Characterization of diastereomers by $^{31}P\{^{1}H\}$ NMR spectroscopy

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ABSTRACT

Many of the more efficient transition-metal catalysts for enantioselective synthesis of organic compounds contain chiral organophosphorus ligands. Phosphorus-31 nuclear magnetic resonance spectroscopic data are given in this review for several representative types of diastereomers that have been of aid in the determination of optical purity and in the study of reaction mechanisms.

1. INTRODUCTION

With the current heightened interest in asymmetric synthesis, especially of drugs [1], there is a demand for non-chiroptical methods for determining the optical purity of dissymmetric compounds. This may often be done by NMR spectroscopy, and the observation of ^{1}H and ^{13}C nuclei for such purposes has been reviewed [2–5]. Since the ^{31}P chemical shift dispersion range is larger than those of ^{1}H and ^{13}C, the ^{31}P chemical shift(s) of diastereomeric substances containing one or more phosphorus nuclei are of considerable potential utility in this regard and have been used for a variety of purposes.

Diastereomers arise whenever a molecule possesses two or more stereocenters [6]. The number of possible diastereomers is equal to 2^n where n is the number of stereocenters. As illustrated by the data in this review, ^{31}P NMR spectroscopy is

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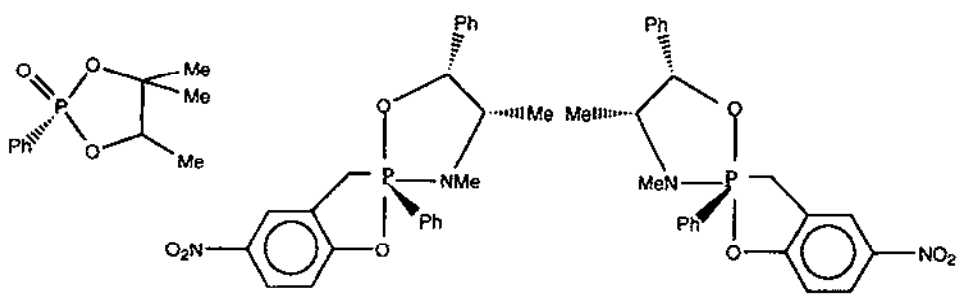
capable of detection and quantitation of diastereomeric ratios even when the observed phosphorus nucleus is not a stereocenter. The ^{31}P NMR data are useful for determining the optical purities of a variety of substances, as well as in the study of reaction mechanisms. Data are given for several types of diastereomers, many of which have been completely characterized by additional techniques such as X-ray crystallography and circular dichroism. The topic coverage is not exhaustive but rather (hopefully) representative. Care has been taken to ensure that all chemical shifts are given positive values when downfield of the reference (external 85% H_3PO_4).

2. PHOSPHINES AND SIMPLE DERIVATIVES

The R_P phosphorus epimers of menthylmethylphenylphosphine oxide (**1**) and neomenthylmethylphenylphosphine oxide (**2**) have been characterized by X-ray crystallography [7]. This allows determination of the absolute configuration of the phosphorus stereocenter in all four diastereomers by ^{31}P NMR, since the absolute configurations of the menthyl and neomenthyl groups are known. ^{31}P NMR ($CHCl_3$, 40.5 MHz): δ $\mathbf{1}_R$, 40.6; $\mathbf{1}_S$, 42.3; $\mathbf{2}_R$, 43.2; $\mathbf{2}_S$, 40.7. The absolute configurations of the two diastereomers of ethylmenthylphenylphosphine oxide (**3**) and menthylphenylisopropylphosphine oxide (**4**) were assigned on the basis of their ^{31}P chemical shifts: $\mathbf{3}_R$, 44.3; $\mathbf{3}_S$, 46.7; $\mathbf{4}_R$, 46.1; $\mathbf{4}_S$, 49.2. Phosphine oxides are reduced by $PhSiH_3$ with retention of configuration at phosphorus [8(a)] and by Si_2Cl_6 with inversion of configuration at phosphorus [8(b)], and oxidation of phosphines by H_2O_2 occurs with retention [8(a),8(b)]. Thus, the absolute configurations and optical purities of diastereomeric phosphines and their oxides may be assessed by ^{31}P NMR spectroscopy.

The diastereomers of 2-{[(R_c)-1-(α-naphthyl)ethyl]amino}-2-thiono-1,3,2-oxathiaphospholane (**5**) and O,S-dimethyl *N*-[(Rc)-1-(a-naphthyl)ethyl] phosphoramidothiolate (**6**) have been characterized by ^{31}P NMR spectroscopy [9]. ^{31}P NMR ($CDCl_3$, 121 MHz): δ $\mathbf{5}R_PR_C$, 94.26; $\mathbf{5}S_PR_C$, 95.06; $\mathbf{6}R_PR_C$, 35.14; $\mathbf{6}S_PR_C$, 34.65. X-ray crystallography confirmed the absolute configurations of **5** and **6** R_PR_C. Two diastereomers of **7** and **8** have been prepared [10].

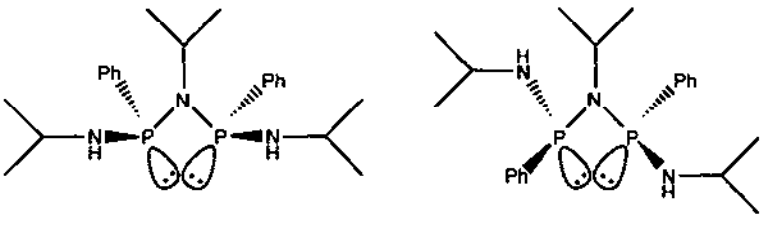


7 **8**

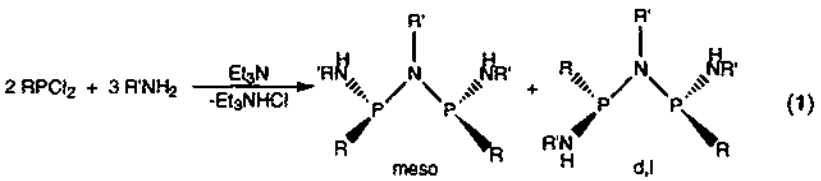
$\delta^{31}P(CDCl_3, 32\ MHz)$

28.5, 29.1 -28.9 -29.5

Two diastereomers of PhOP(OEt) [$N(CH_2)_3CHCO_2Et$] (^{31}P NMR: δ 141.2, 139.9) and their BH_3 adducts (^{31}P NMR: δ 73.3, 70.2) have been reported [11]. The meso and *d,l* diastereomers of the diphosphinoamine i-$C_3H_7N[C_6H_5PNH(i\text{-}C_3H_7)]_2$ (**9**) show phosphorus chemical shifts that differ by 1 ppm [12]:

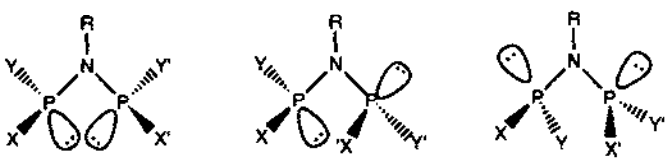


In further studies of similar diphosphinoamines related in part to the diastereoselectivity of their formation, as indicated by the general reaction (1), the data collected in Table 1 have been reported [13–16].



The absolute configurations of i-prN(PPhCl)(PPh i-prNH) [14] and i-prN(PPh iprNH)$_2$ [15] were determined from X-ray crystal structures of their molybdenum tetracarbonyl complexes. The diastereomeric assignments for the other compounds were inferred from the ^{31}P NMR data. Generally, the ^{31}P chemical shift of the meso diastereomer occurs downfield of that for the *d,l* diastereomer. Where observable, the value of $^2J_{PP}$ is greater for the meso than for the *d,l* diastereomer.

Surprisingly [16], two diastereomers were not observed for MeN(PMeCl)$_2$, MeN(PBrCl)$_2$ and MeN[PCl(NMe$_2$)$_2$]. Some of the compounds listed in Table 1 exhibited temperature-dependent $^2J_{PP}$ which decreased with increasing temperature. This was attributed [16] to a temperature dependence of the relative populations of conformers I, II and III for the meso diastereomers and similarly related conformers for the *d,l* diastereomers.



The bis-(1,3,2-oxazaphospholidenes) **10–12** have been synthesized, and two analogs have been characterized by X-ray crystallography [17]. Some of these

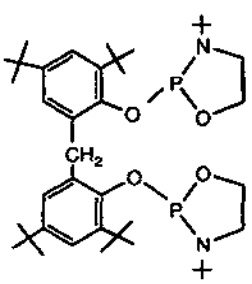
TABLE 1

^{31}P NMR data for diastereomeric diphosphinoamines

Compound	$\delta^{31}P$ (ppm)	$^2J_{PP}$ (Hz)	Diastereomer	Ref.
$MeN(PPhCl)_2$	134.8	341 ± 3	*d,l*	16[a]
	137.1	421 ± 3	meso	16
$MeN[P(pMeC_6H_4)Cl]_2$	137.7		meso	13[b]
	139.7		*d,l*	13
$i\text{-prN(PPhCl)}_2$	128.5		meso	14[c]
	123.7		*d,l*	14
i-prN(PPhCl)(PPh i-prNH)	126.1, 63.1	8.0	erythro	14
	125.8, 65.5	14.0	threo	14
i-prN(PPhEtNH)(PPh i-prNH)	64.6, 60.5	14.6	threo	14
	59.6, 60.9	6.9	erythro	14
$i\text{-prN(PPh i-prNH)}_2$	60.2		meso	15[c]
	59.1		*d,l*	15
$PhN(PPhPhNH)_2$	62.2		meso	15
	61.0		*d,l*	15
$MeN(PMePh)_2$	58.1	278 ± 5	meso	16
	55.1	225 ± 5	*d,l*	16
$MeN(PPhBr)_2$	138.2	310 ± 10	*d,l*	16
	141.2	390 ± 10	meso	16
MeN(PMePh)[P(S)MePh]	41.3, 70.4	78 ± 5	*d,l*	16
	43.8, 71.4	82.5	meso	16
$MeN[P(S)MePh]_2$	69.3	0 ± 5	meso	16
	67.9	0 ± 5	*d,l*	16

[a]Data obtained by $^1H\{^{31}P\}$ double-resonance measurements.
[b]24.3 MHz, CH_2Cl_2.
[c]36.3 MHz, C_6D_6.

molecules exhibit large through-space P–P coupling of about 30 Hz. The absolute configurations of these diastereomers are not known.



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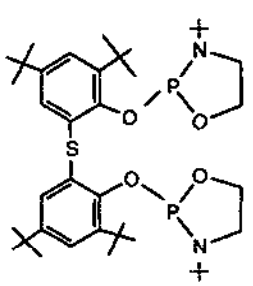
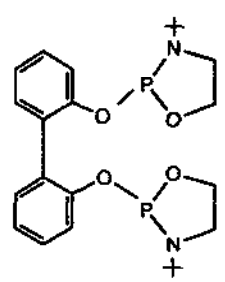
$\delta^{31}P(C_6D_6, 160\ MHz)$

136.6, 137.1



11

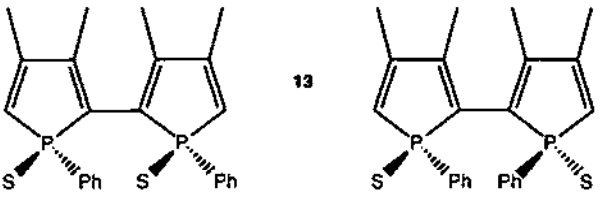
135.7, 136.2



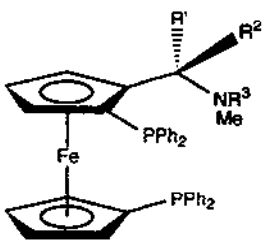
12

130.5, 130.9

The ^{31}P chemical shifts of the meso and *d,l* diastereomers of the diphosphole disulfide **13** differ by 0.6 ppm [18].



In a study of gold(I)-catalyzed asymmetric Aldol reactions, Togni and Pastor [19] have synthesized and characterized the diastereomeric diphosphino-ferrocenes **14**.



14

Diastereomer	R^1	R^2	R^3	^{31}P(121.5 MHz, $CDCl_3$)
(R)–(S)	CH_3	H	$CH_2CH_2NMe_2$	−23.5, −13.0
(S)–(S)	H	CH_3	$CH_2CH_2NMe_2$	−21.5, −17.0
(S)–(S)	H	CH_3	CH_3	−20.8, −16.9
(R)–(S)	CH_3	H	CH_3	−23.0, −16.9

The ^{31}P chemical-shift differences for the diastereomers of P(III, IV and V) derivatives, though not large (0.4 to 3.1 ppm), are sufficient for detection and quantitation of diastereomeric ratios.

3. TRANSITION-METAL COMPLEXES

3.1. Square-planar complexes of monophosphorus donors

Verkade and co-workers [11,20,21] have prepared and chromatographically separated diastereomeric $LL'PtX_2$ complexes as a means of resolving phosphorus ligands. The ^{31}P NMR data are collected in Table 2.

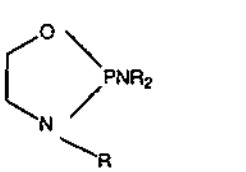
There is no regularity in the relative chemical shifts nor in the magnitude of the chemical-shift differences for the $LL'PtX_2$ complexes. Thus, while optical purity may be assessed by ^{31}P NMR for complexes of this type, absolute configuration cannot.

TABLE 2

36 MHz $^{31}P\{^1H\}$ NMR data for diastereomeric cis-LL'PtX$_2$ complexes in CH_2Cl_2–C_6D_6 [11,20,21]

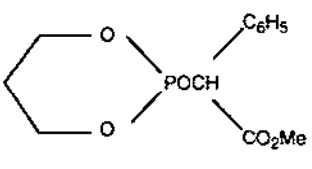
L	L'	X	$\delta^{31}P$ (ppm)	$^1J_{Pt,P}$ (Hz)	Diastereomer
15	**15**	I	70.9	5071	*d,l*
15	**15**	I	73.6	4989	meso
16	**16**	I	75.1	5473	*d,l*
16	**16**	I	75.2	5473	meso
17[a]	**17**	I	70.5	4881	*d,l*
17[a]	**17**	I	68.2	4931	meso
18[b]	**18**	Cl	58.8	5787	?
18[b]	**18**	Cl	68.7	5791	?
15	**16**	I	72.6(**15**), 74.4(**16**)	4677(**15**), 5846(**16**)	+**16**, −**15**
			71.5(**15**), 73.6(**16**)	4690(**15**), 5849(**16**)	+**16**, +**15**
15[a]	**16**	Cl	75.9(**15**), 67.5(**16**)[c]	4785(**15**), 6037(**16**)	+**16**, −**15**
			75.2(**15**), 67.1(**16**)[c]	4798(**15**), 6052(**16**)	+**16**, +**15**
14	**17**	I	76.6(**14**), 66.7(**17**)	5865(**14**), 4469(**17**)	+**14**, ±**17**
			74.5(**14**), 66.1(**17**)	5849(**14**), 4530(**17**)	+**14**, ±**17**
15	**18**	Cl	74.6(**15**), 65.9(**18**)[d]	4797(**15**), 6053(**18**)	*d,l*
			73.3(**15**), 66.2(**18**)[e]	4870(**15**), 6062(**18**)	meso
15	**18**	I	74.8(**15**), 72.1(**18**)	4635(**15**), 5795(**18**)	?
			73.6(**15**), 73.2(**18**)	4696(**15**), 5814(**18**)	?
15	**19**	Cl	71.8(**15**), 68.3(**19**)	5116(**15**), 5307(**19**)	?
			71.5(**15**), 68.7(**19**)	5114(**15**), 5304(**19**)	?
16	**20**	I	64.8(**16**), 63.6(**20**)	5869(**16**), 5481(**20**)	+**16**, +**20**
			66.6(**16**), 64.5(**20**)	5852(**16**), 5487(**20**)	+**16**, −**20**

[a] in C_6D_6.
[b] in $CDCl_3$.
[c] $^2J(PP) = 15$ Hz.
[d] $^2J(PP) = 16.6$ Hz.
[e] $^2J(PP) = 15.5$ Hz.



R=CH_2CH_2Cl

15



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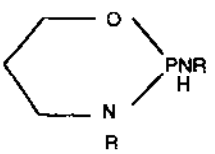
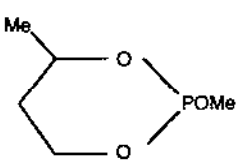


R=CH_2CH_2Cl

17



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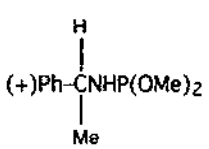


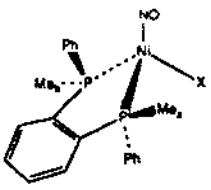
19

(PhO)P(OC_6H_4-pCl)(OC_6H_4-pMe)

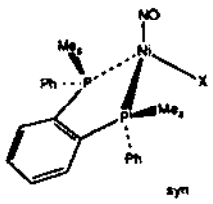
20

3.2. Tetrahedral complexes

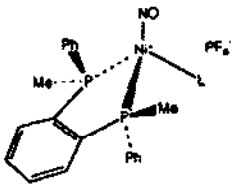
The tetrahedral complexes (R*,R*)-(±)- and (R*,S*)-*anti*[NiX(NO){1,2-C_6H_4(PMePh)2}] (**21**) rearrange in nitrobenzene-d_5 at 25 °C with inversion at the metal stereocenter ($t_{1/2} \approx 5$ s (X=Cl), 9 s (X=NCS) and 3.5 h (X=CN)). The salts (R*,R*)-(±) and (R*,S*)-*anti*[NiL(NO){1,2-C_6H_4($PMePh_2$)$_2$}]PF_6 (**22**) rearrange with $t_{1/2}$ (inversion) of approximately 6 min and $t_{1/2}$ (redistribution) of approximately 12 h (L=PMe_2Ph). The crystal structures of (R*, S*)-*anti*-[NiNCS(NO){1,2-C_6H_4($PMePh_2$)}] and (R*,S*)-*anti*-[NiNO{$P(OMe)_3$}-{1,2-C_6H_4($PMePh_2$)$_2$}] PF_6 provide bases for the assignments of the ^{31}P NMR chemical shifts (Table 3) [22].



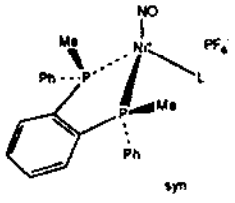
(R*,R*) **21**



(R*,S*) **21**



(R*,R*) **22**



(R*,S*) **22**

3.3. Octahedral complexes of monophosphorus donors

Considering the fact that an η^5-cyclopentadienyl ligand occupies three coordination sites on a transition-metal center, the geometry of complexes of the type CpMLL'L'' is based upon that of an octahedron. The symmetry of these compounds is, however, equivalent to that of a tetrahedral center with four different substituents [23,24]. From either perspective, the metal in such species is a stereocenter [6]*. ^{31}P NMR data for these complexes are collected in Table 4. The first four compounds in Table 4 are configurationally stable [26], but the last is not [27].

* Absolute configurations are assigned according to the Baird Sloan modification of the Cahn–Ingold–Prelog priority rules. See ref. 25.

TABLE 3

80.98 MHz $^{31}P\{^1H\}$ NMR data for **21** and **22** in CD_2Cl_2

Compound	$\delta^{31}P$ (ppm)	$^2J_{PP}$ (Hz)
(*R**,*R**)-**21**(X=Cl)	32.9, 40.7 (ABq)	39.1
(*R**,*R**)-**21**(X=Br)	30.2, 36.6 (ABq)	36.6
(*R**,*R**)-**21**(X=I)	27.0, 31.7 (ABq)	31.7
(*R**,*R**)-**21**(X=CN)	37.0, 41.8 (ABq)	12.2
(*R**,*R**)-**21**(X=NCS)	35.8, 41.7 (ABq)	31.8
(*R**,*S**)-*anti*-**21**(X=Cl)	42.6	
(*R**,*S**)-*anti*-**21**(X=I)	33.1	
(*R**,*S**)-*anti*-**21**(X=CN)	43.4	
(*R**,*S**)-*anti*-**21**(X=NCS)	44.1	
(*R**,*R**)-**22**(L=PMe_3)	−8.5, 37.7, 38.9(ABX)	7.9, 3.7, 4.9
(*R**,*R**)-**22**(L=$PMePh_2$)	19.8, 37.6, 38.3(ABX)	6.9, 4.0, 1.3
(*R**,*R**)-**22**(L=PMe_2Ph)	3.6, 37.8, 38.7(ABX)	7.3, 4.0, 1.8
(*R**,*R**)-**22**(L=PPh_3)	34.6, 35.4, 38.3(ABX)	8.0, 3.7, 8.5
(*R**,*S**)-*anti*-**22**(L=PMe_3)	−7.0t, 34.3d	6.3
(*R**,*S**)-*syn*-**22**(L=PMe_3)	−9.3t, 40.3d	3.9
(*R**,*S**)-*anti*-**22**(L=$PMePh_2$)	20.2t, 34.1d	5.9
(*R**,*S**)-*syn*-**22**(L=$PMePh_2$)	19.1t, 39.5d	2.4
(*R**,*S**)-*anti*-**22**(L=PMe_2Ph)	4.8t, 34.3d	6.3
(*R**,*S**)-*syn*-**22**(L=PMe_2Ph)	3.2t, 40.0d	3.4
(*R**,*S**)-*anti*-**22**(L=PPh_3)	35.0d, 40.5t	6.3
(*R**,*S**)-*anti*-**22**[L=$P(OMe)_3$]	39.0d, 161.2t	26.2
(*R**,*S**)-*syn*-**22**[L=$P(OMe)_3$]	39.5d, 159.5t	25.8

TABLE 4

$^{31}P\{^1H\}$ NMR data for CpMLL'L' type species

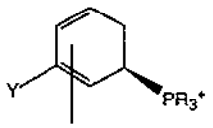
Compound	$\delta^{31}P$ (ppm)	Diastereomer
[Ru(η^5-mcp)(CO)(PPh_2Me)Cl][a]	35.6, 35.8	(+310), (−310)
[Ru(η^5-nmcp)(CO)(PPh_3)I][a]	49.8, 49.4	(*R*), (*S*)
[Ru(η^5-nmcp)(CO)(PPh_3)Cl][a]	50.8, 50.0	(*R*), (*S*)
[Ru(η^5-nmcp)(CO)(PPh_3)Br][a]	46.8, 45.7	(*R*), (*S*)
[(η^6-C_6Me_6)RuN(Ph)CHMeC_6H_4(PMe_3)][b]	46.8, 4.16	(*RS*,*SR*), (*RR*,*SS*)

[a] Ref. 26, 40.48 MHz, toluene-d_8, mcp = *R*-(−)-menthylcyclopentadiene, nmcp = *S*-(+)-neomenthylcyclopentadiene.

[b] Ref. 27, 121 MHz, $CDCl_3$, $t_{1/2}$ = 18 h, 25°C for isomerization.

Dienetricarbonyl iron(0) complexes **23** and a derivative **24** have been reported and resolved [28]. These compounds are configurationally stable.

The compound $Mo(CO)_5$[PMe(OEt)(OH)] (**25**) has been resolved [29] by forming diastereomeric salts with (−)-ephedrine (^{31}P NMR ($CDCl_3/CH_3OH$): δ (−)eph(−) **25**, 155.5; (−)eph(+) **25**, 156.2). The OH group of this compound may

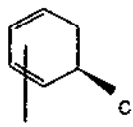


$d^{31}P$ (40.26 MHz, $CDCl_3$)

Y=H

PR_3	
(S)(+)-PMePrPh	31.2, 31.7
(S)(+)-$PPh_2(C_{10}H_{19})$	32.4, 34.2
(S)(+)-$PPh_2(C_5H_{11})$	31.2, 31.7
Y=OMe, PR_3=(S)(+)-$PPh_2(C_{10}H_{19})$	31.7, 33.7

23



70.5, 70.1

$Fe(CO)_2$[(S)(+)-$PPh_2(C_{10}H_{19})$]

24

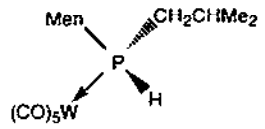
be esterified with retention of configuration at phosphorus. Prochiral L-menthyl phospha-alkene complexes were prepared from the "phospha–Wittig" reagents $[MenP(H)\text{-}P(O)(OR)_2]M(CO)_5$ (M = Mo,W), and several aldehydes [30]. Their catalytic hydrogenation using RhL_2^+ catalysts and their [2+4] cycloaddition with cyclopentadiene proceeded with full diastereoselectivity. A molecular model of such a phospha-alkene complex showed that a preferred conformation exists that minimizes the combined interactions of the isopropyl substituent of the L-menthyl group with the complexing group and the phosphavinylic C–H bond. In this conformation, only the *si* face of the phospha-alkene is accessible to the incoming reagents. Both hydrogenation and [2+4] cycloaddition with cyclopentadiene selectively take place on this face, as demonstrated by the X-ray crystal structure analysis of two of the resulting complexes. A two-step procedure was devised for the conversion of $[MenPH_2]Mo(CO)_5$ into optically pure phosphines. In the first step, the primary phosphine complex was phosphorylated, the resulting phospha–Wittig reagent was allowed to react with an aldehyde, and the phospha-alkene complex thus formed was trapped by cyclopentadiene. The decomplexation of the resulting molybdenum complex was carried out by heating it with $Ph_2PCH_2CH_2PPh_2$. An optically pure 2-L-menthyl-2-phospha-5-norbornene was thus prepared.

The absolute configuration of **27b** was confirmed by X-ray crystallography.

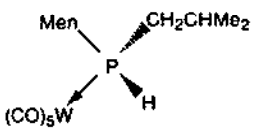
The phosphido complex (η^5-Cp)Re(NO)(PPh_3)(PhPH) undergoes inversion of the coordinated phosphido-phosphorus [31] with $\Delta G^{\ddagger}_{243} = 11.5 \pm 0.1$ kcal mol^{-1}. Approximate ^{31}P chemical shifts are (THF, −64 °C) (RS,SR) 25, −91; (RR,SS) 17, −111).

The aminophospirane complex **28** reacts with 1-hexene to generate two diastereomers of the new aminophosphirane complex **29** according to reaction (2) [32], by way of the aminophosphinidene intermediate, $[Et_2N\text{-}P{=}W(CO)_5]$.

The two diastereomers of **29** slowly equilibrate upon standing at room temperature by reversible formation of the aminophosphinidene intermediate. The absolute configurations of these two diastereomers are not known.



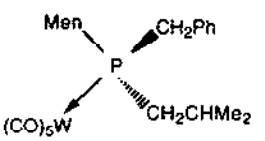
26a



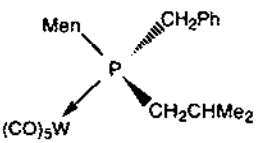
26b

$\delta^{31}P$ (C_6D_6, 32.44 MHz)
-43.5, $^1J(WP)$ = 222.2 Hz

-52.9



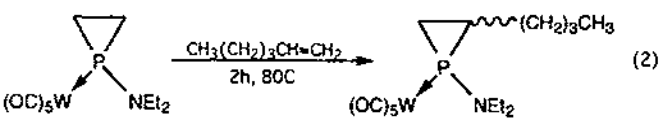
27a



27b

10.2, $^1J(WP)$ = 234 Hz

18.16, $^1J(WP)$ = 236 Hz



(2)

28

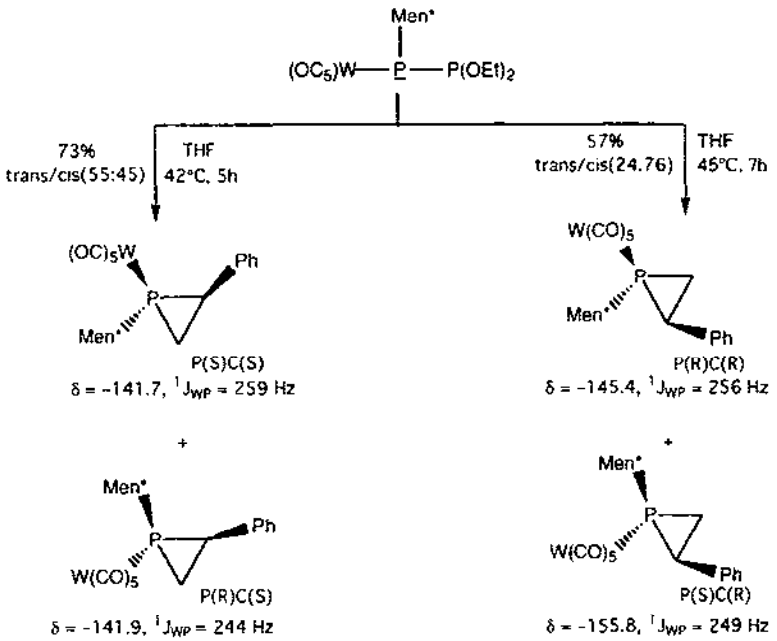
29

$\delta^{31}P$ (32.44 MHz, C_6D_6)
29a: -90.8, $^1J_{WP}$ = 278 Hz; major
29b: -92.4, $^1J_{WP}$ = 273 Hz; minor

"Phospha–Wittig" reactions of pentacarbonyl [(diethoxyphosphoryl)menthylphosphine] tungsten(0) with optically pure styrene oxide proceeds by inversion of the carbon configuration to produce diastereomeric products (reaction (3)) [33]. The absolute configuration of the P(R)C(S) diastereomer was determined by X-ray crystallography. Similar reactions were observed for analogous complexes with other racemic oxiranes but in these cases only the cis and trans isomers could be distinguished by ^{31}P NMR spectroscopy. The data are given in Table 5.

Reactions (3) have also been reported for the analogous molybdenum complexes with optically pure styrene oxide [34]. The four diastereomeric complexes were separated by column chromatography and the free 1-menthyl-s-phenylphosphiranes were liberated from the molybdenum complexes by reaction with $Ph_2PCH_2CH_2PPh_2$. The absolute configuration of the P(R)C(S) diastereomer was confirmed by an X-ray crsytal structure of the $[L_2(COD)Rh]PF_6$ complex. The ^{31}P NMR data are given in Table 6.

The coordination chemical shifts ($\Delta\delta(^{31}P) = \delta(^{31}P)$ complex $- \delta(^{31}P)$ ligand for the molybdenum and tungsten complexes of these diastereomeric phosphiranes may be predicted from the equations [35] $\Lambda\delta^{31}P = -0.142\delta^{31}P(\text{ligand}) + 40.19$ and



(3)

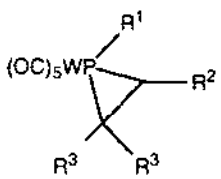
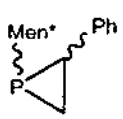


TABLE 5

32.43 MHz ^{31}P NMR data for the compounds in C_6D_6

R^1	R^2	R^3	δ^{31}P (*trans*, *cis*) (ppm)	*trans*/*cis* ratio
Ph	Ph	H	−152.5, −157.6	68:32
t-Bu	Ph	H	−127.5, −136.8	75:25
PhCH=CH	Ph	H	−156.8, −169.6	70:30
PhCH=CH	OMe	Me	−155.0, −147.5	62:38

TABLE 6

81.01 MHz ^{31}P NMR data for the $(OC)_5Mo$–  complexes and the free ligands in toluene

Phosphirane diastereomer	^{31}P (ppm)	
	Mo complex	Free ligand
P(*S*) C(*S*)	−120.0	−170.2
P(*R*) C(*S*)	−122.7	−182.9
P(*R*) C(*R*)	−132.7	−195.0
P(*S*) C(*R*)	−125.3	−181.8

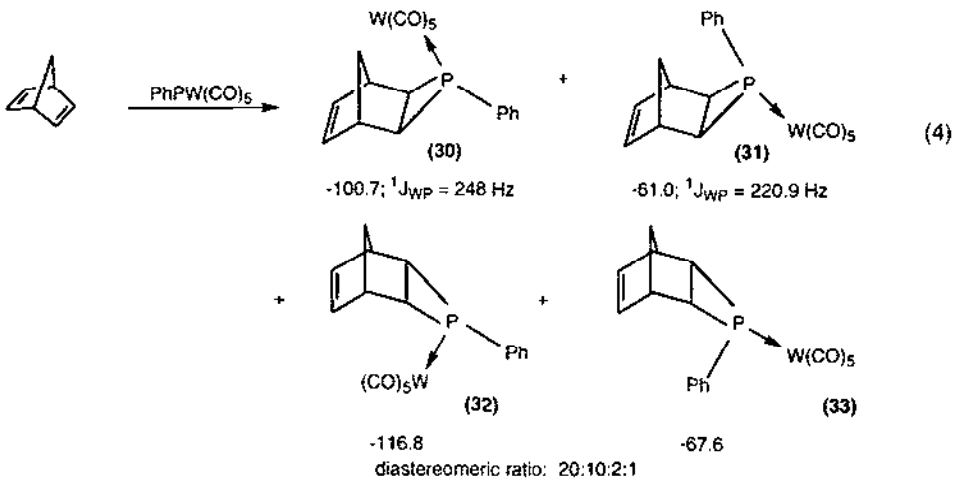
$\Delta\delta^{31}P = 0.128\delta^{31}P(\text{ligand}) + 21.42$ for the Mo and W complexes respectively. The experimental values are compared with the predicted values in Table 7.

As can be seen from the data in Table 7, the observed coordination chemical shifts are all smaller than the predicted values, suggesting that the phosphiranes are poorer donors than typical phosphines.

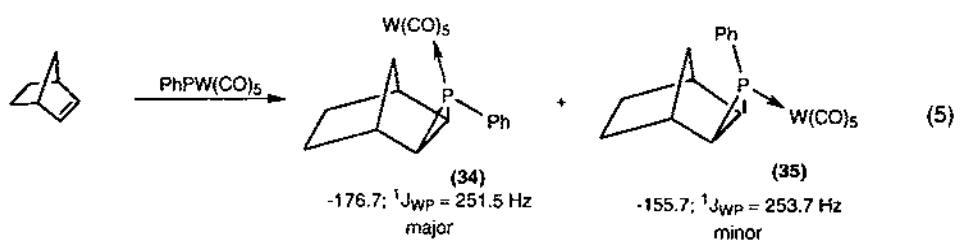
Rhodium complexes of these phosphiranes were evaluated as catalysts for the asymmetric hydrogenation of $RCH=C(Z)CO_2H$ where $Z=NHCOMe$, $R=H,Ph$ and $Z=CH_2CO_2H$, $R=H$. Effective catalytic activity was observed with only moderate optical yields. But, since only ring-opened oxidized phosphorus derivatives were found at the termination of the catalytic reactions, it is not clear that the phosphiranes themselves take part in the catalytic cycle. This is consistent with the low donor ability of the phosphiranes as suggested by the coordination chemical shift data. Only the P(R)C(S) diastereomer shows normal coordination chemical-shift values, and it gave the best optical yields in the catalytic hydrogenation reactions.

Phenylphosphinidene tungsten pentacarbonyl reacts with norbornadiene and norbornene to produce the diastereomers shown in reactions (4)–(7) [36].

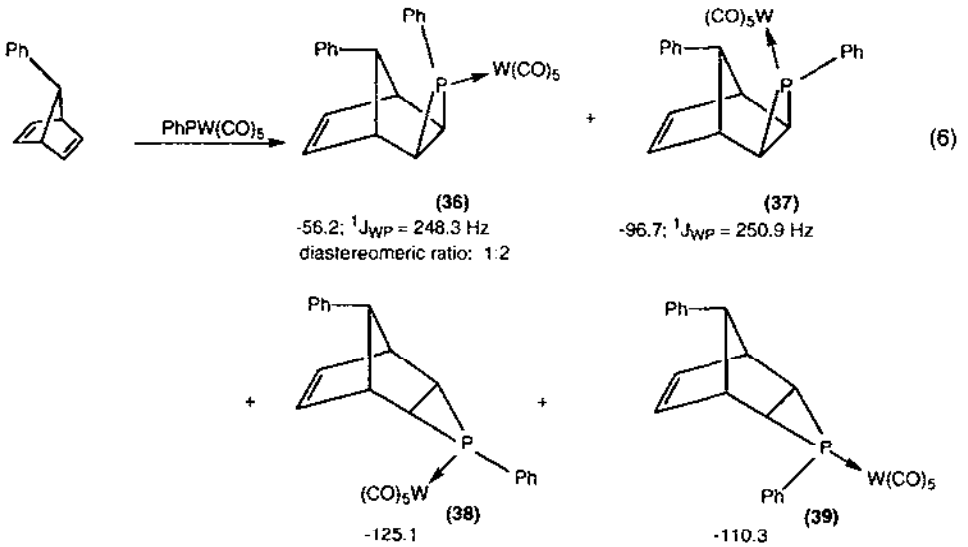
The structure of **30** was confirmed by X-ray crystallography. The ^{31}P chemical



(4)



(5)



shifts of the phosphinidene [1,2]-cycloaddition products of unsubstituted and 7-phenyl-substituted norbornadiene (*i.e.* Z-exo, $\delta = -100.7$ (**30**) and -96.7 (**37**); E-exo, -61.0 (**31**) and -56.2 (**36**); Z-endo, -116.8 (**32**); E-endo, -67.6 (**33**) are strikingly different (a) from the generally much more shielded resonances ($\delta = -130$ to -175 ppm) found for $W(CO)_5$-complexed phosphiranes [37–43] and (b), in particular, from those of the related exo-phosphiranes **34** ($\delta = -176.7$ ppm, major Z isomer) and **35** ($\delta = -155.7$ ppm) that result from the reaction of $PhPW(CO)_5$ with norbornene. This strong deshielding effect ($\Delta\delta = 77$ and 96 ppm for exo **30** and **31**, respectively, relative to the corresponding phosphiranes **34** and **35**) is attributed to

TABLE 7

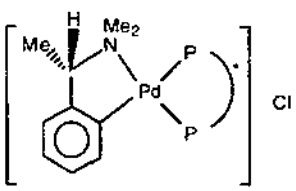
Coordination chemical shifts for the $LMo(CO)_5$ and $LW(CO)_5$ complexes of the diastereomeric phosphiranes

Diastereomer	$\Delta\delta^{31}P$ (ppm)			
	$LMo(CO)_5$		$LW(CO)_5$	
	Observed	Calculated	Observed	Calculated
P(*S*) C(*S*)	50.2	64.4	28.5	43.2
P(*R*) C(*S*)	60.2	66.2	41.0	44.8
P(*R*) C(*R*)	52.3	66.5	39.6	45.1
P(*S*) C(*R*)	56.5	66.0	26	44.7

negative hyperconjungation [44]* between the phosphorus and the remote double bond, which causes P-electron withdrawal and deshielding. The exo- phosphiranes benefit most from this extended δ,π conjugation, and particularly the Z isomer (**30**) owing to its W configuration (C=C,C_2Ph), which thereby indirectly supports the phosphirane product assignments.

4. COMPLEXES OF DIPHOSPHINES

The orthometallated palladium(II) complex (−)-bis(μ-chloro)bis[(R)-dimethyl(α-methylbenzyl)aminato-C^2,N] dipalladium(II) can be used for the resolution of phosphines [45,46]. The ^{31}P NMR spectra of the diastereomeric salts (**40**) formed by reaction of this compound with chiral diphosphines provide a measure of the optical purity of the diphosphines [47] (Table 8). There is no pattern in these data that would lead to ready assignment of absolute configurations.



40

Phospholes undergo intramolecular [4+2] Diels–Alder cycloadditions with vinyl phosphines when both are coordinated mutually cis to Pd(II) or Pt(II) halides [49]. With divinylphenylphosphine, two diastereomers **41** and **42** are formed. The ^{31}P NMR data are given in Table 9.

TABLE 8
^{31}P{^{1}H} ($CDCl_3$) NMR data for diastereomeric salts **40** [47]

Diphosphine	δ^{31}P (ppm)	$^2J_{PP}$ (Hz)
Diop	33.6(*R,R*)[a] 33.7(*SS*)	
1,2-C_6H_4(PMePh)$_2$	44.7, 29.3(*R,R*); 47.6, 31.0(*S,S*)	25(*R,R*); 26(*S,S*)
Dipamp	48.4, 32.1(*R,R*); 45.3, 32.8(*S,S*)	27(*R,R*); 25(*S,S*)
Norphos	48.4(*R,R*); 46.7, 44.6(*S,S*)	5(*S,S*)
Renorphos	42.6, 42.0(*R,R*); 45.5, 44.2(*S,S*)	7(*R,R*); 8(*S,S*)
Binaph[b]	37.78, 11.62(*R,R*); 38.53, 11.00(*SS*)	43.4(*R,R*); 44.3(*S,S*)

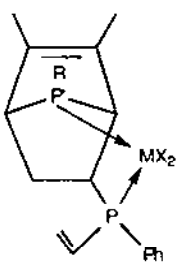
[a] Configurations of the stereocenters in the free phosphine.
[b] Data from Ref. 48.

* The negative hyperconjugation discussed in ref. 44(a) relates to the ^{31}P NMR chemical shifts of 7-phosphanorbornanes and 7-phosphanorbornenes. The system discussed here represents an extension to these earlier studies.

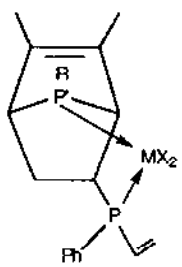
TABLE 9

40.26 MHz ($CDCl_3$) $^{31}P\{^1H\}$ NMR data for **41** and **42**

M	R	X	Diastereomer	$\delta^{31}P$ (ppM)		$^1J_{PtP}$ (Hz)	$^2J_{PP}$ (Hz)
				P′	P		
Pd	Ph	Cl	**41**	123.82	35.42		4.9
Pd	Ph	Cl	**42**	125.76	34.03		4.9
Pd	Ph	Br	**41**	125.60	35.48		1.5
Pd	Ph	Br	**42**	126.06	33.42		0
Pt	Ph	Cl	**41**	96.09	21.22	3254, 3420	17
Pt	Ph	Cl	**42**	97.3	21.1		17
Pt	Ph	Br	**41**	97.75	22.92	3159, 3357	15
Pt	Ph	Br	**42**	99.45	21.83		12
Pt	Ph	I	**41**	98.51	23.12	2957, 3188	10
Pt	Ph	I	**42**	101.40	21.13	2959, 3223	10
Pt	Bzl	I	**41**	102.27	23.95	2959, 3201	10
Pt	Bzl	I	**42**	103.90	22.92	2944, 3271	10



41



42

The structures were confirmed by X-ray crystallography. The chemical-shift differences of the two phosphorus resonances for **42** are always larger than those for **41**, allowing for facile structure assignment.

Similar [4+2] Diels–Alder cycloadditions occur [50] when (DMPP)$Mo(CO)_5$ is reacted with phenyldivinylphosphine or when phenyldivinylphosphinemolybdenumpentacarbonyl is reacted with DMPP. The $^{31}P\{^1H\}$ NMR data for the two diastereomers of the resulting tetracarbonyl complexes are: δ 49.0 (d), 143.4 (d); $^2J_{PP} = 17.1$ Hz and δ 47.2 (d), 142.5 (d); $^2J_{PP} = 17.1$ Hz respectively.

Rearrangements in square-planar and square-pyramidal palladium(II) complexes of (±)-methylphenyl (8-quinolyl)phosphine (**43**) have been studied [51]. This chiral ligand, which could potentially form all the diastereomers shown in Fig. 1, in fact forms only the cis isomers. The data are given in Table 10.

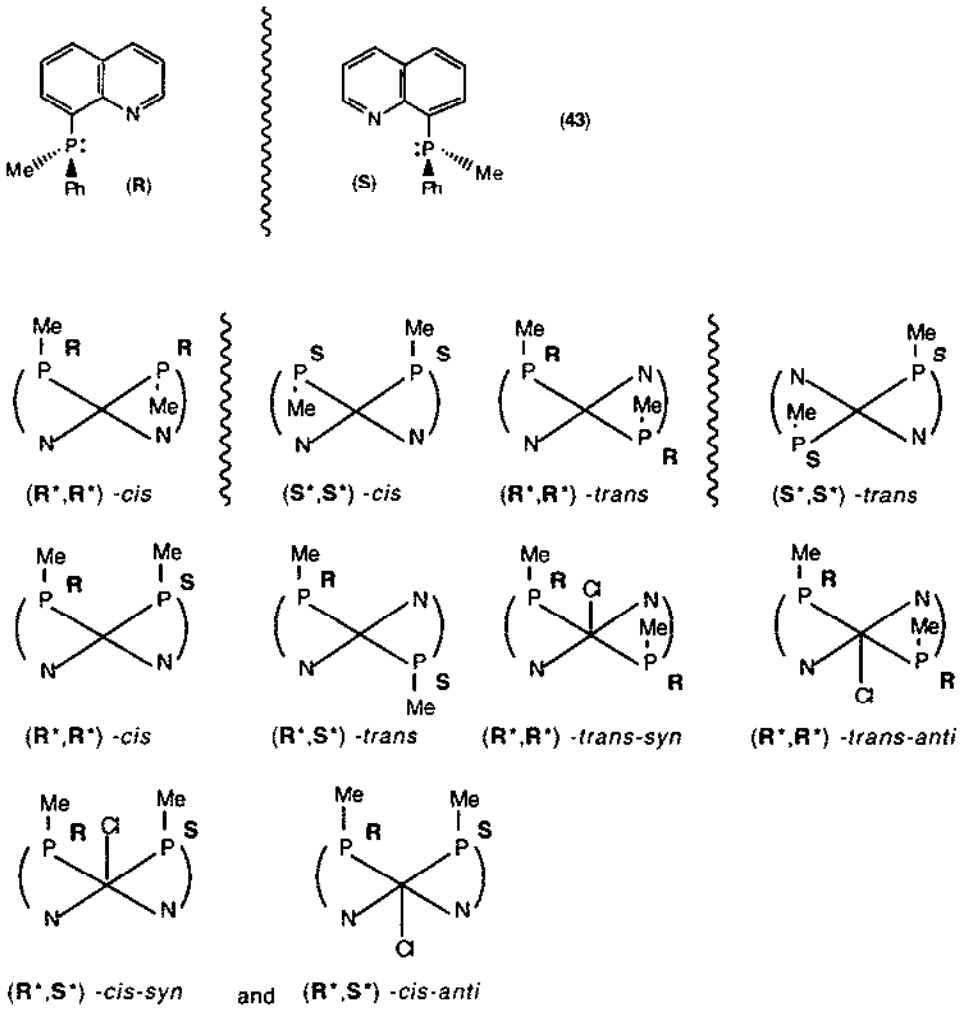
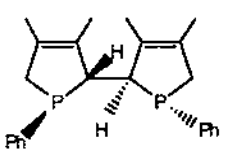


Fig. 1. Diastereomeric Pd(II) and Pt(II) complexes of **43**.

The diphospholene (**44**) [52] forms the meso and *d,l* diastereomers of $[Ni(\mathbf{44})_2](BF_4)_2$ [53] (^{31}P NMR (40.28 MHz, $CDCl_3$) δ meso 80.17, rac (*dd*+*ll*) 82.94), both of which have been characterized by X-ray crystallography.



44

In a series of papers [54–56] concerning the stereochemistry of reactions at the ruthenium stereocenter in complexes of the type $[(\eta^5\text{-}C_5H_5)Ru$

TABLE 10

24.28 MHz (CD_2Cl_2) $^{31}P\{^1H\}$ NMR data for the diastereomeric palladium(II) and platinum(II) complexes of **43**

Compound	$\delta^{31}P$ (ppm)	$^1J_{PtP}$ (Hz)
(*S,S*)-*cis*-[PdCl(P*N)$_2$]Cl	22.7	
(*R*,R**)-*cis*-[PdCl(P*N)$_2$]Cl	22.7	
(*R*,S**)-*cis*-[PdCl(P*N)$_2$]Cl	23.7	
(*S,S*)-*cis*-[PtCl(P*N)$_2$]Cl	1.2	3560
(*R*,R**)-*cis*-[PdCl(P*N)$_2$]Cl	1.2	3560
(*R*,S**)-*cis*-[PdCl(P*N)$_2$]Cl	1.9	3560
(*S,S*)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$[a]	12.1	3310
(*R*,R**)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$[a]	12.1	3310
(*R*,S**)-*cis*-[Pt(P*N)$_2$](PF$_6$)$_2$[a]	12.3	3320

[a] In DMSO-d_6 at 304 K.

(P*P)L]X, Consiglio and co-workers have obtained the ^{31}P NMR data collected in Table 11. They found that ligand substitution generally occurred with retention of

TABLE 11

^{31}P NMR data for (η^5-C_5H_5)Ru(Prophos)X (**45**) and [(η^5-C_5H_5)Ru(Prophos)L](PF$_6$) (**46**) in toluene = d_8

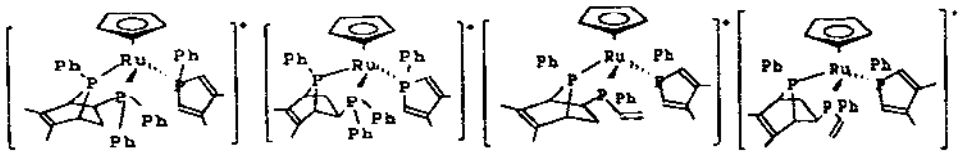
Compound	S_{Ru},R_c		R_{Ru},R_c	
	$\delta^{31}P$ (ppm)	^2J(PP) Hz	$\delta^{31}P$ (ppm)	^2J(PP) Hz
45, X=H[a]	98.1, 77.2	30.0	104.3, 85.7	22.9
45, X=CH_3	100.0, 74.1	35.2	93.6, 85.0	32.2
45, X=C_2H_5	99.1, 72.3	36.4	88.3, 81.6	37.1
45, X=$C_6H_5CH_2$	97.5, 72.9	34.2	93.0, 81.9	32.7
45, X=$C_6H_5CH_2CH_2$	100.4, 74.3	35.7	89.6, 82.4	36.3
45, X=$C_6H_5C{\equiv}C$	91.7, 68.8	31.1	89.0, 79.4	24.7
45, X=Cl	86.4, 61.3	30.3	80.9, 74.1	36.7
45, X=$SnCl_3$[b,c]	81.7, 59.5	30.6	81.8, 64.7	29.0
46, L=CH_3CN[c]	87.3, 63.1	32.9	88.1, 75.7	25.6
46, L=CH=CH_2[c]	88.2, 61.9	31.1	82.4, 58.9	38.5
46, L=C(OCH_3)$CH_2C_6H_5$[c]	92.2, 67.6	32.8	84.0, 76.6	33.1
46, L=C=CHC_6H_5[c]	80.0, 61.0	27.9	83.7, 63.5	29.3
46, L=C=$CHCH_3$[c]	83.1, 67.9	25.8	90.7, 74.1	23.8

[a] In C_6O_6.

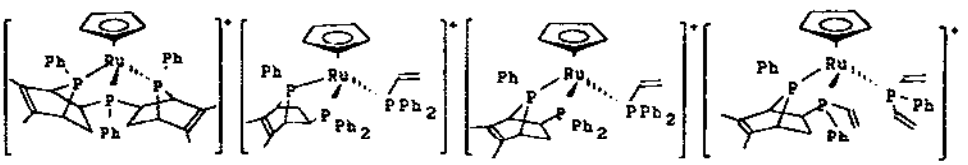
[b] Because of the convention applied in this case the descriptors must be interchanged even though the geometry of the complexes in the two series is the same [25].

[c] In CD_2Cl_2.

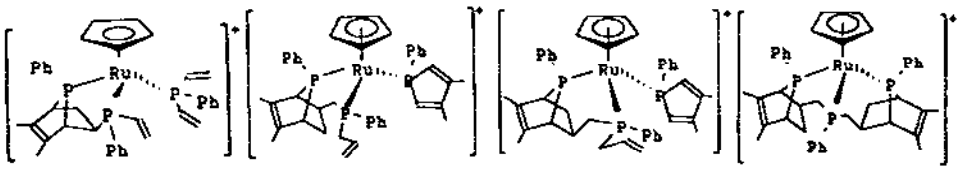
stereochemistry at the ruthenium center [54]. These authors noted empirically that the diastereomers having the $S_{Ru}R_C$ configuration exhibit differences in the ^{31}P chemical shifts for the two phosphorus atoms which are always larger than those for the $R_{Ru}R_C$ diastereomers. This rule seems to apply equally as well to the absolute configurations of the diastereomers formed by intramolecular [4+2] Diels–Alder cycloadditions within the coordination spheres of $[(\eta^5\text{-}C_5H_5)Ru(DMPP)_{3-n}(\text{dienophile})_n]PF_6$ [57] and iron analogs [58]. The data are given in Tables 12 and 13.



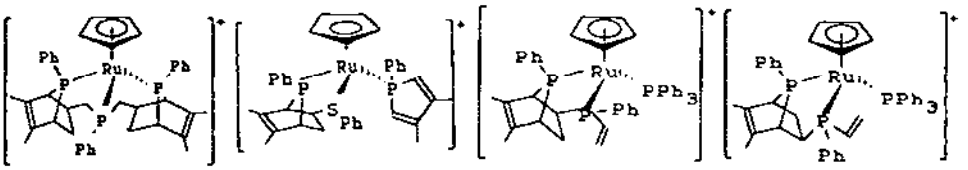
46a 46b 47a 47b



47c 48a 48b 49a



49b 50a 50b 50c



50d 51a,b 52a 52b

are sulfur epimers racemic racemic

The ligand structures **A** or **B** were assigned by comparison with X-ray crystal structures and Consiglio's empirical rule [54] based upon the magnitude of $\Delta\delta$.

TABLE 12

121.65 MHz ($CDCl_3$) $^{31}P\{^1H\}$ NMR data for the complexes **46–52**[a]

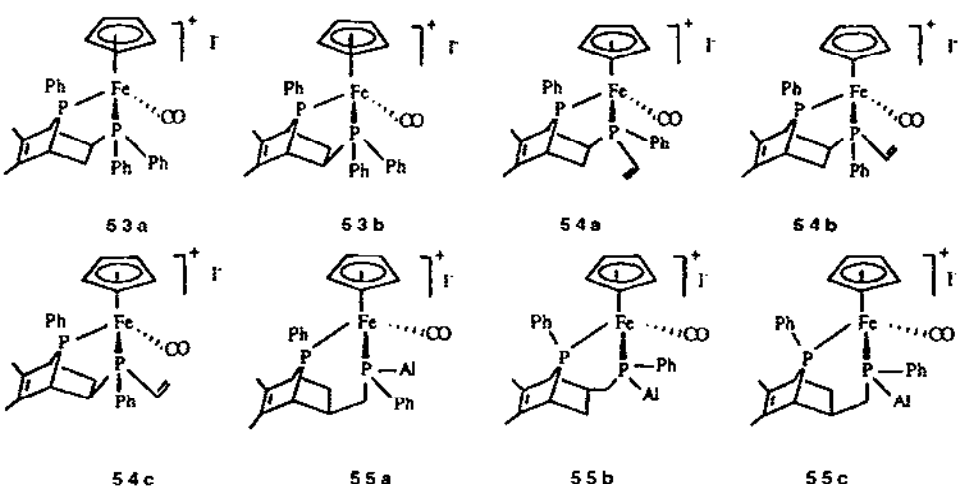
Compound	Ratio[b]	$\delta^{31}P(m)$,[c] (ppm)			$^2J_{PP}$ (Hz)		
		P_1	P_2	P_3	P_1P_2	P_2P_3	P_1P_3
46a	5	151.18(dd)	54.16(dd)	48.84(dd)	41.24	34.55	30.30
46b	1	152.47(dd)	69.57(dd)	40.21(dd)	48.83	39.06	26.90
47a	3	151.50(dd)	56.01(dd)	40.56(dd)	53.71	46.10	37.83
47b	1	154.71(dd)	60.19(dd)	47.84(dd)	48.83	46.39	39.06
47c	4	159.20(d)	78.60(t)		43.94		
48a	9	151.08(dd)	52.18(dd)	42.18(dd)	39.42	37.29	31.51
48b	1	152.35(dd)	68.96(dd)	61.83(dd)	46.23	40.63	23.48
49a	6	151.99(dd)	48.44(dd)	35.24(dd)	43.95	34.18	34.18
49b	1	154.65(dd)	45.78(dd)	39.48(dd)	43.95	34.18	34.18
50a	3	129.46(dd)	44.51(dd)	17.26(dd)	34.18	29.30	43.95
50b	1	123.72(dd)	47.95(dd)	13.33(dd)	29.30	39.07	48.83
50c	1	127.57(AB)	125.19(AB)	6.13(X)	31.23	43.15	44.20
50d		124.11(d)	6.51(t)		45.56		
51a	3[d]	164.81(d)		44.69(d)			35.41
51b	1[d]	159.41(d)		46.50(d)			35.41
52a	3	154.65(dd)	50.01(dd)	41.36(dd)	34.18	29.30	43.94
52b	2	156.83(dd)	45.53(dd)	42.45(dd)	34.18	34.18	43.94

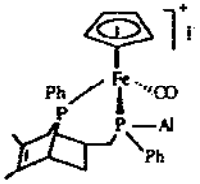
[a] **46a,b**, **47a–c**, **48a,b**, and **49a–d** in CD_3NO_2, the other complexes in $CDCl_3$.

[b] The ratio is among stereoisomers of the same composition.

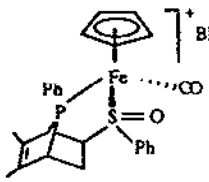
[c] Abbreviations: m, multiciplicity; d, doublet; dd, doublet of doublets; t, triplet; AB, AB quartet, X, X part of ABX.

[d] At −20°C in $CDCl_3$, stopped exchange limit.

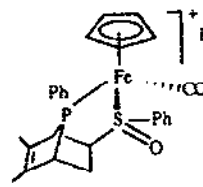




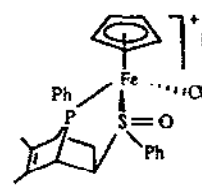
55d



56a



56b



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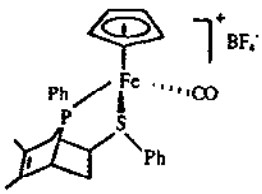
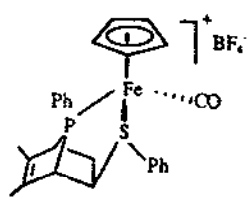


57a

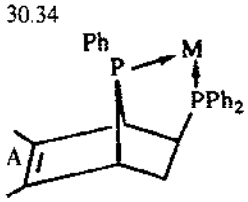
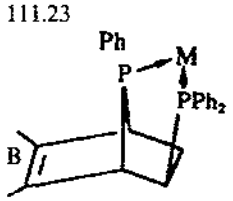


57b

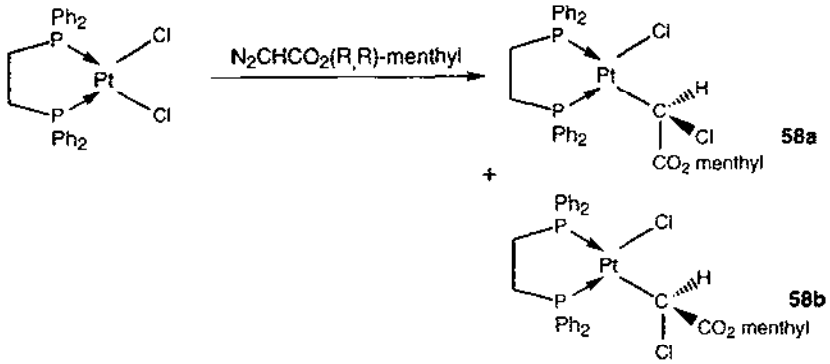
Reactions (7)–(11) have been studied [59] for complexes containing symmetric (reaction (7)) and asymmetric (reactions (8)–(11)) diphosphines. The ^{31}P NMR data for the diastereomers thus obtained are given in Table 14.

TABLE 13

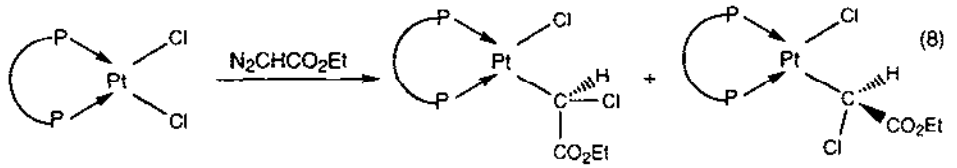
121.65 MHz ($CDCl_3$) $^{31}P\{^1H\}$ NMR data for the complexes **13–17** and ligand structure assignments[a]

Compound	δP_7	δP_2	$\Delta\delta = \delta P_7 - \delta P_2$	Ligand structure
53a	173.10	70.47	102.63	A
53b	171.27	88.09	83.18	B
54a	171.19	64.42	106.77	A
54b	174.43	66.66	107.77	A
54c	168.55	83.39	85.16	B
55a	144.57	38.31	106.26	B
55b	144.27	34.43	109.84	A
55c	145.30	38.79	106.51	B
55d	141.57	30.34	111.23	A
56a	174.2			A
56b	169.8			A
56c	165.8			B
57a	170.1			A
57b	166.9			B

[a] In ppm; P_7 is the 7-phosphaphosphorus atom and P_2 is the exocyclic 2-phosphinophosphorus atom.

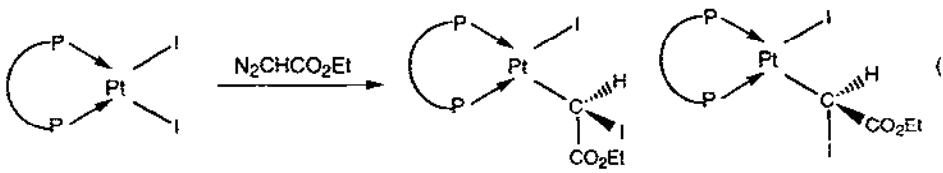


(7)



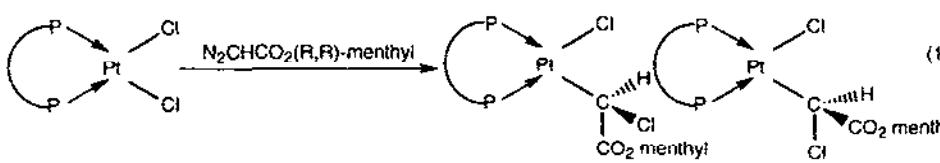
(8)

59a	P∼P = R,R – diop	**60a**	**61a**
59b	P∼P = S,S – skewphos	**60b**	**61b**
59c	P∼P = S,S – chiraphos	**60c**	**61c**



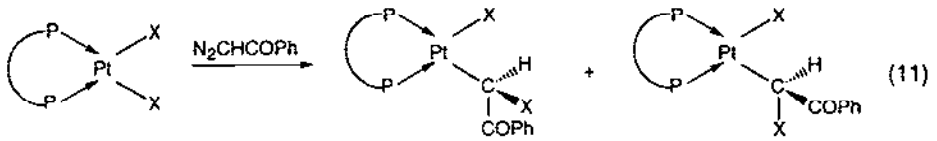
(9)

62a	P∼P = R,R – diop	**63a**	**64a**
62b	P∼P = S,S – skewphos	**63b**	**64c**
62c	P∼P = S,S – chiraphos	**63c**	**64c**



(10)

59a	P∼P = R,R – diop	**65a**	**66a**
59b	P∼P = S,S – skewphos	**65b**	**66b**



(11)

69a	P∼P = R,R – diop, X = Cl	**67a**	**68a**
59b	P∼P = S,S – skewphos, X = Cl	**67b**	**68b**
62c	P∼P = R,R – diop, X = I	**69a**	**70a**
62b	P∼P = S,S – skewphos, X = I	**69b**	**70b**

TABLE 14

36.2 MHz $^{31}P\{^1H\}$ NMR data for complexes **58–70** in $CDCl_3$[a]

Compound	$\delta(P_A)$	$^1J(PtP_A)$	$\delta(P_B)$	$^1J(PtP_B)$	$^2J(P_AP_B)$	Ratio[b]
58a,b	41.4	3972	39.9	2102	5	1.0
	40.9	3984	39.4	2097	5	
60a[c]	1.5	4099	−0.5	1946	20	3.0
61a[c]	1.5	4099	−1.3	1932	20	
61b	11.5	3921	7.3	1902	27	2.0
60b	10.9	3960	8.7	1980	27	
60c,61c	41.3	3872	40.0	2063	15	3.0
	41.3	3972	40.0	1997	15	
63a,64a	−5.3	3894	−8.8	2033	17	3.0
	−4.6	3869	−11.3	2026	17	
63b,64b	4.8	3716	3.8	2053	24	1.0
	6.0	3762	0.7	1997	27	
63c,64c	38.5	3762	37.4	2051	15	1.5
	40.1	3608	37.8	2241	15	
65a,66a	1.2	4076	−0.9	1928	20	2.5
	−0.9	4082	−2.0	1922	20	
65b,66b	11.4	3943	7.1	1924	27	1.0
	11.0	3913	7.1	1924	27	
67a,68a	0.7	4072	−0.6	1995	20	5.0
	−0.2	4072	−1.9	2000	20	
67b,68b	10.4	3885	8.0	2011	27	7.0
	8.9	3909	9.1	1994	27	
69a,70a	−6.9	3884	−8.6	2103	17	5.0
	−6.2	3860	−12.3	2063	19	
69b,70b	3.3	3771	2.6	2092	27	10
	1.8	3715	0.1	2048	27	

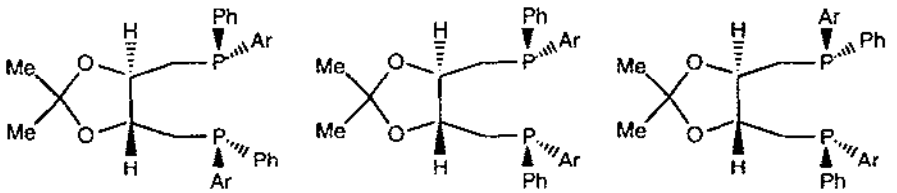
[a] P_A is trans to the halide and P_B is trans to the carbon.

[b] Numbers in this column refer to the ratios of the ^{31}P NMR signals representing the two diastereomers (data for the major diastereomer are given first).

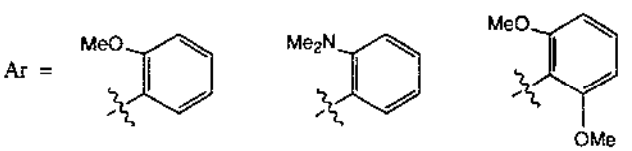
[c] Some of the signals were coincident in $CDCl_3$, but in $(CD_3)_2SO$ they are clearly resolved: **60a**, $\delta(P_A)$ 2.4, $^1J(PtP_A)=4057$, $\delta(P_B)=-0.5$, $^1J(PtP_B)=1970$, $^2J(P_AP_B)=20$; **61a** $\delta(P_A)$ 2.9, $^1J(PtP_A)=4050$, $\delta(P_B)=-1.4$, $^1J(PtP_B)=1965$, $^2J(P_AP_B)=20$.

The absolute configuration of **60a** was determined by X-ray crystallography.The absolute configuration at the α-carbon for the major diastereomer **60b** was determined by conversion of **60a** to **60b** by reaction of **60a** with skewphos.

The stereochemically matched (and mismatched) bisphosphine DIOP-DIPAMP hybrid ligands **71–73** have been prepared, the diastereomers separated and their molybdenum tetracarbonyl complexes have been characterized [60]. The ^{31}P NMR data for these compounds are given in Table 15.



Ar =



71 **72** **73**

The absolute configurations of Rp,Rp(**71**), Rp,Rp(**72**), Rp,Rp(**73**) and Sp,Sp(**73**) were determined from X-ray crystal structures of their $Mo(CO)_4$ complexes.

TABLE 15

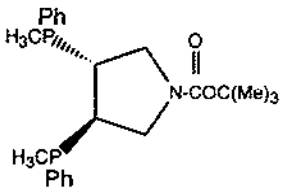
$^{31}P\{^1H\}$ NMR data for the diastereomeric bisphosphines **71** and **72** and the $Mo(CO)_4$ complexes of **71–73** in $CDCl_3$

Compound	Diastereomer	$\delta^{31}P$ (ppm)
71	Rp, Rp	−30.87
	Rp, Sp	−29.87, −30.69
	Sp, Sp	−29.82
72	Rp, Rp	−29.70
	Rp, Sp	−29.90(d), −30.3(d), $^5J_{PP}$ = 1.7 Hz
	Sp, Sp	−30.1
$Mo(CO)_4$ (**71**)	Rp, Rp	18.8
	Rp, Sp	13.67(d), 22.47(d), $^2J_{PP}$ = 20.9 Hz
	Sp, Sp	13.99
$Mo(CO)_4$ (**72**)	Rp, Rp	24.7
	Rp, Sp	11.4(d), 26.0(d), $^2J_{PP}$ = 19.3 Hz
	Sp, Sp	11.5
$Mo(CO)_4$ (**73**)	Rp, Rp	17.9
	Sp, Sp	19.4

The free bisphosphines (**71**) and (**72**) were liberated from their respective $Mo(CO)_4$ complexes without epimerization of the phosphine stereocenters by reduction of the complexes with sodium naphthalenide at −78 °C in THF. This procedure was not successful for Rp,Sp or Rp,Rp**73** but succeeded for Sp,Sp**73**.

In situ formed rhodium complexes of the diastereomers of **71** were evaluated as asymmetric catalysts for hydrogenation of a dehydroaminoacid, for hydrosilylation of phenylethanone and for hydroboration of norbornene, indene and styrene. In each case the enantiomeric excesses were low to moderate (0 to 84%) and the Sp,Sp diastereomer consistently provided the highest enantiomeric excesses.

The diastereomeric bisphosphine (**74**) and its PdI_2 complexes have been separated and characterized [61]. Cyanide displacement of the bisphosphine from the palladium complexes occurs without epimerization of the phosphorus stereocenters.



74

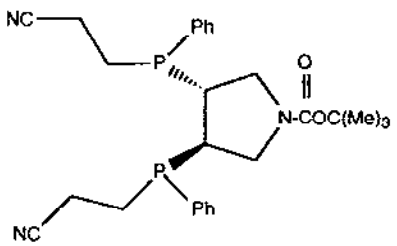
$\delta^{31}P(CD_3OD)$

	ligand	PdI_2 complex
PR, 3R, 4R, P'R	−28.65	23.58
PS, 3R, 4R, P'S	−29.03	27.98
PR, 3R, 4R, P'S	−28.5 to −29.5m	29.39(d), 24.81(d); $^2J_{PP}$ = 27.4 Hz 29.59(d), 24.96(d); $^2J_{PP}$ = 27.4 Hz

$\delta^{31}P$ for [(COD)Rh(**74**)] BF_4 in CD_2Cl_2

PS, 3R, 4R, P'S	21.11(d); $^1J_{RhP}$ = 151.6 Hz
PR, 3R, 4R, P'R	18.00(d); $^1J_{RhP}$ = 147.8 Hz
PR, 3R, 4R, P'S	23.75 (143.4), 20.48 (153.9) ABX; $^2J_{PP}$ = 12.4 Hz 24.07 (143.9), 20.17 (153.4) ABX; $^2J_{PP}$ = 12.4 Hz

Two AB spectra are observed for the palladium complex of the PR, 3R, 4R, P'S diastereomer because of hindered amide rotation. The absolute configuration of PdI_2 (PS,3R,4R,P'S-**74**) was determined by X-ray crystallography. A similar bisphosphine **75** and its palladium iodide complexes have also been reported [62].



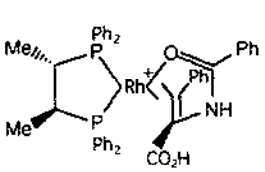
(75)

$\delta^{31}P(CH_2Cl_2/C_6D_6)$

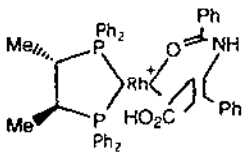
	ligand	PdI_2 complex
PS, 3R, 4R, P'S	−18.01, −18.05 (AB)	36.8 (AB)
PR, 3R, 4R, P'R	−17.98, −18.26 (AB)	33.6 (AB)
PR, 3R, 4R, P'S	−17.92(d), −18.64(d); $^3J_{PP}=21$ Hz	37.77(d), 31.49(d); $^2J_{PP}=19$ Hz 37.52(d), 31.74(d); $^2J_{PP}=19$ Hz

The absolute configuration of the PS, 3R, 4R, P'S diastereomer was determined from the X-ray crystal structure of its PdI_2 complex. These same authors have prepared and characterized the diastereomeric $[(COD)Rh(\mathbf{74})]BF_4$ complexes [63]. From an investigation of catalytic hydrogenation of α-(acetylamino) cinnamic acid and its methyl ester, they concluded that the high enatioselectivities obtained with the rhodium complexes of conformationally rigid bis(diphenylphosphino) ligands are mainly due to the influence of the axially situated phenyl groups at the phosphorus atoms. The equatorially situated phenyl groups play a minor role.

Brown and co-workers, in a series of papers [64–67] relating to the mechanism of rhodium-catalyzed asymmetric hydrogenation, have determined the diastereomeric ratios for $[(P^*P)Rh(alkene)]^+$ complexes exemplified by **76** and **77** (Table 16).



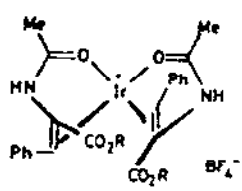
76



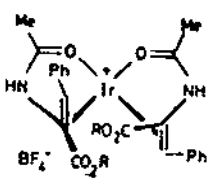
77

These authors found that the prochiral enamides coordinate to the $\{(P^*P)Rh\}^+$ moiety as bidentate ligands binding through the alkene C=C group and the amide oxygen as illustrated in **76** and **77**. The diastereomeric ratios are temperature-dependent and do not correlate with the optical yields observed in catalytic hydrogenation. Landis and Halpern have shown [68], by detailed kinetic studies, that the predominant product of catalytic hydrogenation derives from the minor (less stable) diastereomer by virtue of its much higher reactivity toward H_2.

The resolved enamide complex (+)-**78** or (−)-**78** may be used for the resolution of chiral diphosphines. The crystal structure of (+)-**78** has been determined [69].



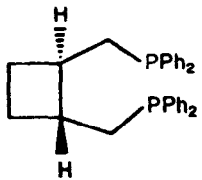
(-)-(**78**) R=(S) - menthyl



(+)-(**78**) R=(R)- menthyl

TABLE 16

36 MHz (CD_3OD) $^{31}P\{^1H\}$ NMR data for $[(P\sim P)Rh(enamide)]^+$

P∼P	Alkene	$\delta^{31}P$ (ppm)		$^1J_{RhP}$ (Hz)		$^2J_{PP}$ (Hz)	Ratio (θ)
		P1	P2	P1	P2		
dipamp	Z-PhCH=C(CO_2H)NHCOPh	70.8	49.5	161	154	39	
		69.6	60.0	156	158	38	92:8/301
	Z-PhCH=C(CO_2Me)NHCOPh	71.2	49.9	162	151	40	
		69.1	59.9	156	160	36	91:9/304
	Z-PhCH=C(CO_2Me)NHCOMe	71.7	48.3	162	150	40	
		69.6	58.1	157	160	38	93:7/303
	Z-PhCH=C(CO_2Bu^t)NHCOMe	72.1	47.6	160	149	40	
		70.7	54.5	149	159	35	87:13/241
	CH_2=C(CO_2H)CH_2CO_2H	67.9	52.2	147	154	22	
		70.2	52.4	151	153	22	7:2/303
	CH_2=C(CO_2H)CH_2CO_2Me	68.2	51.0	150	153	22	
		66.6	50.8	148	151	21	4:1/303
	Z-PhCH=C(CO_2H)NHCOMe	40.3	12.9	154	150	48	
		30.4	14.3	160	162	49	73:27/241
	Z-PhCH=C(CO_2H)NHCOPh	39.1	14.6	153	152	50	
		30.4	16.6	162	165	44	80:20/241
	Z-PhCH=C(CO_2H)NHCOBu^t	38.8	13.6	154	154	50	
		30.3	15.4	162	165	44	52:48/241
	Z-PhCH=C(CO_2H)NHCOAd[a]	38.7	14.3	153	155	50	
		30.2	15.7	162	165	45	65:35/241
	Z-PhCH=C(CO_2Me)NHCOMe	39.5	13.6	152	150	50	

		31.3	14.7	160	159	45	93:7/241
	Z-PhCH=C(CO_2Me)NHCOPh	38.1	14.7	153	155	52	
		30.8	17.8	160	163	46	95:5/274
	Z-PhCH=C(CO_2Me)NHCOAd[a]	36.8	13.8	155	160	51	
		30.1	16.3	160	162	46	77:23/305
	Z-PhCH=C($CO_2CH_2CF_3$)NHCOMe	39.3	14.0	151	150	50	
		38.5	15.0	149	150	50	13:87/241
	Z-MeCH=C(CO_2Me)NHCOH	40.0	14.0	154	147	49	
		36.1	11.2	154	147	46	41:59/241
	Z-EtCH=C(CO_2Me)NHCOH	40.6	14.4	153	144	49	
		36.4	10.7	152	144	46	48:52/241
	Z-Pr^{i}CH=C(CO_2Me)NHCOH	45.5	4.3	159	122	34	
		32.6	12.7	162	154	43	67:33/241
	Z-CF_3CH=C(CO_2Me)NHCOH	41.8	9.2	144	123	37	
		33.9	11.6	140	124	38	65:35/274
diop	*Z*-PhCH=C(CO_2Pr^i)NHCOMe	35.0	10.0	152	153	52	
		28.6	10.3	159	159	47	69:18/241
	cis-PhCH=CH(CO_2H)	35.3	15.1	176	170	52	
		41.3	12.7	176	168	52	3:1/230
	CH_2=CPh(CO_2H) + NEt_3	35.5	13.6	173	168	50	
		39.3	10.6	173	170	50	3:2/235
	E-PhCH=CPh(CO_2H) + NEt_3	31.8	16.0	178	171	50	
		35.6	11.6	178	170	51	3:2/303
	o-$OCH_3C_6H_4C(CO_2H)$=CH_2	37.1	14.7	173	172	53	
		42.0	10.2	170	172	52	4:1/252
	E-PhCH=C(CO_2H)NHBzl	38.4	11.6	178	166	52	
		33.3	15.4	178	170	52	1:1/295
	CH_2=CPh($CONMe_2$)	39.3	14.1	173	168	53	
		35.9	10.3	174	170	53	3:2/236
	CH_2=CHPh($CONH_2$)	43.3	6.7	163	162	52	
		36.9	12.4	172	168	51	5:4/228
	o-$OCH_3C_6H_4C(CONMe_2)$=CH_2	37.3	13.4	171	168	52	

TABLE 16 (*continued*)

P∼P	Alkene	δ^{31}P (ppm)		$^{1}J_{RhP}$ (Hz)		$^{2}J_{PP}$ (Hz)	Ratio (θ)
		P1	P2	P1	P2		
		41.2	9.2	171	167	53	3:1/252
	2-Methylpropenoic acid + NEt_3	39.4	13.1	170	173	53	
		34.6	14.4	171	173	53	1:1/252
	2-Methylpropenoic acid	30.7	29.7	161	137	39	
		31.4	17.6	140	134	41	5:1/252
	Propenoic acid	31.5	18.3	140	134	41	
		30.5	30.5	161	141	–	6:1/228
	CH_2=CPh(CH_2NHAc)[a]	38.9	12.6	174	155	50	
		40.5	10.5	171	154	49	3:2/228
	CH_2=CH(CH_2NHAc)[a]	41.6	12.1	179	153	48	
		42.0	10.5	179	153	49	1:1/252

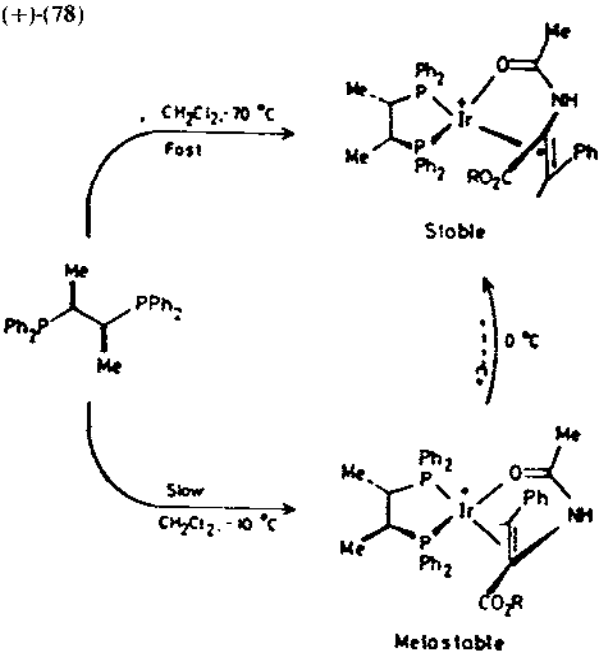
[a] Ad = 1-adamantyl, Ac = CH_3CO_2.

TABLE 17

Reaction products from chiral diphosphines and (+)-(78) or its enantiomer (−)-(78)

Initial iridium complex	Biphosphine	δ (ppm), J (Hz); θ (°C); solvent	Isomer
(+)-(78)	(*S*,*S*)-Chiraphos	45.7; 26.6; 26; −70; CH_2Cl_2	Stable, C_α^{re}
(−)-(78)	(*S*,*S*)-Chiraphos	54.7; 30.0; Br; 0; CH_2Cl_2	Metastable, C_α^{si}
(−)-(78)	(*S*,*S*)-Chiraphos	46.4; 27.1; 26:25; CH_2Cl_2	Stable, C_α^{re}
(+)-(78)	(*R*,*R*)-Dipamp	37.1; 23.6; small; 0; CH_2Cl_2	Metastable, C_α^{re}
(+)-(78)	(*R*,*R*)-Dipamp	45.6; 24.8; small; 0; CH_2Cl_2	Stable, C_α^{si}
(+)-(78)	(*R*,*R*)-Diop	−2.5; −17.0; 20; 10; MeOH	Stable, C_α^{re}
(−)-(78)	(*R*,*R*)-Diop	−1.4; −22.3; 22.5; MeOH	Metastable, C_α^{si}
(−)-(78)	(*R*,*R*)-Diop	−2.6; −16.5; 5:20; 10; MeOH	Stable, C_α^{re}

(+)-(78)

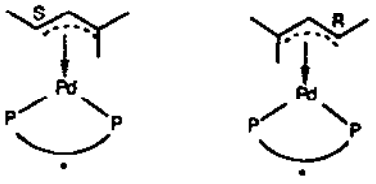


(+)-(78)

Complex **78** forms the diastereomers (Table 17) upon reaction with chiral diphosphines. One diastereomer is metastable and slowly converts to the stable diastereomer as illustrated above for (S,S)-chiraphos.

The chiral palladium(0) and platinum(0) complexes [(R,R)-Diop]M(CH_2CH_2) (**79**) act as derivatizing agents for the ^{31}P NMR assay of the enantiomeric purity of certain chiral alkenes and allenes as they readily displace the ethene ligand from **79** [70]. ^{31}P NMR data are given in Table 18. There is no enantioselectivity in binding of the *Si* or *Re* faces of the C=C double bond to the metal.

Diastereomers of [Pd(P*P)(chiral π-allyl)]$^+$ complexes have been characterized by ^{31}P NMR in the course of studies relating to catalytic allyllation [71–73]. Diastereomers of the types **80** and **81** result. ^{31}P NMR data are collected in Table 19.



major minor

80 **81**

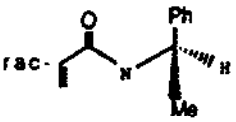
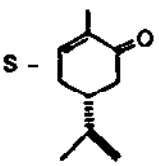
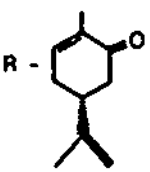
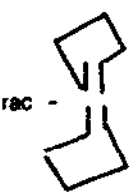
The crystal structure of the major diastereomer of [Pd(η^3-C(Xyl)$_2$CHCHPh)(S,S-chiraphos)]BPh_4 has been reported [74]. It has been found in a study of the mechanism of asymmetric catalytic allylation [75] that the π-allyl intermediates epimerize 10 to 100 times faster than nucleophilic attack occurs. The nucleophilic attack is the turnover-limiting step as well as being the enantioselective step. In contrast to asymmetric catalytic hydrogenation [68,76–79], the major diastereomeric intermediate produces the major product enantiomer.

5. CONCLUSIONS

The synthetic applications of enantioselective organotransition-metal-mediated reactions have recently been reviewed [80,81]. A large majority of the catalysts employed thus far contain asymmetric phosphines. Chirality transfer is generally believed to occur by way of diastereomeric transition states. Many of the early studies did not take advantage of the broad utility of ^{31}P NMR spectroscopy. Hopefully, the data provided in this review will promote a more general application of this spectroscopic technique.

TABLE 18

$^{31}P\{^{1}H\}$ (C_6D_6, 298 K) NMR data for the diastereomers formed upon reaction of **79**, M = Pt, with chiral alkenes and allenes

Ligand	Isomer	$\delta^{31}P$ (ppm)		J (Hz)		
		P(1)	P(2)	Pt(P1)	Pt(P2)	P(1)P(2)
	(i)[a]	12.8	9.9	3801	3759	57
	(ii)	12.7	11.3	3512	3477	61
	(iii)	13.6	9.6	3828	3752	57
	(iv)	13.3	10.8	3470	3500	64
		12.5[b]	10.8	3409	3881	65
		13.8	9.9	3537	3938	65
	(i)[c]	17.6	11.0	3246	3057	71
	(iii)	17.3	10.3	3250	3060	71

[a] (i) and (ii) [and (iii) and (iv)] are unassigned constitutional isomers related by *Si*- or *Re*-binding of the alkene, while (i) and (iii) [and (ii) and (iv)] are diastereomers related by binding of the S and R enantiomers of the alkene by the same face.

[b] A figure shows the ^{31}P NMR spectra observed for (S)(+)- and (R)(−)-carvone and various mixtues of the two.

[c] Binding occurs only to the less hindered face.

TABLE 19

$^{31}P\{^{1}H\}$ NMR data for $[Pd(P^{*}P)(\text{chiral } \pi\text{-allyl})]^{+}$ complexes

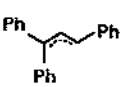
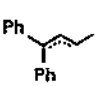
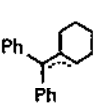
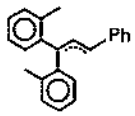
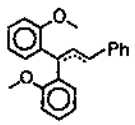
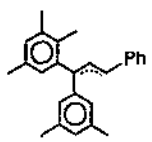
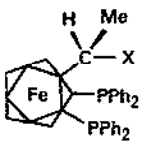
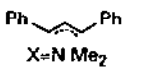
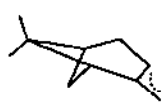
Diphosphine	Allyl	Major / Minor diastereomer		^{31}P NMR[a] J	Diastereomer ratios[b]	
					$CDCl_3$	DMF
		$\delta(P_1)$	$\delta(P_2)$			
S–S chiraphos		50.58	49.38	51.17	1:1	1:1(−20°C)[f,e]
		51.02	49.02	50.84		
		53.29	48.49	53.79		
		49.44	48.38	52.15	1.7:1	1.9:1(−20°C)[f,e]
		51.75	46.89	52.15		
		47.45	47.09	—[c]		1.6:1(60°C)
		53.42	47.52	55.76		
		48.78	47.12	54.45	1.2:1	[f,e]
		50.64	49.26	50.18		
		50.38	48.92	49.20	1.8:1	[f,e]
		52.26	50.20	59.04		
		52.34	48.50	58.38	1:1	1:1(−20°C)[f,e]
		55.75	44.47	64.62		
		51.28	50.56	—[c]	6:1	9.7:1(−20°C)[f,e]
		57.74	45.84	73.80		
		52.33	49.81	73.47	5.5:1	6:1(3.7:1 in THF)
		55.60	42.22	67.57		
		50.86	50.36	—[c]	4:1	6:1
		53.78	42.60	61.01		
		49.52	48.62	—[c]	5:1	7.4:1
		54.74	44.86	58.38		
		50.32	48.72	—[c]	3.1:1	[f,e]

TABLE 19 (*continued*)

Diphosphine	Allyl	Major diastereomer $\delta(P_1)$	Major diastereomer $\delta(P_2)$	Minor diastereomer $\delta(P_1)$	^{31}P NMR[a] J	Diastereomer ratios[b] $CDCl_3$	Diastereomer ratios[b] DMF
		57.76	44.18	52.15	73.47	1.5:1	2.8:1 (1.6:1 in Me_2SO)
		57.06	45.98	51.89	76.75	<2:1[d]	<2:1[d] 11.7:1
		55.22	47.44	52.54	76.75		12.5:1 (Me_2SO) 11:1 (THF)
		22.00	25.81	23.74	58.8 28.45	63.2	20:1[f]
		23.03	28.37	24.25	59.9 31.24	60.3	2:1[g]
S-Binap		27.5[h]	22.9	22.8	50 19.6	52	
R-Binap							

[a] Chemical shifts in ppm relative to 85% H_3PO_4; $\delta(P_1)$ are the chemical shifts of the phosphorus atoms of the major (top row) and minor (lower row) diastereomers; J is the coupling constant in Hz; spectra were run in $CDCl_3$ at 32.3 MHz and are proton-decoupled.

[b] Ratios were determined at 35°C unless otherwise noted.

[c] Only two peaks are observed and are assumed to be the inner peaks of an AB quartet. The quoted chemical shifts are based on this assumption and on the assumption that the coupling constant is the same as that of the major diastereomer.

[d] Large error.

[e] f = fluxional at 35°C.

[f] 40°C [72].

[g] −10°C [72].

[h] [73].

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APPENDIX: ABBREVIATIONS