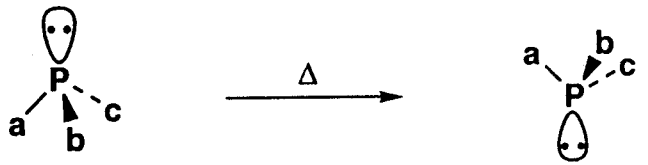
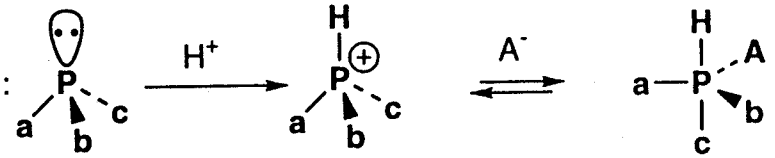
Some racemisation pathways for optically active phosphorus

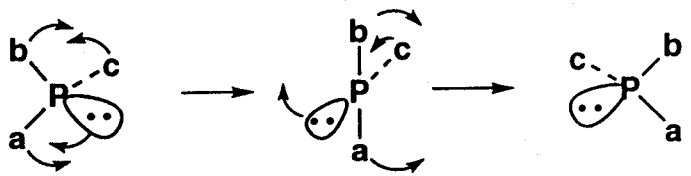
Pyramidal inversion :



Berry pseudorotation :



Edge inversion :

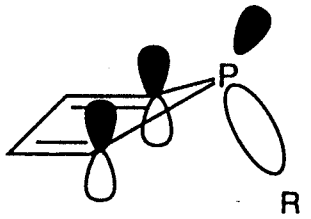


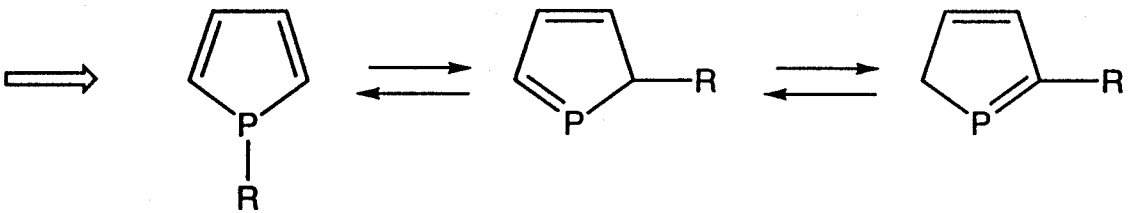
planar T-shaped

Arduengo ..., JACS,**108**, 2461 (1986)

The Phosphole - Cyclopentadiene Analogy

σ,π overlap in pyramidal phospholes:

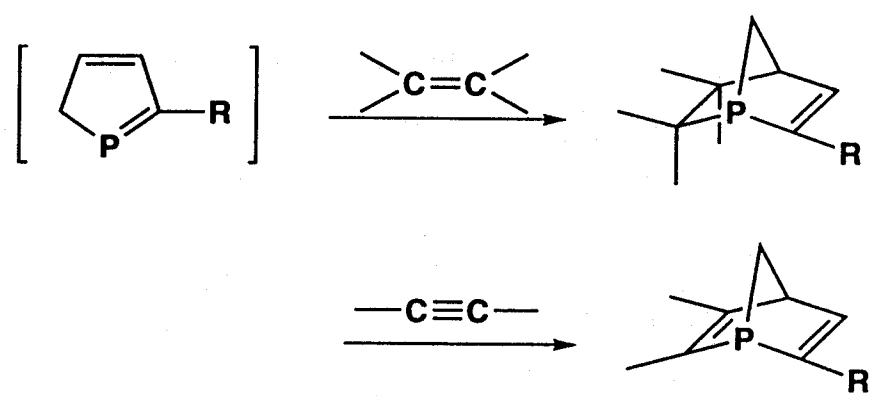




R migrates rather easily: H << 0°C, Ar ≈150°C, sp carbons (-C≡N, -C≡CPh) ≈100°C, also -SR, -PR_2, -SiR_3. No competition with 3*H*- phospholes. They are much higher in energy [Bachrach, JOC, **58**, 5414 (1993)].

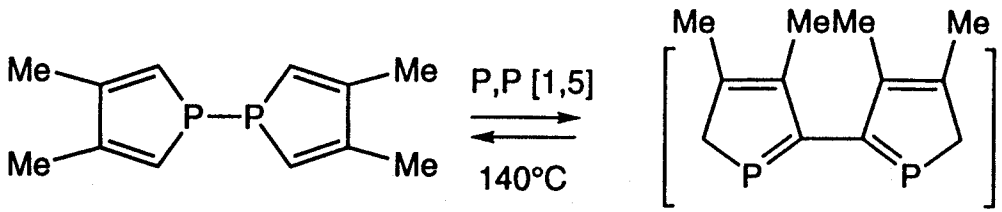
C. Charrier, H. Bonnard, G. de Lauzon, F. Mathey, JACS, 1983;
F. Laporte, F. Mercier, L. Ricard, F. Mathey, BSCF, 1993

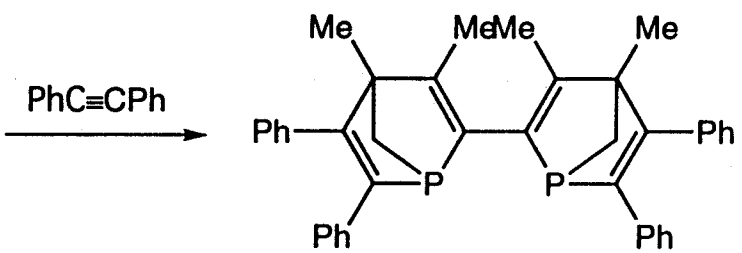
2-*H*-phospholes as 1-phosphadienes



LeGoff, Mathey, Ricard, *J. Org. Chem.* (1989)
Mathey, Mercier, Charrier, Fischer, Mitschler, *J. Am. Chem. Soc.* (1981)

Synthesis of a bis-phosphanorbornadiene



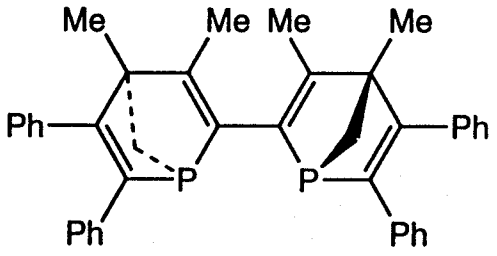


meso + racemate (30%)

The two diastereomers can be separated as their $PdCl_2$ complexes

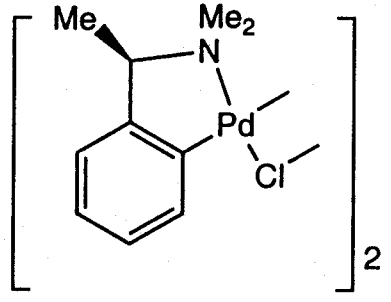
M.-O. Bévierre, F. Mercier, L. Ricard, F. Mathey,BSCF, 1992

The Performances of BIPNOR in Asymmetric Catalysis



(*R,R*)-(+)
(*S,S*)-(-) - BIPNOR

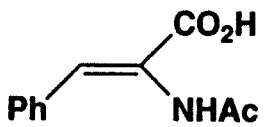
resolution by chromatography of the two diastereomeric Pd-BIPNOR-Pd dinuclear complexes obtained by reaction with the (*R*)-homochiral Pd_2 complex



preliminary experiments indicate ee's in the same range as those obtained with BINAP in the Rh-catalyzed asymmetric hydrogenation of dehydroaminoacids

F. Robin, F. Mercier, L. Ricard, F. Mathey, M. Spagnol

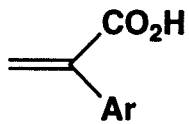
Asymmetric hydrogenation of functional alkenes



H_2 3 atm, cat. 1%
EtOH, 25°C, 2h

$PhCH_2$-CH(NHAc)CO_2H

>98% ee (*S*)
100% conversion

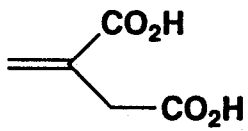


H_2 4 atm, cat. 1%
MeOH, 25°C, 2h

Ar = 6-methoxy-2-naphthyl

$PhCH_2$-CH(Ar)CO_2H

98% ee
30% conversion

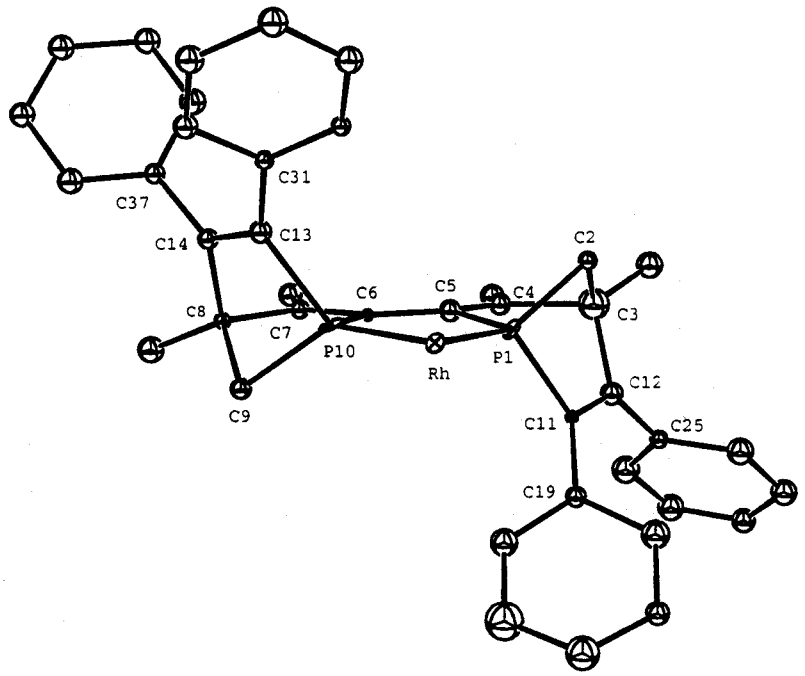


H_2 3 atm, cat. 0.5%
MeOH, 25°C, 40 min.

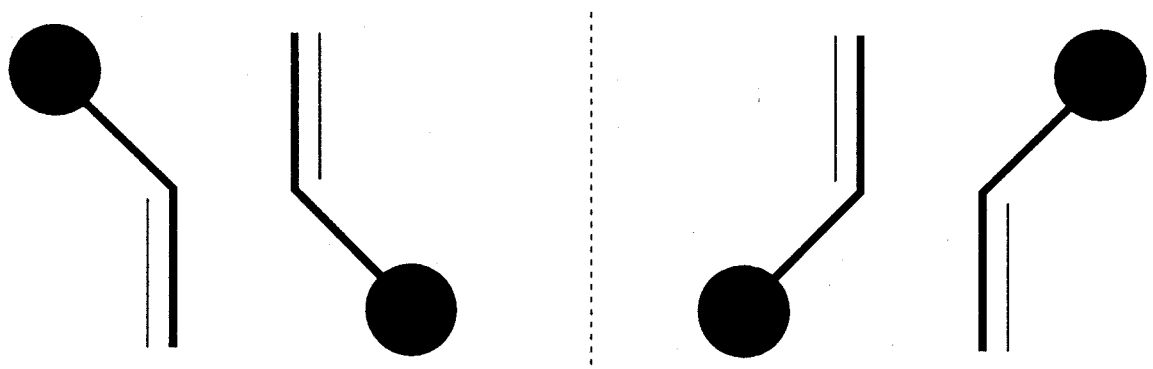
$PhCH_2$-CH(CO_2H)CH_2CO_2H

93% ee (*S*)
100% conversion

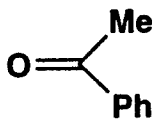
catalyst: [Rh(cod)(-)-BIPNOR)]$^+PF_6^-$ for cases 1 and 2
[Rh(cod)(+)-BIPNOR)]$^+PF_6^-$ for case 3



View of the [Rh(-)-BIPNOR] moiety of [Rh(cod)(-)-BIPNOR]$^{+}PF_6^{-}$ from the PRhP plane

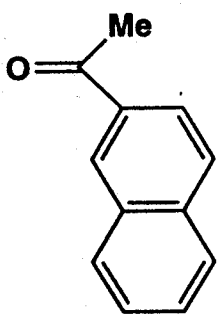


Asymmetric hydrogenation of ketones



H_2 60 atm, cat. 0.5%
MeOH, 50°C, 48h

PhCH(OH)Me
60% ee
30% conversion

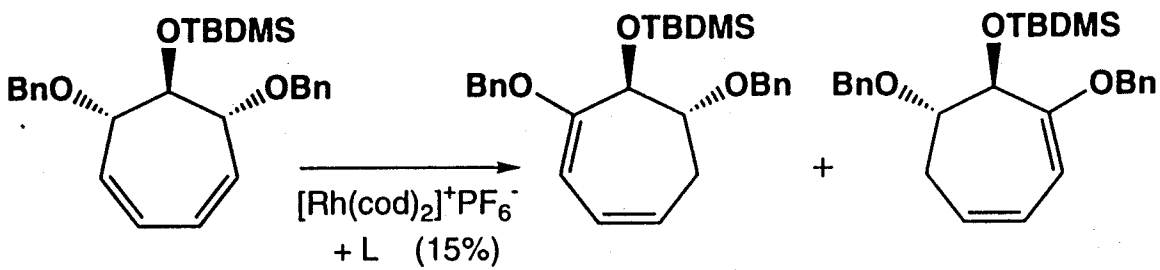


H_2 5 atm, cat. 0.2%
^{i}PrOH, 28°C, 10h

ArCH(OH)Me
81% ee (*R*)
65% conversion

catalyst: [$RuBr_2$(+)-BIPNOR)] for case 1
[$RuBr_2$(+)-BIPNOR)] + KOH + (*S,S*)-1,2-diphenyl-1,2-ethanediamine for case 2

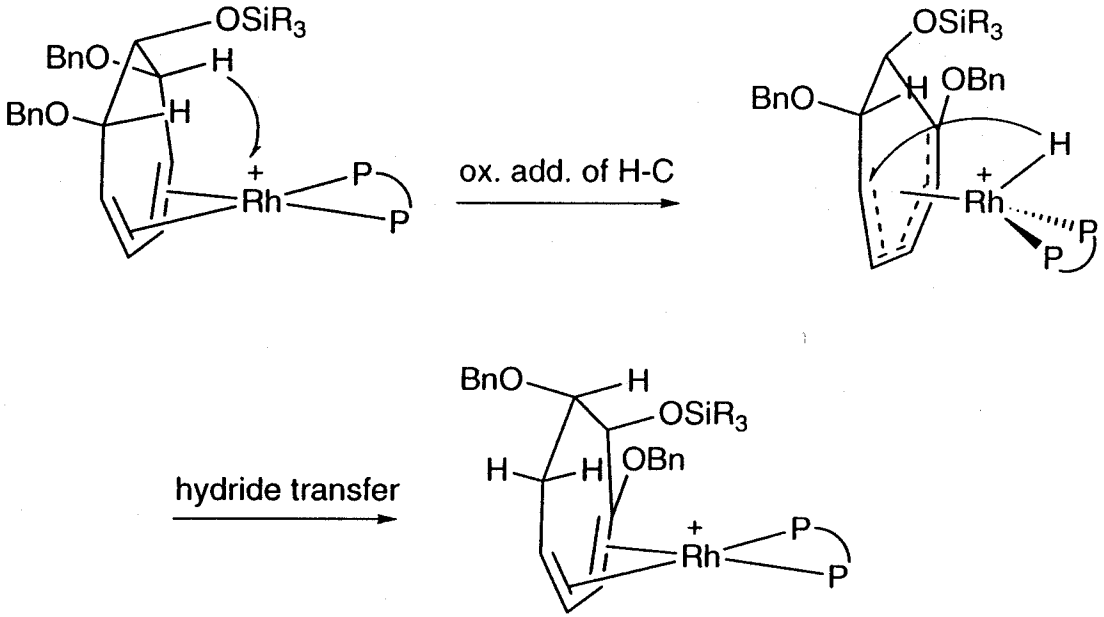
Asymmetric isomerisation of a cyclic diene



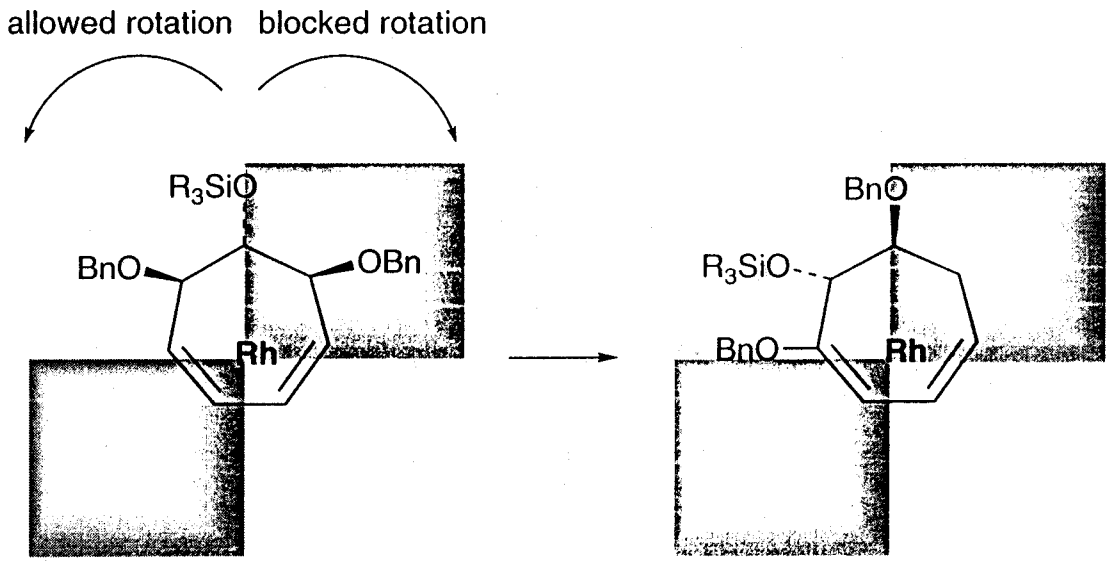
L	Solvents	T°C	t (100% conv.)	ee
(+)-BIPNOR	THF/tol (1:1)	50°C	32 h	55
(+)-BINAP	"	"	24h	31
(+)-BIPNOR	DME/tol (1:3)	90°C	5min.	91
(+)-BINAP	"	"	15min.	11

Th. Faitg, J. Soulié, J.-Y. Lallemand, F. Robin, F. Mercier, F. Mathey, to be published.

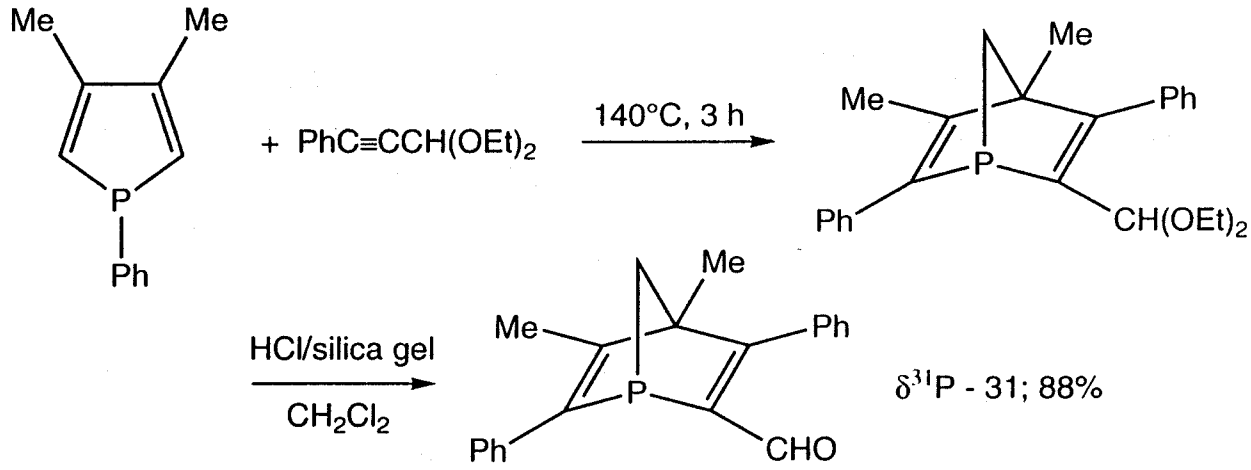
Proposed mechanism for the isomerisation of the cyclic diene



Origin of the enantioselectivity in the isomerisation of the cyclic diene

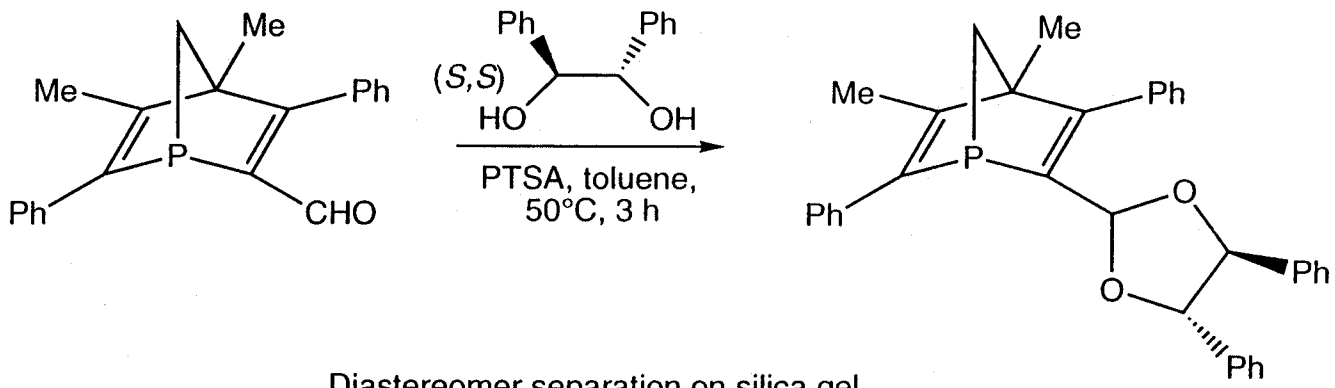


Synthesis of a 1-Phosphanorbornadiene-2-carboxaldehyde



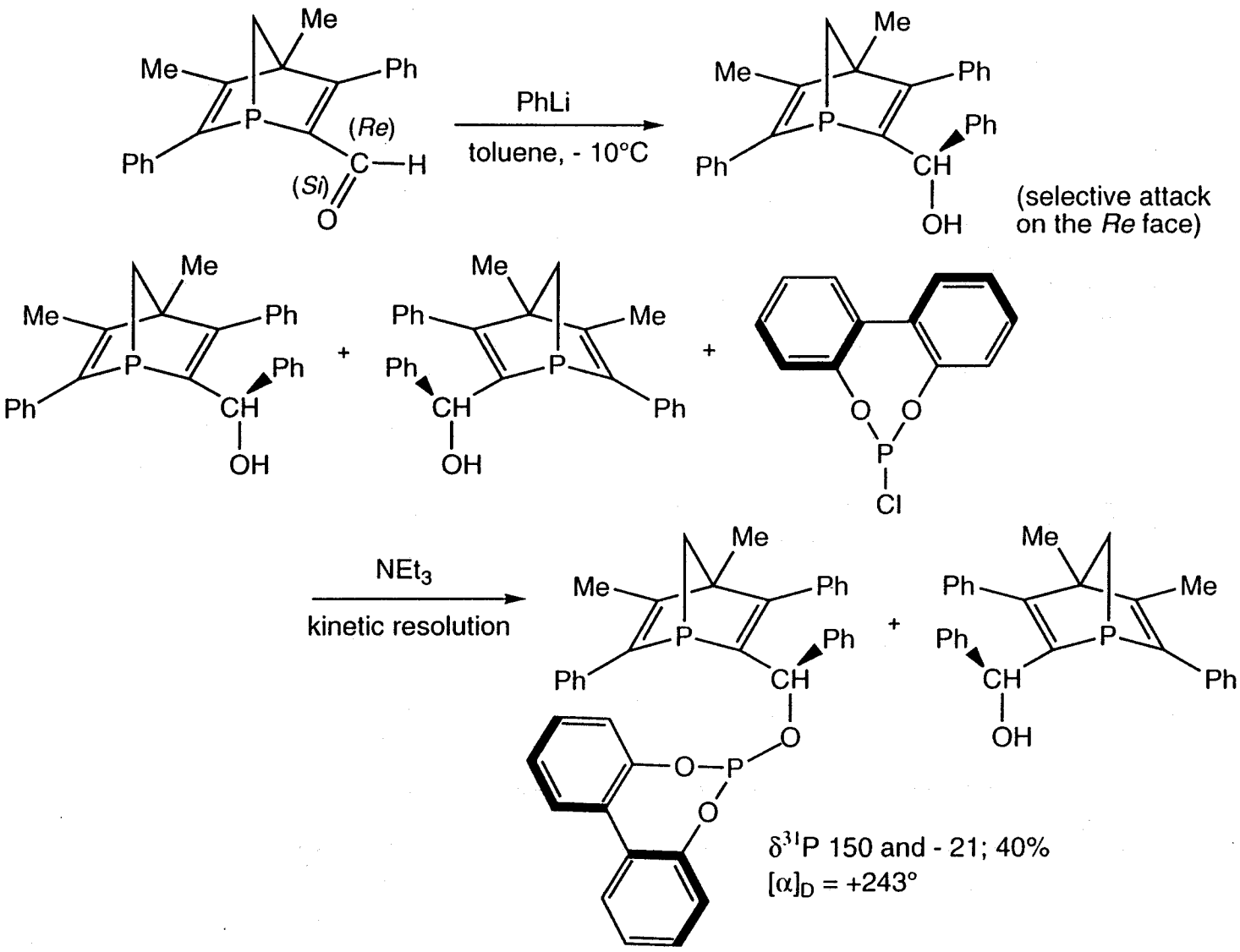
S. Lelièvre, F. Mercier, F. Mathey (1998)

Resolution of the Phosphanorbornadiene-1-carboxaldehyde

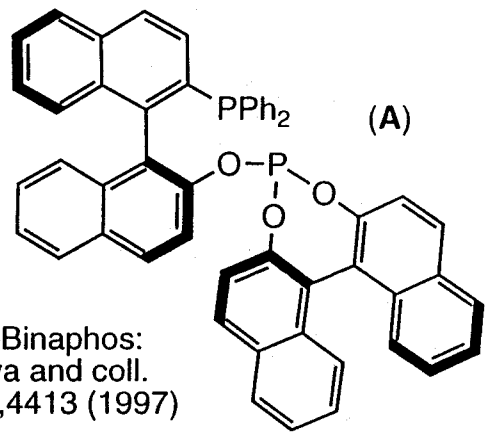


Diastereomer separation on silica gel
with hexane/dichloromethane 7/3
$[\alpha]_D$ = + 41.6 and + 200° (c =1, CH_2Cl_2)
Deprotection with HCl/silica gel/acetone
$[\alpha]_D$ = + 134.5 and - 133 (c =0.55, $CDCl_3$)

Synthesis of enantiopure Phosphanorbornadiene-phosphites

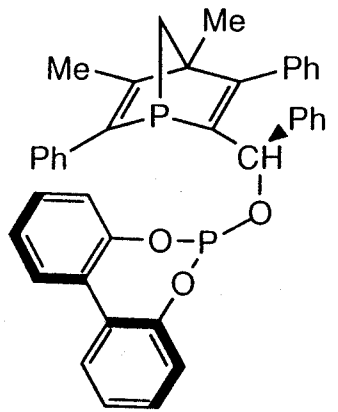


Hydroformylation of Styrene



(**A**)

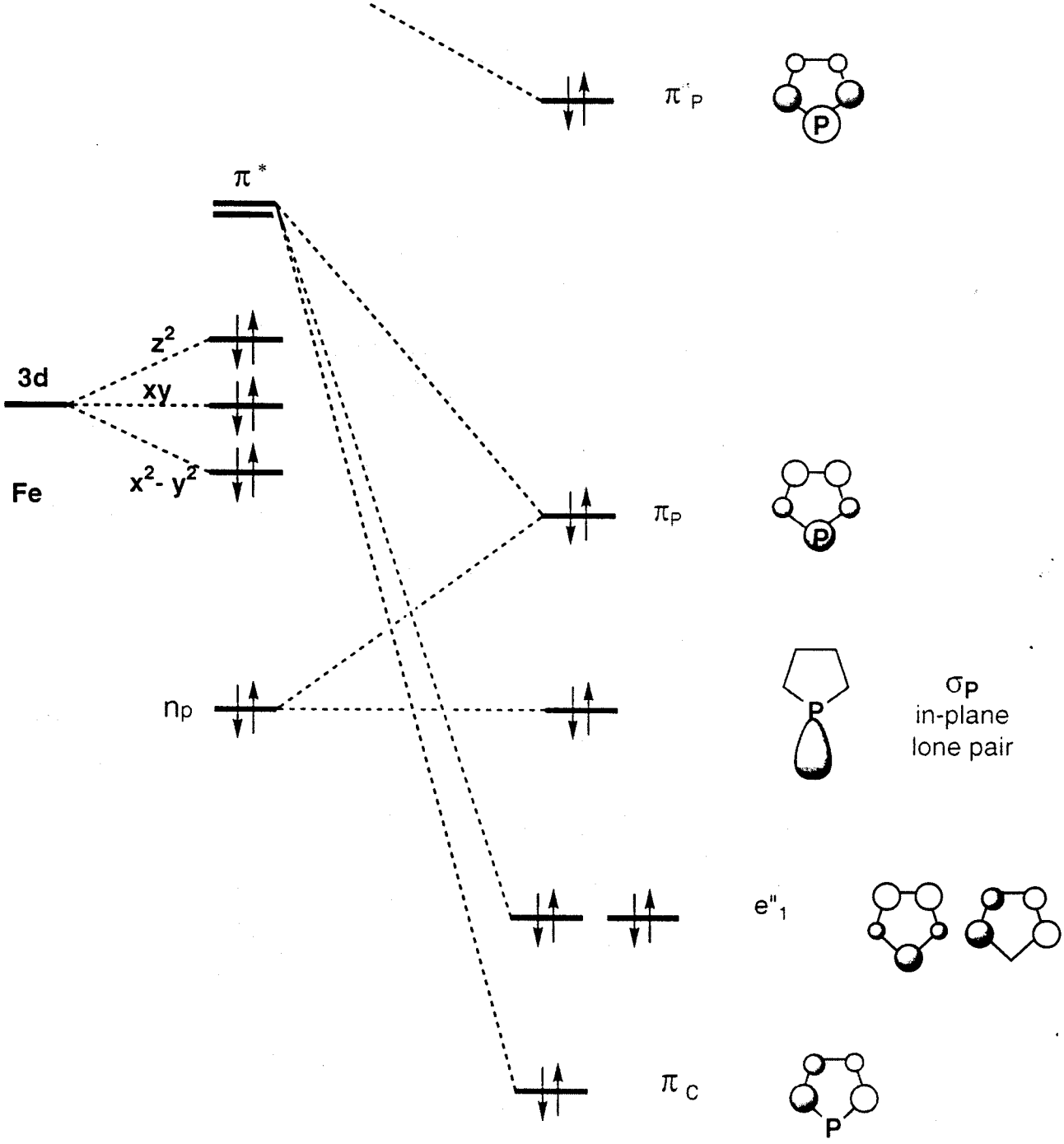
(*S,R*)-Binaphos:
Takaya and coll.
JACS,4413 (1997)



(**B**)

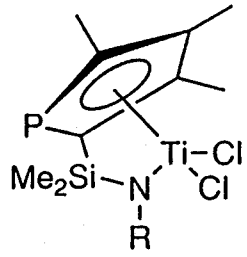
phosphine	solvent	P atm	T°C	Rh/P	b/l	ee	TOF h^{-1}
(**A**)	(C_6H_6)	100	50	1/8	88/12	94	46
(**B**)	toluene	100	50	1/2	92/8	0	91
(**B**)	MeOH	150	40	1/8	94/6	21	14

Electronic structure of phosphaferrocene

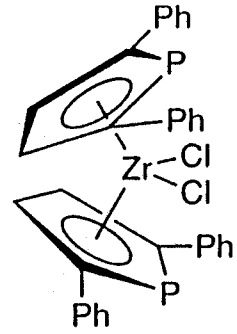


Phosphametallocenes in catalysis

Olefin polymerization

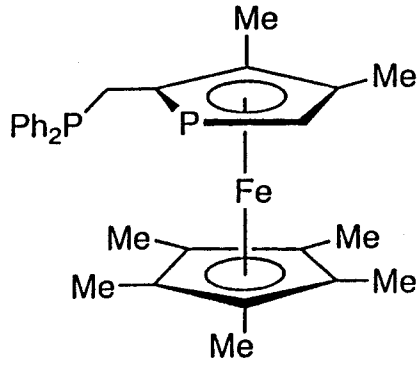


S.J Brown et al., *Organometallics*, **17**, 5445 (1998)



E.J.M. de Boer et al., *J. Mol. Cat. A*, **128**, 155 (1998)

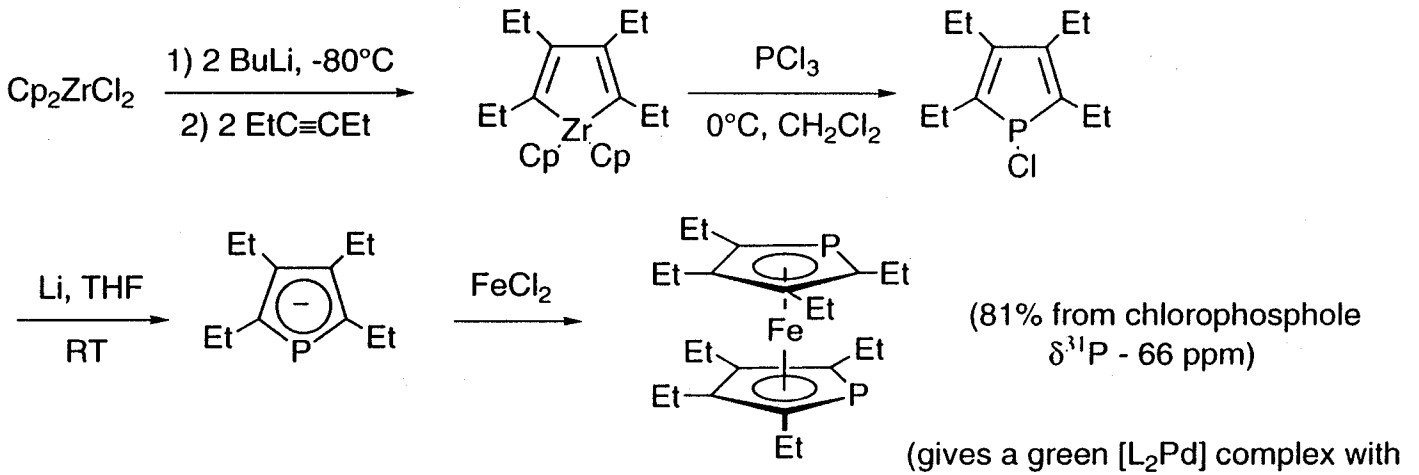
Asymmetric hydrogenation



(-)-P_2

S. Qiao, G.C. Fu, *J. Org. Chem.*, **63**, 4168 (1998)

Synthesis of Octaethyl-1,1'-Diphosphaferrocene



(81% from chlorophosphole
$\delta^{31}P$ - 66 ppm)

(gives a green $[L_2Pd]$ complex with
$[Pd(dba)_2]$ at RT in THF, $\delta^{31}P$ - 125)

X. Sava, L. Ricard, P. Le Floch , F. Mathey (1999)

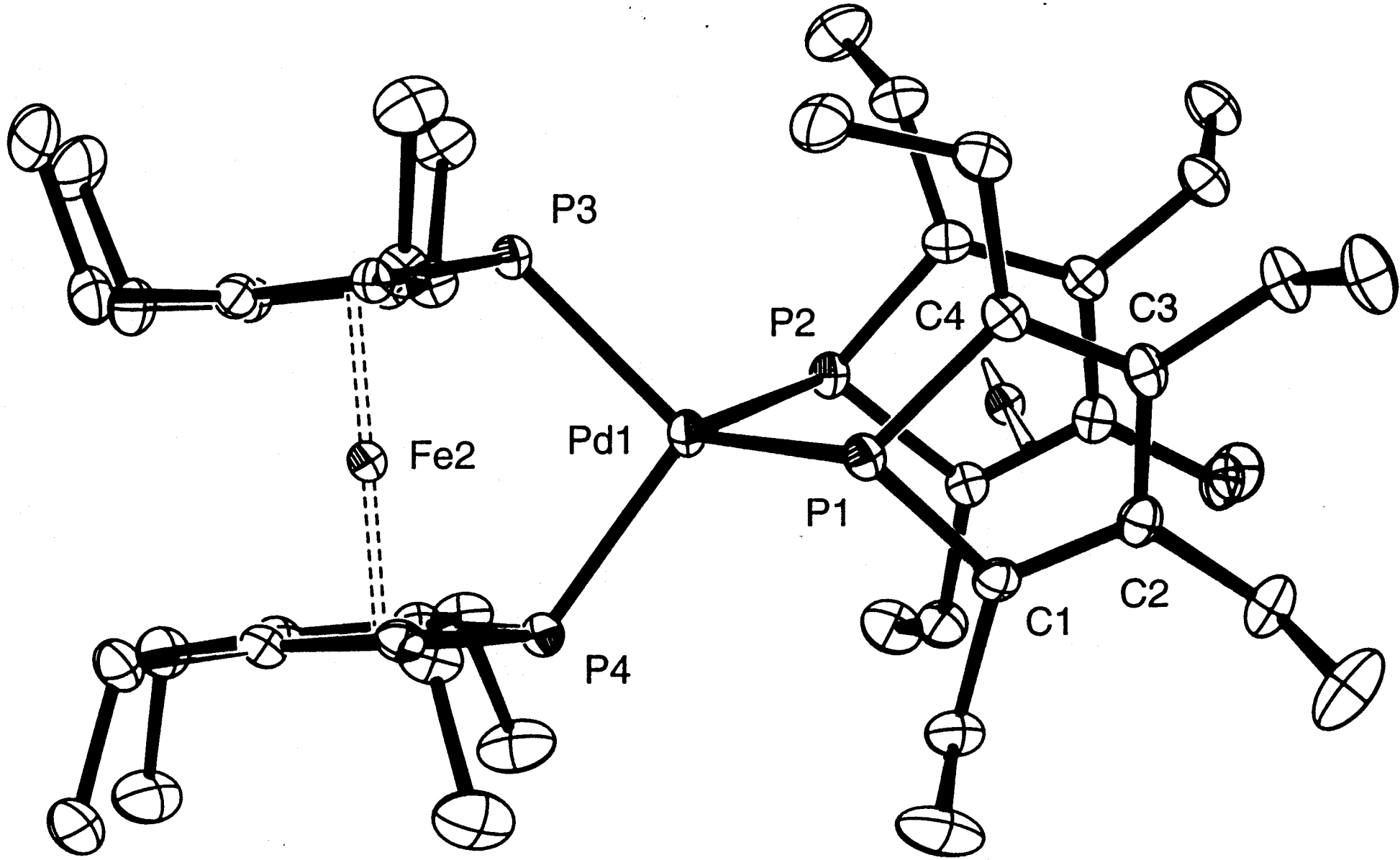
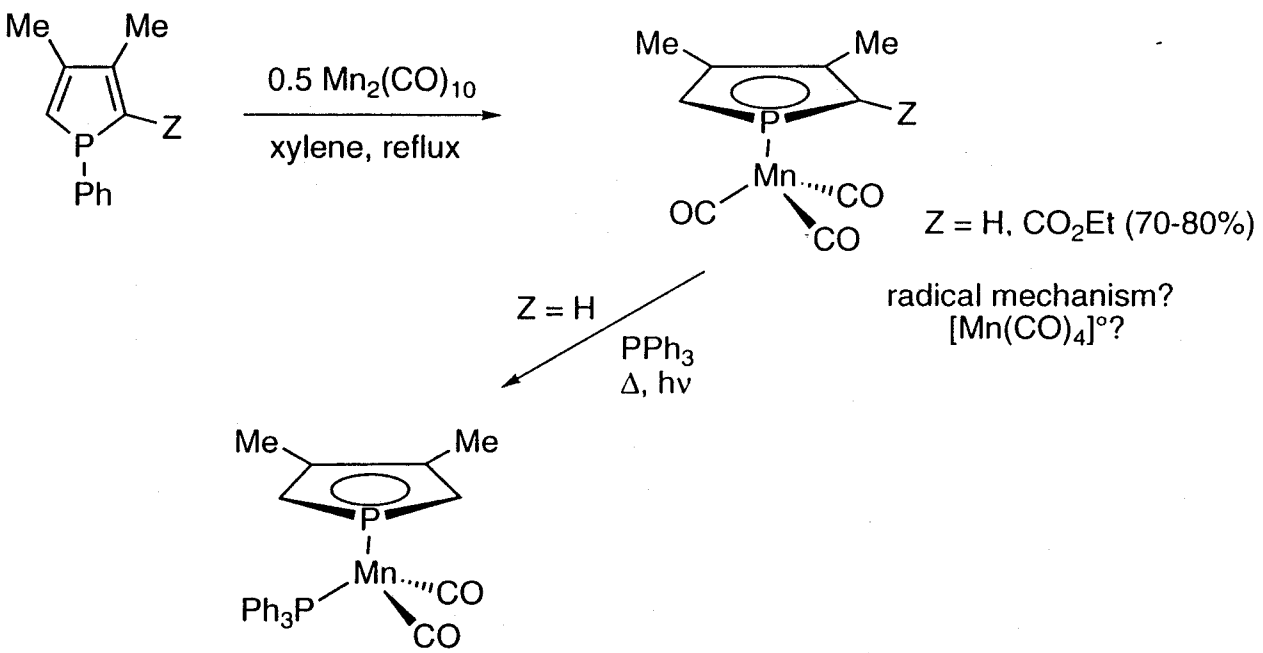

P3
P2
C4
C3
Fe2
Pd1
P1
C1
C2
P4

Table Suzuki Coupling of Aryl Bromides

Aryl bromide	mol%Pd	*t*/h	Conversion(%)	TON
4-bromoacetophenone	0.0001	1	77	770000
4-bromoacetophenone	0.0001	20	98	980000
3-bromothiophene	0.005	1	80	16000
3-bromothiophene	0.005	20	96	19200
2-bromoanisole	0.005	1	67	13400
2-bromoanisole	0.005	20	96	19200
bromobenzene	0.0001	1	46	460000

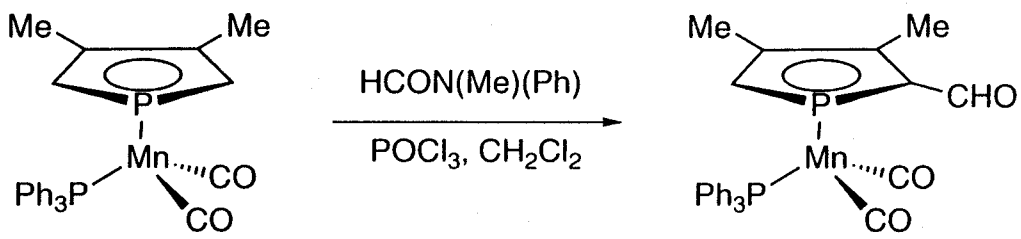
Reaction conditions : 1.0 equiv of aryl bromide, 1.5 equiv of phenylboronic acid, 2.0 equiv. K_2CO_3. Temperature : 110°C, TON are expressed in mol product(mol Pd)$^{-1}$.

Synthesis of phosphacymantrenes



F. Mathey, *Tetrahedron Lett.* (1976)
B. Deschamps, L. Ricard, F. Mathey, *Organometallics* (1999)

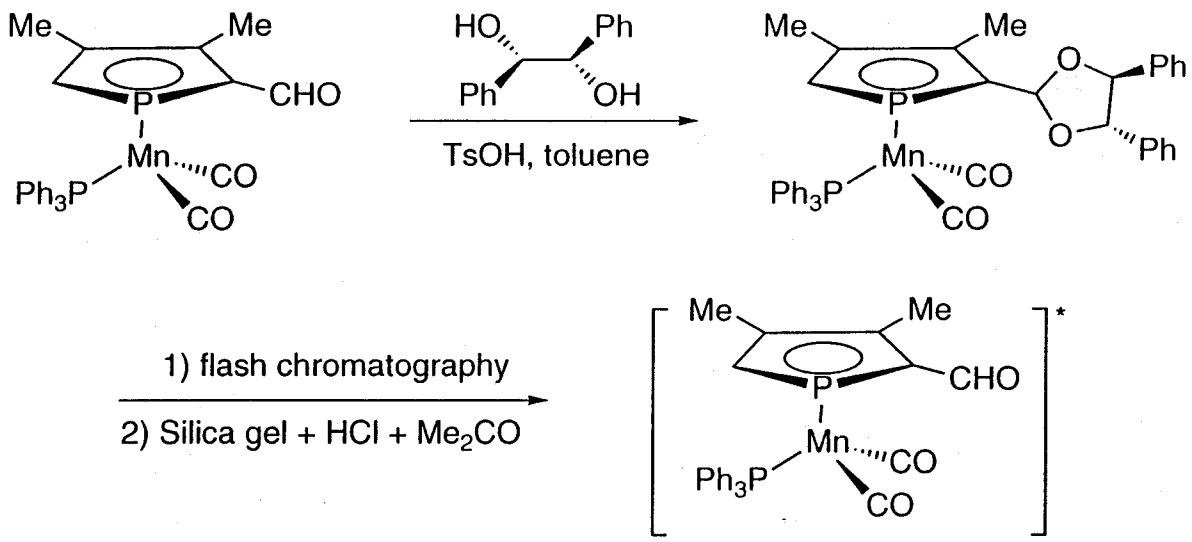
Synthesis of a phosphacymantrene-2-carboxaldehyde



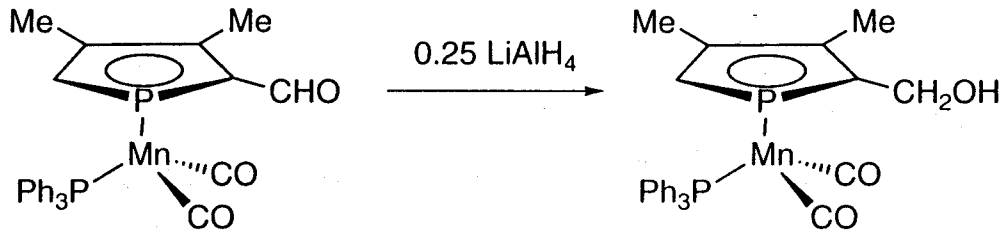
(50-70%) $\delta^{31}P$ +86 and -19.8

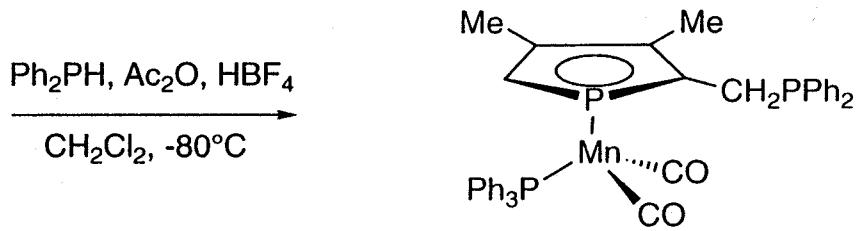
B. Deschamps, L. Ricard, F. Mathey (1999)

Separation of the enantiomers of a phosphacymantrene 2-carboxaldehyde



Synthesis of a 2-(phosphinomethyl)-phosphacymantrene





cyclic P: $\delta^{31}P$ -40 ppm (AB)
PPh_2: $\delta^{31}P$ -9 ppm (AB, $^3J_{AB}$ = 25 Hz)
PPh_3: $\delta^{31}P$ +89 ppm