride, methanol from magnesium turnings. All experiments with organometallic elements were performed in a nitrogen-filled dry box or by using standard Schlenk techniques.^1H and ^{13}C Nuclear Magnetic Resonance (NMR). Spectra were recorded on a Bruker AM-250 or Bruker AM-200 Fourier transform spectrometer.Spectra were obtained in benzene-*d* or chloroform-*d*. Chemical shifts are reported in parts per million (ppm) with TMS as an internal reference, and coupling constants are reported in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin-Elmer 297 spectrometer.

Preparation of 1/n $(CODRuCl_2)_n$[18]

2.45 g (9.4 mmol) of ruthenium (III) chloride trihydrate were dissolved in 95 % ethanol (100 mL). To this solution was added cyclooctadiene (9 ml, 75 mmol). The reaction medium was heated under reflux for 3 days. The deep green coloration disappeared and a brown precipitate was observed. After cooling to room temperature, the suspension was filtered off. The solid was washed with ethanol (2 x 30 mL) and dried in vacuo. 2.6 g of insoluble polymer were obtained (yield : 99 %).

Preparation of $(COD)Ru(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: following a modification of the literature procedure [12]
To a suspension of dichloro-[cyclo-octa-1,5-diene]-yl-ruthenium (II) (2.8g, 10 mM) in 30 mL of anhydrous ether was added a diethyl ether solution of 2-methylallyl magnesium chloride (60 mM, 0.4M). The mixture was stirred under argon for 2 hours. The resulting grey suspension was then filtered through celite. The filtrate was cooled to 0°C and hydrolyzed with 150mL of a mixture of ice-water and extracted with 2 x 100 mL of ether. The organic layers were dried ($CaCl_2$), filtered through alumina and evaporated to dryness.The resulting black residue was washed with 10mL of cold methanol to provide a pale grey solid (2.9g, yield 91%) which was recrystallized in a mixture of petroleum ether and methanol.

Preparation of chiral ruthenium (II) catalysts $(P^*P)Ru(\eta^3\text{-}(CH_2)_2CCH_3)_2$

General procedure :

$(COD)Ru(\eta^3\text{-}(CH_2)_2CHCH_3)_2$ (0.5 mM) and the chiral diphosphine (1 equiv.) were introduced in a Schlenk vessel. To these solids were added 2mL of degassed hexane and the mixture was then heated to 70°C (oil bath temperature) for 5 hours. A solid precipitated during the course of the reaction. The resulting solid was filtered under argon and washed with 1mL of degassed hexane. The diphosphineRu(methylallyl)$_2$ complexes obtained were stored under argon. For the preparation of Binap and BiphempRu(2-methylallyl)$_2$, the same procedure was employed except that hexane was replaced by toluene and the solution heated to 110°C for 5h. The reaction mixture was then cooled, evaporated in vacuo and washed with 1mL of degassed hexane.

(-)-DIOPRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 1.0 (m, 2H) ; 1.3 (s, 6H) ; 1.32 (q, J = 14.5 Hz, 4H) ; 2.04 (s, 6H) ; 2.55 (m, 2H) ; 2.79 (dd, J_1 = 8.5 Hz, J_2 = 13 Hz, 6H) ; 3.25 (t, J = 13 Hz, 6H) 4.15 (m, 2H) ; 6.8-8.0 (m, 20H, aromatics). ^{13}C NMR (62 MHz, C_6D_6) : 25.77 ; 27.2 ; 31.5 (m) ; 42.5 ; 48.31 (m) ; 78.8 ; 95.7 ; 107.9 ; 127 140 (aromatics). ^{31}P NMR (100 MHz, C_6D_6) : 36 (ref : H_3PO_4 85%). IR (Nujol) : 1595, 1240 cm^{-1} $[\alpha]_D^{25}$ – +202 (c = 0.43, toluene). m.p. = 204°C (decomposition).

(-)-CHIRAPHOSRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 1.06 (d, J = 6.5 Hz, 2H) ; 1.12 (d, J = 6.5 Hz, 2H) ; 1.24 (q, J = 2.5 Hz, 6H) ; 1.61 (d, J = 2.5 Hz, 2H) ; 1.74 (d, J = 2.5 Hz, 2H ; 2.15 (s, 6H) ; 6.8-8.0 (m, 20H, aromatics). ^{13}C NMR (62 MHz, C_6D_6) : 18.4 ; 26.1; 40.3 (m) ; 44.3 (d, J = 28 Hz) ; 44. 7 (d, J = 28 Hz) ; 45.9 ; 97.1 ; 127-133 (aromatics). ^{31}P NMR (100 MHz, C_6D_6) : 87.6 (ref : H_3PO_4 85%). IR (Nujol) : 1580, 1085, 1015, 760, 720 cm^{-1}.$[\alpha]_D^{25}$ = +60 (c = 0.2, toluene). m.p. = 183°C (decomposition).

(-)-BPPMRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{13}C NMR (62 MHz, C_6D_6) : 24.9 ; 26.8 ; 28.6 ; 31.2 ; MS (EI, 70 e. V.) : 707 ; 651 ; 605 ; 551 ; 526. 31.8 (d, J = 15 Hz) ; 34.7 ; 42.7 ; 43.8 (d, J = 25 Hz) $[a]_D^{20}$ = -183 (c = 0.4, toluene) 46.9 (d, J – 20 Hz) ; 49.7 ; 54.9 ; 56.6 (d, J – 25 Hz) m.p. = 160-165°C (decomposition).^{31}P NMR (100 MHz, C_6D_6) : 35.56 (ref : H_3PO_4 85%) IR (KBr) : 3047 ; 1698 ; 1681 cm^{-1}.

(+)-DIMPCRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 1.15 (m, 1H) ; 1.25 (d, J – 125 Hz, 2H) ; 1.50 (d, J – 100 Hz, 1H) ; 1.55 (m, 1H) ; 1.80 (s, 1H) ; 1.90 (d, J = 125 Hz, 1H) ; 2.00 (sl, 1H) ; 2.35 (s, 3H) ; 2.65 (dd, J = 5 Hz, J_2 = 12 Hz, 1H) ; 2.80 (t, J = 12 Hz, 1H) ; 3.15 (sl, 1H) ; 6.80-8.10 (m, 10H) ^{13}C (50 MHz, C_6D_6) : 25.8 ; 26.2 ; 38.2 ; 38.5 ; 40.6 ; 95.0 ; 126-135. ^{31}P NMR (100 MHz, C_6D_6) : 21 (ref : H_3PO_4 85%) IR : 697 ; 1432; 2919 cm^{-1}.$[\alpha]_D^{20}$ = -166 (c = 0.35, toluene). m.p. = 170°C. Anal. Calc. for $C_{40}H_{48}P_2Ru$ = C, 69.46 ; H, 6.95 ; P, 8.97 ; Ru, 14.62. Found C, 68.68 ; H, 6.99 ; P, 8.41 ; Ru, 15.46.

(-)-CBDRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 1.06 (dd, J = 17.5 Hz, J_2 = 5.0 Hz, 1H) 1.35 (m, 2H) ; 1.51 (d, J = 150 Hz, 1H) ; 1.63 (dl, J = 5.0 Hz, 1H) ; 2.10 (s, 3H) ; 2.18 (s, 1H) ; 2.50 (m, 3H) ; 6.95-8.00 (m, 10H).^{13}C NMR (50 MHz, C_6D_6) : 25.2 ; 27.0 ; 27.1 ; 39.5 ; 42.1 ; 94.2 ; 126-134. ^{31}P NMR (100 MHz, C_6D_6) : 21 (ref : H_3PO_4 85%) IR (KBr) : 697 ; 1026 ; 1087 ; 1432 2946. $[a]_D^{20}$ = -236 (c = 0.5, toluene). m.p. = 174-176°C (decomposition). Anal. Calc. for $C_{38}H_{44}P_2Ru$ = C, 68.78 ; H, 6.54 ; P, 9.35 Ru, 15.23 Found C, 66.92 ; H, 6.91 ; P, 8.55 ; Ru 16.65.

(+)-DEGUPHOSRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 0.70 (dd, J = 29.0 Hz, J_2 = 11.0 Hz, 2H) ; 1.35 (s, 1H) ; 2.00 (s, 3H) ; 2.10 (m, 1H) ; 2.90 (dl, J = 25.0 Hz, 2H) ; 3.30 (dd, J = 54.0 Hz, J_2 = 14.0 Hz, 1H) ; 3.85 (ls, 1H) ; 6.50-7.70 (m, 15H). ^{13}C NMR (62 MHz, C_6D_6) : 26.0 ; 30.0 (d, J = 7 Hz) ; 41.0 ; 43.0 ; 53.0 ; 61.0 ; 95.0 ; 125.0. ^{31}P NMR (100 MHz, C_6D_6) : 64 (ref : H_3PO_4 85%) IR (KBr) 523 ; 698 ; 1022 ; 2917 ; 3051. $[\alpha]_D^{20}$ = +40 (c = 0.14, toluene).

(+)-PROPHOSRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 1.05 (d, J = 5.0 Hz, 1H) ; 1.28 (d, J – 5.0 Hz, 1H) ; 1.48 (t, J = 6.0 Hz, 2H) ; 1.72 (t, J = 3.0 Hz; 3H) ; 2.0 (sl, 2H) ; 2.17 (d, J = 1.0 Hz, 1H) ; 2.49 (s, 3H) ; 2.66 (s, 3H) ; 2.7 (d, J = 1 Hz, 1H) ; 2.90 (m, 1H) ; 3.50 (m, 2H) ; 6.8-8.0 (m, 20H). ^{13}C NMR (62 MHz, C_6D_6) : 18.8 (dd, J = 10 Hz, J_2 = 30 Hz) ; 26.4 ; 26.6 ; 40.1 (dd, J = 32 Hz, J_2 = 38.0 Hz). ^{31}P NMR (100 MHz, C_6D_6) : 89.2 ; 71.2 (ref : H_3PO_4 85%). m.p. 195°C (decomposition).

(-)-BDPPRu$(\eta^3\text{-}(CH_2)_2CHCH_3)_2$: ^{1}H NMR (200 MHz, C_6D_6) : 0.83 (m, CH) ; 1.28 (m, 2H) ; 1.41 (sl, 2H) ; 2.12 (sl, 7H) ; 2.22 (sl, 4H) ; 2.78 (sl, 3H) , 5.60 (s, 1H) ; 7.10-7.60 (m, 20H). ^{13}C NMR (50 MHz, C_6D_6) : 18.7 ; 26.3 ; 28.3 ; 30.2 ; 31.9 ; 39.1 ; 90.5 ; 127-136. ^{31}P NMR (100 MHz, C_6D_6) : 51.7 (ref : H_3PO_4 85%). $[\alpha]_D^{20}$ = +255 (c = 0.32, toluene).

(-)-DIPAMPSiRu(η^3-$(CH_2)_2CHCH_3)_2$: ^{1}H NMR (250 MHz, C_6D_6) : 0.30 (s, 3H) ; 1.30 (dd, J = 12.0 Hz, J_2 = 15.5 Hz, 1H) ; 2.50 (s, 1H) ; 1.60 (t, J = 13.0 Hz, 1H) ; 1.80 (m, 2H) ; 2.30 (s, 3H) ; 2.94 (s, 1H) ; 2.97 (s, 3H) ; 6.40-7.66 (m, 9H). ^{13}C NMR (62 MHz, C_6D_6) : 25 ; 20.1 ; 26.6 ; 40.7 ; 49.0 (d, J = 24 Hz) ; 54.5 ; 96.1 ; 111.2-159.8. ^{31}P NMR (100 MHz, C_6D_6) : 38.7 (ref : H_3PO_4 85%).IR : 798 ; 1024 ; 1247 ; 1433 1477 ; 1569 ; 2944 . $[\alpha]_D^{20}$ = +186 (c = 0.5, toluene) m.p. = 180°C.

(-)-DIPAMPRu(η^3-$(CH_2)_2CHCH_3)_2$: MS (DCI/NH_3, au/z = 671, 615 (100%). ^{1}H NMR (250 MHz, C_6D_6) : 0.25 (d, J = 15.0 Hz, 2H) ; 1.10 (dd, J = 15 Hz, J_2 = 5.0 Hz, 2H) ; 1.70 (b, 2H) ; 2.22 (d, J = 2.0 Hz, 2H) ; 2.31 (s, 6H) ; 2.92 (s, 6H) ; 3.40 (m, 4H) ; 6.50-8.10 (m, 18H). ^{13}C NMR (62 MHz, C_6D_6) : 26.6 32.5 (dd, J = 27 Hz, J_2 = 2 Hz) ; 42.4 (d, J = 25 Hz) ; 44.3 ; 54.0 ; 96.1 ; 110.6 ; 120.6 ; 126.1-130.0 ; 134.6 142.3 ; 159.9. ^{31}P NMR (100 MHz, C_6D_6) : 85.0 (ref : H_3PO_4 85%).IR (nujol) : 750 ; 800 ; 1240 ; 1380 ; 1460. $[\alpha]_D^{20}$ = -43 (c = 0.23, toluene) m.p. = 183-185°C (decomposition). Calc. for $C_{36}H_{42}O_2P_2Ru$ = C, 64.57 ; H, 6.29 ; O, 4.78 ; P, 9.27 ; Ru, 15.10 found C, 64.84 ; H, 6.42 ; P, 8.28, Ru, 15.30.

β-PO-OP(η^3-$(CH_2)_2CHCH_3)_2$: ^{31}P NMR (100 MHz, C_6D_6) : 133.03 (ref. H_3PO_4 85 %). $[\alpha]_D^{20}$ = -180 (c = 0.5, $CHCl_3$).

(+)-BINAP or (+)-BIPHEMP)Ru(η^3-$(CH_2)_2CHCH_3)_2$: ^{31}P NMR (100MHz) -15; 27; 40 (ref : H_3PO_4 85%)

Preparation of dihalogenodiphosphine ruthenium (II) complexes: $[P^*PRuX_2]_2$

General procedure :

(COD)Ru(η3-$(CH_2)_2CCH_3)_2$ complex was dissolved in 1ml degassed acetone. To this solution were slowly added 2.2 equiv. of HX in methanol (X=Cl; Br; I). The resulting dark red solution was stirred for 1/2 hour, the solvent was removed under reduced pressure to give dihalogeno complexes which were used directly as hydrogenation catalysts as shown in the following paper.

Preparation of *in situ* dihalogenodiphosphine ruthenium(II) complexes: $[P^*PRuX_2]_2$

General procedure :

(COD)Ru(η3-$(CH_2)_2CCH_3)_2$ complex and the chiral diphosphine (1.2 equiv) were dissolved in 1ml degassed acetone and 2.2 equiv. of HX in methanol (X=Cl, Br, I) were slowly added. The resulting orange solution was stirred for 1/2 hour, the solvent was removed under reduced pressure to give dihalogeno complexes which were used directly as hydrogenation catalysts.

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