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Reactions of coordinated phosphines and arsines: stereoselective reactions at the chlorophosphine-*P* stereocentre in the complex [(*R**), (*R**, *R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}-Fe(PClMePh)]$PF_6 \cdot CH_2Cl_2$

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Abstract

The reaction of (*R**, *R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(NCMe)]PF_6 with (±)-chloromethylphenylphosphine in boiling dichloromethane affords a separable mixture of two diastereomeric iron complexes, epimeric at the chlorophosphine-*P* stereocentre, *viz*. [(*R**), (*R**, *R**)]-(±)- and [(*S**), (*R**, *R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(PClMePh)]PF_6, with the diastereomeric ratio (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 3/1. The crystal structure of the (*R**), (*R**, *R**) diastereomer (with one molecule of solvation of dichloromethane) has been determined. By use of the optically active acetonitrile complex, optically pure [*R*-[(*S**), (*R**, *R**)]]-(+)$_{589}$-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(PClMePh)]$PF_6 \cdot Me_2CO$ was obtained, the first complex to be isolated containing resolved (±)-PClMePh. Alkylations of the diastereomeric chlorophosphine-iron complexes with Grignard reagents in tetrahydrofuran at 20°C are highly stereoselective, with predominant retention of configuration at phosphorus. The reaction of ethylmagnesium bromide with the (*R**), (*R**, *R**) diastereomer of the (±)-chloromethylphenylphosphine-iron complexes gives the (±)-ethylmethylphenylphosphine-iron complex with (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 1/3; benzylmagnesium bromide gives the (±)-benzylmethylphenylphosphine iron complex with (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 1/8. Sodium borohydride reductions of the (±)-chloromethylphenylphosphine-iron complexes are also stereoselective, with predominant retention of configuration at phosphorus in each case. Thallium(I) phenoxide, however, when allowed to react with the (*R**), (*R**, *R**) diastereomer of the (±)-chloromethylphenyl-phosphine-iron complex in boiling tetrahydrofuran, gives the corresponding (±)-methylphenoxyphenylphosphine-iron complex, with predominant inversion of configuration at phosphorus ((*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 1/6).

1. Introduction

Trivalent chlorophosphines form metal complexes that are useful intermediates for the synthesis of a variety of coordinated phosphines by substitution of chloride [1]. Hitherto, however, the stereoselectivity of substitution at phosphorus in chlorophosphine complexes does not appear to have been investigated, although alkylations of primary and secondary phosphines [2] (and secondary arsines [3]) coordinated to iron(II) have been shown to be highly stereoselective when performed at low temperatures. Herein we report that (±)-chloromethylphenylphosphine can be resolved in certain organometallic iron(II) complexes and that substitution of chloride in the resulting configurationally homogeneous diastereomers by Grignard reagents, sodium borohydride, or thallium(I) phenoxide is highly stereoselective at phosphorus.

2. Results

The complex (*R**, *R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(NCMe)]PF_6, (*R**, *R**)-**1**, is readily prepared as a racemate or in homochiral form from (η^5-C_5H_5)$Fe(CO)_2Br$ and the appropriate form of the bis(tertiary phosphine) [4]. The optically pure forms of the complex are convenient resolving agents for chiral ligands capable of displacing the acetonitrile. Thus, with (±)-chloromethylphenylphosphine in boiling dichloromethane, (*R**, *R**)-**1** affords the diastereomers

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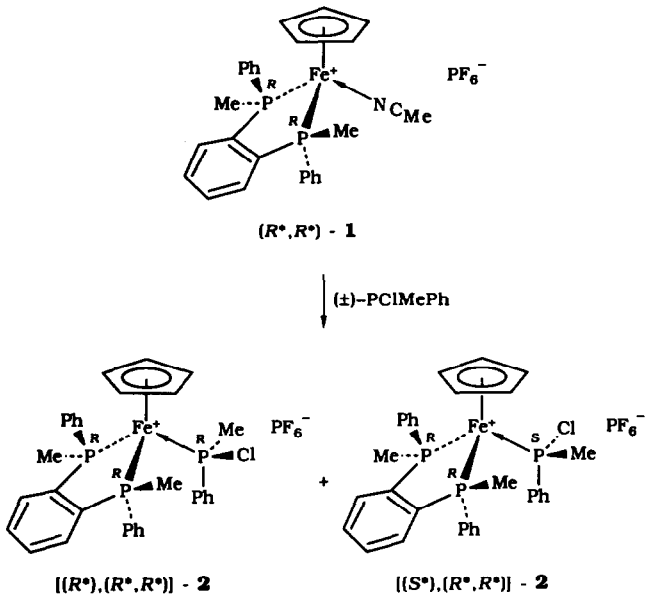


Fig. 1. Synthesis of chiral secondary chlorophosphine–iron complexes. One enantiomer of each diastereomer is depicted.

[(*R**), (*R**, *R**)]-(±)- and [(*S**), (*R**, *R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4($PMePh_2$)}Fe(PClMePh)]PF_6, [(*R**), (*R**, *R**)]- and [(*S**), (*R**, *R**)]-**2**, with the diastereomeric ratio (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 3/1 (Fig. 1) [5*]. The major diastereomer crystallizes from dichloromethane–petroleum ether (b.p. 60–80°C) as the *1:1 dichloromethane solvate*; the minor diastereomer was recovered from the mother liquor after evaporation and recrystallization of the residue from acetone–diethyl ether. The more soluble diastereomer crystallizes as a *1:1 acetone solvate*. Selected ^{1}H NMR data for the two complexes are given in Table 1. For each diastereomer, a pair of resonances in the range δ 2.12–2.52 was observed in dichloromethane-d_2 for the non-equivalent P*Me* groups of the bis(tertiary phosphine). The resonances for the chlorophosphine P*Me* groups in **2** occur at δ 1.38 for the (*R**), (*R**, *R**) diastereomer and at δ 2.34 for the (*S**), (*R**, *R**) diastereomer (Table 1). In the $^{31}P\{^1H\}$ NMR spectra of

* Reference number with asterisk indicates a note in the list of references.

TABLE 1. Selected ^{1}H NMR data for diastereomers of **2** and **3** [a]

Diastereomer	R	δ(C_5H_5)	1,2-C_6H_4-($PMePh_2$)$_2$		PMeRPh
			δ(PMe)	δ(PMe)	δ(PMe)
(*R**), (*R**, *R**)	Cl	4.31 q	2.12 d	2.33 d	1.38 d
(*S**), (*R**, *R**)	Cl	4.40 q	2.15 d	2.52 d	2.34 d
(*R**), (*R**, *R**)	Et	4.10 q	2.09 d	2.45 d	0.64 d
(*S**), (*R**, *R**)	Et	4.10 q	2.07 d	2.32 d	1.40 d
(*R**), (*R**, *R**)	Bn	4.24 q	2.13 d	2.61 d	0.46 d
(*S**), (*R**, *R**)	Bn	4.24 q	2.14 d	2.22 d	1.06 d
(*R**), (*R**, *R**)	OPh	4.17 q	2.37 d	2.43 d	1.13 d
(*S**), (*R**, *R**)	OPh	4.09 q	2.08 d	2.45 d	2.16 d
(*R**), (*R**, *R**)	OMe [b]	4.06 q	2.13 d	2.32 d	0.92 d
(*S**), (*R**, *R**)	OMe [b]	4.04 q	2.06 d	2.38 d	2.04 d
(*R**), (*R**, *R**)	H [c]	4.39 q	1.60 d	2.23 d	0.64 dd
(*S**), (*R**, *R**)	H [c]	4.36 q	2.20 d	2.32 d	1.55 dd

[a] Chemical shift values quoted in ppm relative to Me_4Si in CD_2Cl_2 at 20°C.
[b] Diastereomers not isolated.
[c] Data taken from ref. 2(c).

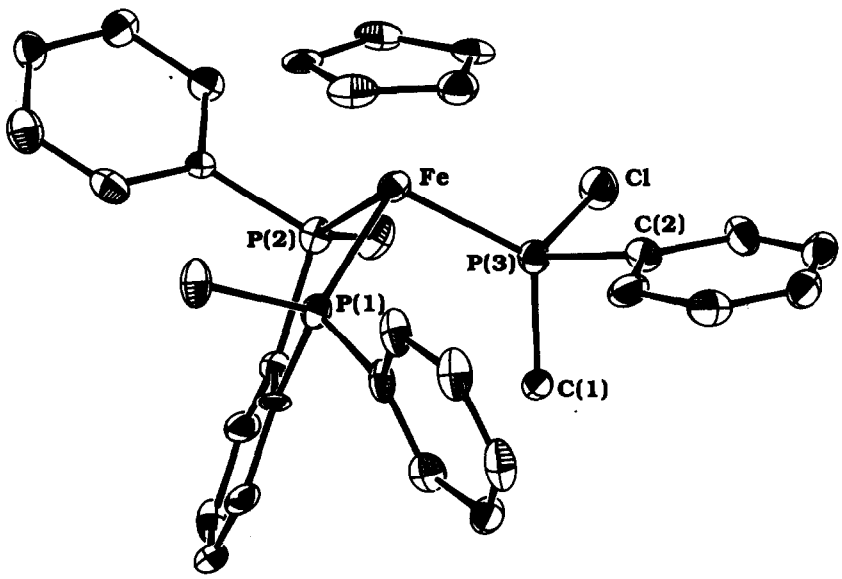


Fig. 2. Molecular structure of the cation in [(*R**), (*R**, *R**)]-**2** · CH_2Cl_2. The *R* enantiomer of the molecule is depicted. Atom labelling corresponds to data in Table 4.

the complexes in the same solvent, ABX spin patterns for the three phosphorus nuclei are observed.

When homochiral [*R*-(*R**, *R**)]-**1** is used, the reaction with (±)-PClMePh yields optically active **2** with [*R*-[(*R**), (*R**, *R**)]]/[*R*-[(*S**), (*R**, *R**)]] = 3/1. Fractional crystallization of the mixture from acetone–diethyl ether yields orange prisms of the minor diastereomer [*R*-[(*S**), (*R**, *R**)]]-**2** · Me_2CO, $[\alpha]_D$ + 261° (CH_2Cl_2). The major diastereomer could not be obtained in a crystalline state. The isolation of this complex represents the first resolution of a coordinated secondary chlorophosphine.

The dichlorophenylphosphine compound (*R**, *R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(PCl_2Ph)]PF_6 was also prepared (from (*R**, *R**)-**1** and an excess of dichlorophenylphosphine in boiling dichloromethane), but attempts to replace the diastereotopic chlorine atoms in the complex stepwise by use of Grignard reagents or sodium borohydride were unsuccessful.

2.1. X-Ray crystal structure of [(*R**), (*R**, *R**)]-2 · CH_2Cl_2

The structure of the cation in [(*R**), (*R**, *R**)]-**2** · CH_2Cl_2 is depicted in Fig. 2. The salt crystallizes in the space group $P2_1/n$ with both enantiomers of the molecular cations present in the unit cells of the crystal. Crystal data for the complex are given in Table 2. Structure solution was by Patterson synthesis and ΔF syntheses using SHELXS. Refinement was by full matrix least squares with all non-H atoms anisotropic, H atoms fixed in calculated positions and not refined, and taking account of disorder in the PF_6^- ion. Table 3 lists the positional parameters, and Table 4 lists the important distances and angles. Complete data are available in the supplementary material [7*].

The three chirotopic phosphorus stereocentres in the complex have the same relative configurations, *viz.* (*R**), (*R**, *R**). In other respects the structural data are similar to those for related complexes [2(c),8].

TABLE 2. Crystal parameters and experimental data for [(*R**), (*R**, *R**)]-**2**·CH_2Cl_2

Formula	$C_{32}H_{33}ClF_6FeP_4 \cdot CH_2Cl_2$
F.W.	831.73
Lattice type	monoclinic
space group	$P2_1/n$
Cell dimensions	
a (Å)	13.525(4)
b (Å)	14.502(3)
c (Å)	17.838(4)
β (°)	97.69(2)
V (Å^3)	3467.2
Z	4
D_c (g cm^{-3})	1.593
Data collection instrument	Nicolet XRD P3
Radiation (graphite monochromator)	Mo Kα
μ (Mo Kα) (cm^{-1})	9.1
λ (Mo Kα) (cm^{-1})	0.71073
Temperature (°C)	−113
Scan method	θ–2θ
Scan range (2θ) (°)	4–50
No. of unique data	6323
No. of data used ($I > 3\sigma(I)$)	2502
No. of parameters refined	416
R [a]	0.062
R_w [b]	0.070
S [c]	1.54
Largest shift/e.s.d., final cycle	0.5 in disorder, 0.1 elsewhere
Largest peak (e Å^{-3})	1.0 (near PF_6^-)

[a] $R = \Sigma \| F_o | - | F_c \| / | F_o |$.
[b] $R_w = [\Sigma w(| F_o | - | F_c |)^2 / \Sigma w | F_o |^2]^{1/2}$.
[c] $S = [\Sigma w(| F_o | - | F_c |)^2 / (N_{observns} - N_{params})]^{1/2}$.

2.2. Stereoselective reactions of (±)-chloromethylphenylphosphine-iron complexes (Fig. 3)

2.2.1. Reactions with Grignard reagents

Treatment of a solution of [(*R**), (*R**, *R**)]-**2** · CH_2Cl_2 in tetrahydrofuran at 20°C with ethylmagnesium bromide in the same solvent affords the corresponding (±)-ethylmethylphenylphosphine-iron complex **3** (R ≡ Et) with (*R**, *R**), (*R**)/(*R**, *R**), (*S**) = 1/3 (Table 1). The stereochemical assignments are based upon those adduced for pure [(*S**), (*R**, *R**)]-**3** (R ≡ Et) prepared from a structurally authenticated sample of [(*R**), (*R**, *R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(PHMePh)]PF_6 · 0.5CH_2Cl_2[2(c)]. By reaction with benzylmagnesium bromide, [(*R**), (*R**, *R**)]-**2** · CH_2Cl_2 affords the (±)-benzylmethylphosphine complex **3** (R ≡ Bn) with (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 1/8. Thus, in each case, alkylation of the chlorophosphine complex by the Grignard reagent proceeds with predominant retention of configuration at phosphorus. Reaction of the epimeric secondary chlorophosphine precursor [(*S**), (*R**, *R**)]-**2** · Me_2CO with ethyl- or benzyl-magnesium bromide under similar conditions gives the epimeric chiral tertiary phosphine-iron complexes **3** (R = Et or Bn) with similar degrees of retention of configuration at phosphorus.

2.2.2. Reactions with sodium borohydride

Treatment of a solution of [(*R**) (*R**, *R**)]-**2** · CH_2Cl_2 in tetrahydrofuran at 20°C with sodium borohydride produces the corresponding secondary phosphine-iron complex **3** (R = H) with (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 3/1 (predominant retention of configuration at phosphorus). Under similar conditions, [(*S**), (*R**, *R**)]-**2** · Me_2CO gives **3** (R = H) with (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 1/3.

2.2.3. Reactions with metal alkoxides

Complex [(R^*), (R^*, R^*)]-**2** · CH_2Cl_2 reacted with thallium(I) phenoxide in boiling tetrahydrofuran, to afford the air-stable (±)-methylphenoxyphenylphosphine-iron complex **3** (R ≡ OPh) with (R^*), (R^*, R^*)/(S^*), (R^*, R^*) = 1/6 (predominant inversion of configuration at phosphorus). With sodium phenoxide, the diastereoselectivity of the reaction was (R^*), (R^*, R^*)/(S^*), (R^*, R^*) = 1/3. The addition of TlOPh or NaOPh to solutions of the mixtures did not affect the diastereomeric ratios. Reactions of [(R^*), (R^*, R^*)]-**2** · CH_2Cl_2 or [(S^*), (R^*, R^*)]-**2** · Me_2CO with sodium methoxide

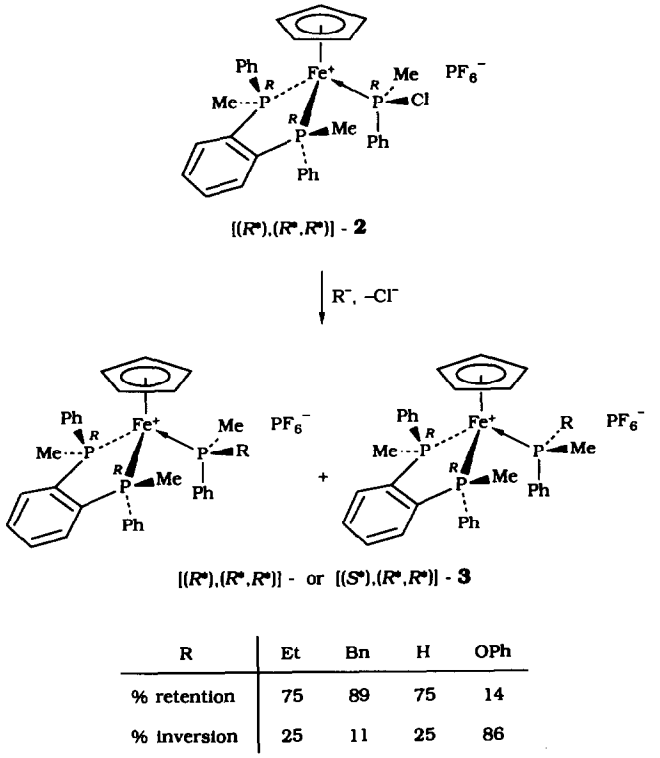
TABLE 3. Atomic coordinates and equivalent isotropic displacement parameters for [(R^*), (R^*, R^*)]-**2** · CH_2Cl_2

Atom [a]	x	y	z	U_{eq} (Å^2)
Fe	0.1027(1)	0.3421(1)	0.28088(8)	0.0177(8)
P(1)	0.1276(2)	0.4886(2)	0.2619(2)	0.018(1)
P(2)	−0.0383(2)	0.3622(2)	0.2058(2)	0.019(2)
C(1)	0.2009(8)	0.5181(9)	0.1855(6)	0.028(6)
C(11)	0.1914(8)	0.5577(8)	0.3396(6)	0.022(6)
C(12)	0.1426(8)	0.6164(8)	0.3834(6)	0.024(6)
C(13)	0.1929(8)	0.6579(8)	0.4479(6)	0.027(6)
C(14)	0.2943(9)	0.6406(9)	0.4674(6)	0.031(7)
C(15)	0.3438(8)	0.5830(9)	0.4241(6)	0.029(7)
C(16)	0.2926(7)	0.5425(8)	0.3603(6)	0.025(6)
C(2)	−0.1551(8)	0.3101(8)	0.2228(6)	0.027(6)
C(21)	−0.0347(7)	0.3269(7)	0.1069(5)	0.016(6)
C(22)	0.0046(8)	0.3834(8)	0.0557(6)	0.025(6)
C(23)	0.0106(8)	0.3556(9)	−0.0170(6)	0.029(7)
C(24)	−0.0233(8)	0.2681(9)	−0.0407(6)	0.025(6)
C(25)	−0.0628(8)	0.2102(8)	0.0098(6)	0.024(6)
C(26)	−0.0680(8)	0.2390(8)	0.0838(6)	0.021(6)
C(31)	0.0103(7)	0.5457(8)	0.2285(5)	0.015(5)
C(32)	−0.0683(7)	0.4861(8)	0.2018(5)	0.015(5)
C(33)	−0.1616(8)	0.5206(8)	0.1724(6)	0.024(6)
C(34)	−0.1770(8)	0.6141(9)	0.1707(6)	0.027(7)
C(35)	−0.1001(9)	0.6743(8)	0.1961(5)	0.026(6)
C(36)	−0.0055(8)	0.6406(8)	0.2251(5)	0.021(6)
P(4)	0.0322(2)	0.3496(2)	0.3823(1)	0.019(1)
Cl(4)	−0.0615(2)	0.2361(2)	0.3908(2)	0.030(2)
C(4)	−0.0557(8)	0.4391(7)	0.3962(5)	0.017(6)
C(41)	0.1047(7)	0.3429(8)	0.4762(5)	0.021(5)
C(42)	0.0791(8)	0.2903(9)	0.5366(6)	0.030(7)
C(43)	0.1303(9)	0.3013(9)	0.6080(6)	0.032(7)
C(44)	0.2050(8)	0.3662(9)	0.6224(6)	0.029(7)
C(45)	0.2329(8)	0.4184(8)	0.5651(6)	0.028(6)
C(46)	0.1840(9)	0.4072(9)	0.4919(6)	0.027(6)
C(51)	0.1808(8)	0.2750(8)	0.2027(6)	0.023(6)
C(52)	0.1220(8)	0.2111(8)	0.2379(7)	0.029(7)
C(53)	0.1526(9)	0.2117(8)	0.3159(7)	0.029(7)
C(54)	0.2320(8)	0.2758(8)	0.3315(6)	0.028(7)
C(55)	0.2506(8)	0.3130(8)	0.2616(7)	0.031(7)
P(6)	0.5526(2)	0.4644(3)	0.2501(2)	0.037(2)
F(61)	0.4500(5)	0.5051(6)	0.2086(4)	0.059(5)
F(62A)*	0.492(1)	0.382(1)	0.282(1)	0.072(4)
F(62B)*	0.513(1)	0.362(1)	0.223(1)	0.072(4)
F(63A)*	0.532(1)	0.523(1)	0.3250(9)	0.063(3)
F(63B)*	0.505(1)	0.448(1)	0.3252(9)	0.063(3)
F(64)	0.6538(5)	0.4233(6)	0.2927(5)	0.070(6)
F(65A)*	0.618(1)	0.551(1)	0.231(1)	0.069(4)
F(65B)*	0.589(1)	0.564(1)	0.272(1)	0.069(4)
F(66A)*	0.576(1)	0.407(1)	0.1834(9)	0.067(4)
F(66B)*	0.592(1)	0.478(1)	0.1702(9)	0.067(4)
C(7)	−0.3674(9)	0.476(1)	−0.0126(7)	0.054(9)
Cl(71)	−0.2645(3)	0.4037(3)	−0.0038(2)	0.049(2)
Cl(72)	−0.3290(5)	0.5928(4)	−0.0276(2)	0.106(4)

[a] Starred atoms have occupancies 0.5 and were refined isotropically with constraints U(FnmB) = U(FnmA). Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter where U_{eq} is one-third of the trace of the orthogonalized U_{ij} matrix.

TABLE 4. Selected bond distances and bond angles for [(R^*), (R^*, R^*)]-**2** · CH_2Cl_2

Bond	Distance (Å)	Bond	Angle (°)
Fe–P(1)	2.184(4)	P(1)–Fe–P(2)	85.2(1)
Fe–P(2)	2.197(3)	P(1)–Fe–P(3)	100.2(1)
Fe–P(3)	2.158(3)	P(2)–Fe–P(3)	93.4(1)
Fe–C(Cp)$_{av}$	2.09(1)	Fe–P(3)–C(1)	121.7(4)
P(3)–C(1)	1.800(11)	Fe–P(3)–C(2)	121.6(4)
P(3)–C(2)	1.827(9)	Fe–P(3)–Cl	111.1(2)
P(3)–Cl	2.096(4)	C(1)–P(3)–C(2)	101.3(5)
		C(1)–P(3)–Cl	98.0(4)
		C(2)–P(3)–Cl	98.5(4)



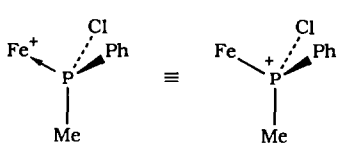
R	Et	Bn	H	OPh
% retention	75	89	75	14
% inversion	25	11	25	86

Fig. 3. Synthesis of chiral tertiary phosphine–iron complexes with summary showing predominant retention of configuration at phosphorus with Grignard reagents and sodium borohydride, but inversion for reaction of the chlorophosphine complex with thallium(I) phenoxide [5*].

in tetrahydrofuran at 20°C, however, gave **3** (R = OMe) with (*R**), (*R**, *R**)/(*S**), (*R**, *R**) = 13/1, in thermodynamically controlled reactions. The identical mixture of phosphite complexes resulted when (*R**, *R**)-**1** reacted with (±)-chloromethylphenylphosphine in boiling methanol. In the latter reaction, the phosphite is formed from the chlorophosphine prior to coordination, since the (±)-chloromethylphenylphosphine-iron complexes remain unchanged in boiling methanol. In a similar reaction, dichlorophenylphosphine reacts with (*R**, *R**)-**1** in boiling methanol to give the corresponding dimethoxyphenylphosphine complex.

3. Discussion

Nucleophilic substitutions at non-cyclic three-coordinate phosphorus stereocentres proceed, in most cases, with complete inversion under conditions in which the reactants and products are configurationally stable [9]. With certain cyclic phosphinous chlorides [10], however, substitutions with complete retention of configuration at phosphorus occur, consistent with mechanisms involving four-coordinate phosphoranide intermediates that decay by rules laid down for true trigonal bipyramidal species [11]. A trivalent phosphine in a positively charged metal complex may be regarded formally as a tetrahedral phosphonium ion containing a large and electronegative substituent, as depicted below:



Trans-attack of a nucleophile at the phosphonium-*P* stereocentre of the phosphonium ion will produce a five-coordinate intermediate that can eliminate chloride directly from the axial position, that is, before pseudorotation, giving inversion of configuration at phosphorus or, if the intermediate is more stable, retention of configuration at phosphorus by elimination of chloride from any one of the three equatorial positions after two pseudorotations [11], as indicated in Fig. 4. Thus, whether inversion or retention of configuration at phosphorus will occur during substitution will depend upon the energies of the trigonal bipyramidal intermediates, which, in turn, will be determined by the electronegativities and π-bonding abilities of the various ligands present. In the present system, the predominant pathway for substitution of chloride at phosphorus by the phenoxide ion is presumably a typical S_N2 process involving a relatively short-lived phosphorus(V) intermediate, whereas the carbon nucleophiles and borohydride replace chloride via more stable intermediates after pseudorotation. It would be hazardous to attempt to predict the stereochemical outcome of substitution reactions at coordinated chlorophosphine stereocentres on the basis of the present data alone, however; for example, the most common outcome of substitution of ligands in organo-transition-metal complexes is retention of configuration at the metal via a concerted pathway [12], whereas substitution of chloride or bromide at silicon proceeds with inversion, whatever the nucleophile [13]. It should be emphasized that misleading results will be obtained in stereochemical investigations of this kind if starting materials or products are not configurationally stable under the experimental conditions employed (that is, reactions must proceed under kinetic control) or product diastereomers are separated inadvertently during work-up.

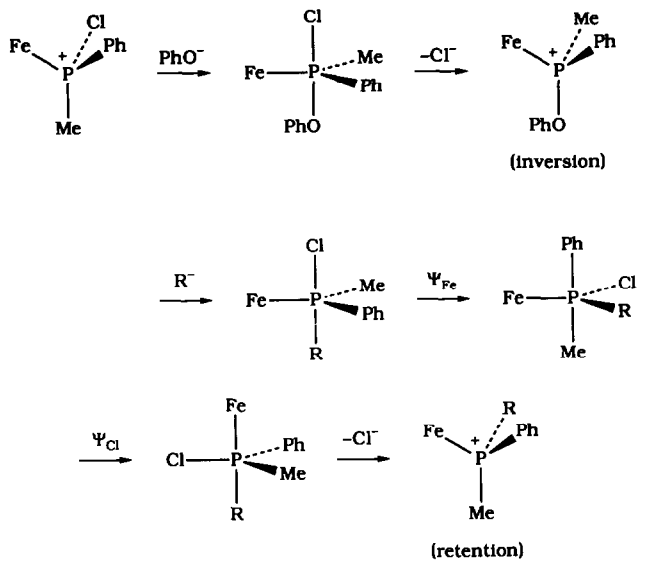


Fig. 4. Reaction pathways for substitution of chloride in [(*R**), (*R**, *R**)]-**2**·CH_2Cl_2.

4. Experimental details

Reactions were performed under argon by use of Schlenk techniques. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian VXR-300 spectrometer or a Bruker CXP-200 spectrometer at 20°C in dichloromethane-d_2 with chemical shift values quoted relative to $Me_4Si(^1H)$ or 85% H_3PO_4 ($^{31}P\{^1H\}$). Optical rotations were measured with a Perkin–Elmer Model 241 polarimeter in a 1 dm cell at 20°C. Elemental analyses were performed by staff within the Research School of Chemistry.

4.1. [(R), (R*, R*)]-(±)-(chloromethylphenylphosphine)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate–1-dichloromethane ([(R*), (R*, R*)]-2 · CH_2Cl_2)*

A mixture of (*R**, *R**)-**1** (2.0 g, 3.2 mmol) [2(c)] and (±)-chloromethylphenylphosphine [14] (9.8 g, 62 mmol) in dichloromethane (30 ml) was heated under reflux for 12 h. The orange solution was then diluted with diethyl ether, which precipitated the product as the major component of a 3/1 mixture of itself with the corresponding (*S**), (*R**, *R**) diastereomer. Fractional crystallization of the mixture from dichloromethane (10 ml) by the slow addition of petroleum ether (b.p. 40–60°C) gave the pure (*R**), (*R**, *R**) diastereomer as orange needles of the 1:1-dichloromethane solvate: m.p. 169–170°C; yield 1.8 g (69%). Anal. Found: C, 47.7; H, 4.3; P, 15.6; Cl, 12.7. $C_{33}H_{35}Cl_3F_6FeP_4$ calc.: C, 47.7; H, 4.2; P, 14.9; Cl, 12.8%. ^{1}H NMR: δ 1.38 (d, 3H, ^2J(PH) = 5.7 Hz, PCl*Me*Ph), 2.12 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 9.0$ Hz, P*Me*), 2.33 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 10.1$ Hz, P*Me*), 4.31 (q, 5H, ^3J(PH) = 1.8 Hz, η^5-C_5H_5), 7.10–7.73 (m, 19H, aromatics). ^{31}P {^{1}H} NMR: δ 78.5, 78.7, 168.7 (ABX m, 3P, $|^2J(AB)| = 43.8$ Hz, $|^2J(AX)| = 67.2$ Hz, $|^2J(BX)| = 51.7$ Hz).

4.2. [(S), (R*, R*)]-(±)-(chloromethylphenylphosphine)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate–1-acetone ([(S*), (R*, R*)]-2 · Me_2CO)*

The mother liquor from the isolation of [(*R**), (*R**, *R**)]-**2** · CH_2Cl_2 was evaporated to dryness and the residue was recrystallized from acetone–diethyl ether to give orange needles of [(*S**), (*R**, *R**)]-**2** · Me_2CO: m.p. 162–164°C; yield 0.4 g (15%). Anal. Found: C, 52.0; H, 4.8; P, 15.1; Cl, 4.3. $C_{35}H_{39}ClF_6FeOP_4$ calc.: C, 52.2; H, 4.9; P, 15.4; Cl, 4.4%. ^{1}H NMR: δ 2.12 (s, 6H, Me_2CO), 2.15 (d, 3H, ^2J(PH) = 8.4 Hz, P*Me*), 2.34 (d, 3H, ^2J(PH) = 5.5 Hz, PCl*Me*Ph), 2.52 (d, 3H, ^2J(PH) = 9.2 Hz, P*Me*), 4.40 (q, 5H, ^3J(PH) = 1.8 Hz, η^5-C_5H_5), 6.97–8.02 (m, 19H, aromatics). ^{31}P{^{1}H} NMR: δ 77.5, 79.1, 169.6 (ABX m, 3P, $|^2J(AB)| = 42.6$ Hz, $|^2J(AX)| = 66.3$ Hz, $|^2J(BX)| = 65.0$ Hz).

4.3. [R-[(S), (R*, R*)]]-(+)-(chloromethylphenylphosphine)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate–1-acetone ([R-[(S*), (R*, R*)]]-2 · Me_2CO)*

Reaction of [*R*-(*R**, *R**)]-**1** with (±)-PClMePh by the method described for the corresponding racemate gave the pure enantiomer as the first fraction from the acetone–diethyl ether recrystallization of the initial 1:3 mixture of optically active diastereomers, orange prisms: m.p. 219–220°C; 10% yield; $[\alpha]_D + 261°$ (*c* 0.033, CH_2Cl_2). Anal. Found: C, 52.1; H, 4.9; P, 15.1; Cl, 4.3. $C_{35}H_{39}ClF_6FeOP_4$ calc.: C, 52.2; H, 4.9; P, 15.4; Cl, 4.4%. ^{1}H and ^{31}P{^{1}H} NMR: identical with those of the corresponding racemate.

4.4. [(R, R*),(R*)]-(±)- and [(R*, R*), (S*)]-(±)-(η^5-cyclopentadienyl)(ethylmethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ([(R*, R*), (R*)]- and [(R*, R*), (S*)]-3)*

A solution of [(*R**), (*R**, *R**)]-**2** · Me_2CO (0.05 g, 0.06 mmol) in tetrahydrofuran (30 ml) was treated with a solution of ethylmagnesium bromide in diethyl ether (3 ml, 0.22 M). After 2.5 h, methanol (1 ml) was added to destroy the excess of the Grignard reagent and the solvent was evaporated off. The residue was dissolved in dichloromethane (50 ml) and the extract washed with aqueous NH_4PF_6. After drying over $MgSO_4$, the organic layer was concentration to *ca.* 2 ml and diluted with diethyl ether. The product was obtained as a mixture of diastereomers with (*R**, *R**), (*R**)/(*R**, *R**), (*S**) = 1/3. ^{1}H and ^{31}P{^{1}H} NMR for the diastereomers were identical with those reported previously for the same complexes prepared by a different route [2c]. The reaction of [(*S**), (*R**, *R**)]-**2** · CH_2Cl_2 with ethylmagnesium bromide under the same conditions gave a similar mixture with (*R**, *R**), (*R**)/(*R**, *R**), (*S**) = 3/1.

4.5. [(R, R*), (R*)]-(±)- and [(R*, R*), (S*)]-(±)-benzylmethylphenylphosphine)-(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ([(R*, R*), (R*)]- and [(R*, R*), (S*)]-4)*

This compound was prepared by the method described above, but starting from benzylmagnesium bromide. The product was isolated as orange needles from dichloromethane–diethyl ether with (*R**, *R**), (*R**)/(*R**, *R**), (*S**) = 1/8. (^{1}H and ^{31}P{^{1}H} NMR data identical with those reported for the pure diastereomers [2c]. The reaction of [(*S**), (*R**, *R**)]-**2** with benzylmagnesium bromide under similar conditions gave the same compound with (*R**, *R**), (*R**)/(*R**, *R**), (*S**) = 8/1.

4.6. [(R, R*), (R*)]-(±)- and [(R*, R*), (S*)]-(±)-(η^5-cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ([(R*, R*), (R*)]- and [(R*, R*), (S*)]-7)*

Sodium borohydride (0.012 g, 0.3 mmol) was added to a stirred solution of [(*R**), (*R**, *R**)]-**2** · CH_2Cl_2 (0.05 g, 0.06 mmol) in tetrahydrofuran (30 ml). After 12 h the solvent was evaporated off, the residue extracted into dichloromethane, and the extract shaken with aqueous NH_4PF_6. The organic layer was dried over $MgSO_4$ and concentrated to *ca.* 2 ml. Diethyl ether was added to precipitate the product as an (*R**, *R**),

$(R^*)/(R^*, R^*)$, $(S^*) = 3/1$ mixture of diastereomers. ^1H and ^{31}P $\{^1H\}$ NMR data were in agreement with those reported for the pure diastereomers [2c]. The reaction of $[(S^*), (R^*, R^*)]$-**2** · Me_2CO with sodium borohydride under similar conditions gave the product with (R^*, R^*), $(R^*)/(R^*, R^*)$, $(S^*) = 1/3$.

4.7. [(R), (R*, R*)]-(±)- and [(S*), (R*, R*)]-(±)-(η⁵-cyclopentadienyl)(methylphenoxyphenylphosphine)-[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ([(R*), (R*, R*)]- and [(S*), (R*, R*)]-5*

4.7.1. Method 1

A mixture of $[(R^*), (R^*, R^*)]$-**2** · CH_2Cl_2 (0.05 g, 0.06 mmol) and thallium(I) phenoxide (0.02 g, 0.07 mmol) in tetrahydrofuran was heated under reflux for 12 h in the absence of light. The solvent was evaporated off, the residue was extracted with dichloromethane (50 ml), and the extract shaken with aqueous NH_4PF_6. The organic layer, after drying over $MgSO_4$, was concentrated to *ca.* 2 ml, and diluted with diethyl ether to afford yellow plates of the product with (R^*), $(R^*, R^*)/(S^*)$, $(R^*, R^*) = 1/6$: m.p. 140–142°C; yield 0.035 g (73%). Anal. Found: C, 56.1; H, 4.6; P, 15.1. $C_{38}H_{38}F_6FeOP_4$ calc.: C, 56.7; H, 4.7; P, 15.4%. ^1H NMR: δ 1.13 (d, 0.4H, $|^2J(PH) + {}^4J(P'H)| = 8.8$ Hz, P*Me*(OPh)Ph-minor), 2.08 (d, 2.6H, $|^2J(PH) + {}^4J(P'H)| = 8.6$ Hz, P*Me*-major), 2.16 (d, 2.6H, $^2J(PH) = 6.2$ Hz, P*Me*(OPh)Ph-major), 2.37 (d, 0.4H, $|^2J(PH) + {}^4J(P'H)| = 9.7$ Hz, P*Me*-minor), 2.43 (d, 0.4H, $|^2J(PH) + {}^4J(P'H)| = 10.7$ Hz, P*Me*-minor), 2.45 (d, 2.6H, $|^2J(PH) + {}^4J(P'H)| = 9.9$ Hz, P*Me*-major), 4.09 (q, 4.3H, $^3J(PH) = 1.9$ Hz, η^5-C_5H_5-major), 4.17 (q, 0.7H, $^3J(PH) = 2.0$ Hz, η^5-C_5H_5-minor), 5.80–8.04 (m, 24H, aromatics). $^{31}P\{^1H\}$ NMR: δ 78.7, 79.1, 176.9 (ABX m, 2.6P, $|^2J(AB)| = 42.5$ Hz, $|^2J(AX)| = 75.8$ Hz, $|^2J(BX)| = 72.2$ Hz, major), 80.3, 81.0, 176.9 (ABX m, 0.4P, $|^2J(AB)| = 43.5$ Hz, $|^2J(AX)| = 77.4$ Hz, $|^2J(BX)| = 62.7$ Hz, minor).

4.7.2. Method 2

A solution of $[(R^*), (R^*, R^*)]$-**2** · CH_2Cl_2 (0.1 g, 0.12 mmol) in tetrahydrofuran (30 ml) was treated with a solution of sodium phenoxide in tetrahydrofuran (5 ml, 0.03 M) at room temperature. After 12 h, the solvent was evaporated off, the residue extracted with dichloromethane (50 ml), and the extract washed with aqueous NH_4PF_6. The organic layer was dried over $MgSO_4$ concentrated to *ca.* 2 ml, and diluted with diethyl ether to yield the product with (R^*), $(R^*, R^*)/(S^*)$, $(R^*, R^*) = 1/3$. The reaction of $[(S^*), (R^*, R^*)]$-**2** · Me_2CO with thallium(I) phenoxide under conditions similar to those described above gave the product with (R^*), $(R^*, R^*)/(S^*)$, $(R^*, R^*) = 6/1$.

4.8. [(R), (R*, R*)]-(±)- and [(S*), (R*, R*)]-(±)-(η⁵-cyclopentadienyl)(methoxymethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ([R*), (R*, R*)]- and [(S*), (R*, R*)]-6)*

Reaction of $[(R^*), (R^*, R^*)]$-**2** · CH_2Cl_2 (0.2 g, 0.24 mmol) and sodium methoxide (3 ml, 0.09 M) (method 2) over 3 h gave the product with (R^*), $(R^*, R^*)/(S^*)$, $(R^*, R^*) = 13/1$: m.p. 272°C; yield 0.15 g (75%). Anal. Found: C, 53.6; H, 5.2; P, 16.7. $C_{33}H_{36}F_6FeOP_4$ calc.: C, 53.4; H, 4.9; P, 16.7%. ^1H NMR: δ 0.92 (d, 2.8H, $^2J(PH) = 6.4$Hz, P*Me*(OMe)Ph-major), 2.04 (d, 0.2H, $^2J(PH) = 6.5$ Hz, P*Me*(OMe)Ph-minor), 2.06 (d, 0.2H, $|^2J(PH) + {}^4J(P'H)| = 8.6$ Hz, P*Me*-minor), 2.13 (d, 2.8H, $|^2J(PH) + {}^4J(P'H)| = 8.8$ Hz, P*Me*-major), 2.32 (d, 2.8H, $|^2J(PH) + {}^4J(P'H)| = 10.3$Hz, P*Me*-major), 2.38 (d, 0.2H, $|^2J(PH) + {}^4J(P'H)| = 10.1$Hz, P*Me*-minor), 2.89 (d, 0.2H, $^3J(PH) = 11.4$Hz, PMe(O-*Me*)Ph-minor), 3.16 (d, 2.8H, $^2J(PH) = 11.2$Hz, PMe (O*Me*)Ph-major), 4.04 (q, 0.4H, $^3J(PH) = 1.8$Hz, η^5-C_5H_5-minor), 4.06 (q, 4.6H, $^3J(PH) = 1.8$ Hz, η^5-C_5H_5-major), 6.51–7.68 (m, 19H, aromatics). $^{31}P\{^1H\}$ NMR: δ 81.5, 82.2, 171.2 (ABX m, 2.8P, $|^2J(AB)| = 44.4$ Hz, $|^2J_{(AX)}| = 59.5$ Hz, $|^2J(BX)| = 77.2$ Hz, major), 79.9, 80.1, 171.2 (ABX m, 0.2P, $|^2J(AB)| = 43.43$ Hz, $|^2J(AX)| = 70.5$ Hz, $|^2J(BX)| = 74.4$ Hz, minor). The reaction of $[(S^*), (R^*, R^*)]$-**2** · Me_2CO with sodium methoxide under similar conditions gave the same compound with (R^*), $(R^*, R^*)/(S^*)$, $(R^*, R^*) = 13/1$.

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phosphorus: (*R*)-PhMeClP^{+}–Fe → (*S*)-PhMeEt(or Bn)P^{+}–Fe, (*R*)-PhMeHP^{+}–Fe, or (*R*)-PhMe(OR)P^{+}–Fe.

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