STEREOSELECTIVE REACTIONS OF COORDINATED HALOGENO-ARSINES AND -PHOSPHINES

by

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B. Sc. (Hons) (The University of Wollongong, 1986)

A thesis submitted for the degree of
Doctor of Philosophy
of the
Australian National University

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June 1990
DECLARATION

The work presented in this thesis is my own except where due reference has been made to others in the text. It was carried out within the Research School of Chemistry of the Australian National University, under the supervision of Dr S. B. Wild. None of the material has been submitted in support of an application for any other degree.

Geoffrey B. Shaw
ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Dr S. B. Wild for his enthusiasm and guidance throughout the course of this work.

The author also gratefully acknowledges the encouragement and assistance provided by Dr G. Salem. Dr A. C. Willis is thanked for the crystal structure analyses, and Ms L. Hunt for the typing of this thesis. The author is particularly indebted to his wife for her patience and constant encouragement during the course of this work.

The author is grateful for a Commonwealth Postgraduate Research Award provided by the Department of Education.
ABSTRACT

The UV irradiation of $[(\eta^5\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCl}]$ with $(R^*,S^*)$-1,2-$\text{C}_6\text{H}_4(\text{PMePh})_2$ in acetonitrile produces a syn - anti mixture of the complex $(R^*,S^*)$-$[(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe(NCMe)}]PF_6$, which can be separated by fractional crystallization;

the major diastereomer has the syn stereochemistry (methyl groups adjacent to
cyclopentadienyl ring) according to an X-ray crystal structure analysis. The pure
diastereomers are stable to epimerization at iron in solution at room temperature, but they
rearrange when heated in boiling methanol with $t_{1/2}$ ca 50 min at 50 °C and formation of
a syn:anti = 3:1 equilibrium mixture of diastereomers. Exchange of the coordinated
acetonitrile was also observed when the pure syn complex was warmed in

$[\text{H}_3]\text{acetonitrile}$. Under similar conditions, $[R-(R^*,R^*)]-(+)$- or $(R^*,R^*)-(\pm)$-1,2-$\text{C}_6\text{H}_4(\text{PMePh})_2$ react with $[(\eta^5\text{C}_5\text{H}_5)(\text{CO})_2\text{FeCl}]$ in acetonitrile to give $[R-(R^*,R^*)]$-

$(+)$- and $(R^*,R^*)-(\pm)$-$[(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe(NCMe)}]PF_6$, respectively.

Both the $(R^*,S^*)$- and $(R^*,R^*)$- forms of the acetonitrile complex react with
methylmagnesium bromide or lithium aluminium hydride to give the corresponding
methyl- or hydrido-iron complexes. The X-ray crystal structure of $(R^*,R^*)-(\pm)$-

$[(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{FeCH}_3]$ has been determined at 196 °C; the bond
lengths and angles in the complex are normal, but the Fe-CH$_3$ group protons were found
to undergo unusually facile exchange with water protons. The reaction of pure $(R^*,S^*)$-

$\text{syn}$-$[(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe(NCMe)}]PF_6$, or a syn:anti = 1:2 mixture of the
same complex, with $\text{MeMgBr}$ produced diastereomerically homogeneous $(R^*,S^*)$-$\text{syn}$-

$[(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{FeCH}_3]$. Diastereomerically pure $(R^*,S^*)$-$\text{syn}$-

$[(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{FeH}]$ was also produced when the pure syn or a

syn:anti = 1:2 mixture of the acetonitrile complex was treated with lithium aluminium
hydride.

The complex $(R^*,R^*)-(\pm)$-$[\mu-$

$\text{N}_2\{(\eta^5\text{C}_5\text{H}_5)\{1,2-$

$\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}_2]\text{(PF}_6\text{)}_2$

has been prepared and used as a substrate for ligand substitution at iron.
(R*,R*)-(±)-[(η⁵C₅H₅)(1,2-C₆H₄(PMePh)₂)Fe(NCMe)]PF₆ reacts with (±)-PClMePh in boiling dichloromethane to give [(R*),(R*,R*)]/[(S*),(R*,R*)]-(±)-[(η⁵C₅H₅)(1,2-C₆H₄(PMePh)₂)Fe(PClMePh)]PF₆ with (R*),(R*,R*):(S*),(R*,R*) = 3:1. The diastereomers, epimeric at the halogenophosphine-P stereocentre, were separated by fractional crystallization, and the crystal structure of the major (R*),(R*,R*) diastereomer was determined by X-ray analysis. Treatment of either pure diastereomer of the chlorophosphine complex with a Grignard reagent gave the corresponding tertiary phosphine complex with predominant retention of configuration at the unidentate phosphorus stereocentre. Lithium aluminium hydride reductions of the pure chlorophosphine complex diastereomers produced the corresponding (±)-methylphenylphosphine complexes with predominant retention of configuration at phosphorus. Substitution of the chlorine in the chlorophosphine complex by phenoxide, however, gave the (±)-PMe(OPh)Ph complex with predominant inversion of configuration at phosphorus, although the corresponding reaction with methoxide gave the (±)-PMe(OMe)Ph complex as a thermodynamic mixture [(R*),(R*,R*):(S*),(R*,R*) = 13:1].

The compound (±)-AsFMePh has been prepared for the first time by reacting (±)-AsBrMePh with AgF in acetone. It reacts with (R*,R*)-(±)-[(η⁵C₅H₅)(1,2-C₆H₄(PMePh)₂)Fe(NCMe)]PF₆ in boiling dichloromethane (in the dark) to give [(R*),(R*,R*)]/[(S*),(R*,R*)]-(±)-[(η⁵C₅H₅)(1,2-C₆H₄(PMePh)₂)Fe-(AsFMePh)]PF₆ with (R*),(R*,R*):(S*),(R*,R*) = 3:1. The crystal and molecular structure of the major (R*),(R*,R*) diastereomer has been determined by X-ray analysis. Fluorine in the fluoroarsine complex is substituted with predominant inversion of the configuration at arsenic by Grignard reagents. Hydrolysis of the As-F bond in the fluoroarsine complex also occurs with inversion at arsenic to give the corresponding arsinous acid complex, but in this case the reaction is completely stereoselective. The hydroxy group in the arsinous acid complex can be deprotonated and methylated with retention of configuration at arsenic to give the complex of the arsinous acid methyl ester, which can also be obtained from the fluoroarsine complex and sodium methoxide. Upon
treatment of the complexes of the arsinous acid or the arsinous acid ester with thionyl chloride, inseparable mixtures of the diastereomers of the (±)-AsClMePh complexes were obtained. Similarly, an inseparable mixture of the diastereomers of the (±)-AsBrMePh complex were obtained from the reaction between (R*,R*)-(±)-[(η⁵C₅H₅){1,2-C₆H₄-(PMePh)₂}Fe(NCMe)]PF₆ and (±)-AsBrMePh in boiling dichloromethane. When the R*,R* acetonitrile complex was reacted with (±)-AsBrMePh in boiling methanol, diastereomerically pure [(R*),(R*,R*)]-(±)-[(η⁵C₅H₅){1,2-C₆H₄(PMePh)₂}Fe(AsBrMePh)]PF₆ crystallized out.
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FORMAT AND NOMENCLATURE

The format of the thesis is based upon the text and notation in the journal *Organometallics*. The nomenclature used is consistent with that recommended in the Chemical Abstracts Index Guide.139 A brief of the relevant guidelines for stereochemical descriptors is as follows:

(i) The assignment of absolute terms (descriptors) $R$ and $S$ should conform with the Sequence Rule specifications of Cahn, Ingold, and Prelog.45

(ii) The symbols $R^*$ and $S^*$ are *relative* descriptors; the lowest numbered (first cited, highest priority) asymmetric centre is arbitrarily assigned an $R^*$ descriptor.

(iii) The descriptors are employed to express the total stereochemical information for a chemical substance. The stereochemical descriptor appears in square brackets before the systematic name or formula of the substance. When only one chiral element is present, the absolute descriptor $R$ or $S$ is used to define absolute configuration of the molecule. When two or more chiral elements are present, the reference centre that has the highest ranking according to the Sequence Rule is assigned an $R^*$ or $S^*$ descriptor. When the absolute stereochemistry is described, the sign of the rotation, $(+)$, $(-)$, or $(\pm)$ can be omitted. For substances having more than one asymmetric centre, the sign of the rotation is cited together with a relative descriptor.

(iv) The absolute descriptor is cited first, followed by the relative descriptors, if any, in parenthesis. For example, for a molecule containing two chiral centres of the same helicity, say $R$, the stereochemical descriptors preceding the systematic name or formula of the substance and the optical information will appear thus: 

$[R-(R^*,R^*)]-(+)\text{ or } [R-(R^*,R^*)]-(\pm)$. 


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10b $^1$H NMR spectrum in $[2H_2]$dichloromethane of $[(R^*),(R^*,R^*)]-$
$(\pm)-[(\eta^5C_5H_5)\{1,2-C_6H_4(PMePh)\}_2Fe(AsFMePh)]PF_6\cdot CH_2Cl_2.$

10c $^1$H NMR spectrum in $[2H_2]$dichloromethane of $[(S^*),(R^*,R^*)]$
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CHAPTER ONE

Introduction
Trifluorophosphine has been extensively employed as a ligand for transition metals.\textsuperscript{1-3} The $\pi$-accepting capacity of trifluorophosphine is exceptional and therefore it forms particularly stable complexes of metals in low oxidation states, analogous to those formed by carbon monoxide.\textsuperscript{4} The first trifluorophosphine complexes to be identified were $[\text{PtCl}_2(\text{PF}_3)_2]$ and $[\text{PtCl}_2(\text{PF}_3)]_2$.\textsuperscript{5} In the same year, 1951, the liquid complex $[\text{Ni}(\text{PF}_3)_4]$ was also synthesized and found to possess considerably greater thermal stability than $[\text{Ni(\text{CO})}_4]$.\textsuperscript{6} Indeed, the thermal stabilities of all metal trifluorophosphine complexes are greater than those of the corresponding metal carbonyls with $[\text{Pd}(\text{PF}_3)_4]$ being the only metal trifluorophosphine compound unstable at room temperature.

The trifluorophosphine ligand can be displaced from the metal by another donor ligand such as an isonitrile, phosphine, phosphite, amine, or carbon monoxide. The degree of substitution depends upon the donor and acceptor properties of the incoming ligand, and increases with increasing $\pi$-acceptor strength. For example, carbon monoxide can replace all of the trifluorophosphine ligands in tetrakis-(trifluorophosphine)nickel(0):\textsuperscript{7,8}

$$[\text{Ni}(\text{PF}_3)_4] + 4\text{CO} \rightarrow [\text{Ni(\text{CO})}_4] + 4\text{PF}_3$$

Triphenylphosphine, however, reacts with $[\text{M}(\text{PF}_3)_4]$ to give $[\text{M}(\text{PF}_3)_{4-n}(\text{PPh}_3)_n]$ (where $\text{M} = \text{Ni}$, $n = 1$ or 2; $\text{M} = \text{Pd}$, $n = 2$; $\text{M} = \text{Pt}$, $n = 1$ or 2) and with $\text{Fe}(\text{PF}_3)_5$ to give $[\text{Fe}(\text{PF}_3)_3(\text{PPh}_3)_2]$\textsuperscript{4}

In protic solvents rapid solvolysis of the P-F bonds in M-PF$_3$ complexes occurs with elimination of HF. An example of one of these reactions is the following:\textsuperscript{9}

$$[\text{Fe(\text{CO})}_n(\text{PF}_3)_{5-n}] + n\text{CH}_3\text{OH} \rightarrow [\text{Fe(\text{CO})}_n(\text{PF}_2\text{OCH}_3)_{5-n}] + n\text{HF}$$
Although sequential solvolysis of P-F bonds in M-PF$_3$ complexes occurs in methanol, the extent of cleavage is much greater when the complexes are reacted with sodium methoxide$^{10}$ or a metal hydroxide:$^{11,12}$

$$\text{[Co(NO)(PF$_3$)$_3$]} \xrightarrow{\text{NaOMe}} \text{[Co(NO)(PF$_3$)$_n$(PF$_2$OMe)$_{3-n}$]} + n\text{HF}$$

(n = 1 or 2)

$$\text{[Fe(NO)$_2$(PF$_3$)$_2$]} \xrightarrow{\text{Ba(OH)$_2$}} \text{[Fe(NO)$_2$(PF$_3$)(PF$_2$O)]}^- \xrightarrow{\text{R$_3$O}} \text{[Fe(NO)$_2$(PF$_3$)(PF$_2$OR)]}$$

Thus, the nucleophilic displacement of fluoride by alkoxide or hydroxide provides a route into trialkoxy-, difluoroalkoxy-, and difluorohydroxy-phosphine complexes that are inaccessible or difficult to prepare by other methods. Indeed, a series of alkoxy- and aryloxy-fluorophosphine complexes of platinum(II) and palladium(II) of the type trans-[MCIL$_2$(PF$_2$O)] (where M = Pt or Pd; L = P$\text{Et}_3$-$n$Ph$_n$; n = 0-3) has been synthesized by Schmutzler and Grosse.$^{13}$

In similar reactions, weak bases, such as secondary amines, were shown to rapidly cleave the P-F bonds in M-PF$_3$ complexes:$^{14}$

$$\text{[Ni(PF$_3$)$_4$]} \xrightarrow{2n\text{R$_2$NH}} \text{[Ni(PF$_3$)$_{4-n}$(PF$_2$NR$_2$)$_n$]} + n\text{[R$_2$NH$_2$]F}$$

(R = Me, Et, n-Pr; n = 2-4)

Treatment of a difluoro(dimethylamino)phosphine complex of nickel(0) with gaseous hydrochloric acid at room temperature led to the isolation of the first chlorodifluorophosphine complex.$^9$

$$\text{[Ni(PF$_2$N(CH$_3$_2)$_4$]} + 8\text{HCl} \xrightarrow{} \text{[Ni(PF$_2$Cl)$_4$]} + 4\text{[(CH$_3$_2)NH$_2$]Cl}$$
More recently, fluorine atoms in \([\text{Ni}(\text{PF}_3)_4]\) have been substituted by organic groups with use of RLi or RMgCl to yield the complexes \([\text{Ni}(\text{PF}_3)_{4-n}(\text{PF}_2\text{R})_n]\) \((n = 1-3)\), \([\text{Ni}(\text{PF}_3)_3(\text{PF}_2\text{R})]\), \([\text{Ni}(\text{PF}_3)_3(\text{PR}_3)]\) (where R = alkyl group).\(^{15}\) A four-centred intermediate has been proposed for these reactions.

The complex \(\left(\eta^6\text{C}_6\text{H}_6\right)\text{Mo(H)(dppe)(PFPh}_2\right)\text{PF}_6\) [where dppe = bis(diphenylphosphino)ethane] is stable for several weeks in solution under nitrogen in the absence of water.\(^{16}\) An X-ray crystal structure analysis of the compound revealed a P-F bond length of 1.641 Å and a relatively short Mo-P bond length of 2.377 Å; these distances are comparable to those for the P-F and M-P bonds in \(\text{trans}-[\text{Mo(CO)}_4(\text{PPh}_2\text{NH}_2)(\text{PFPh}_2)]\), the only other related compound to be characterized by X-ray crystallography.\(^{17}\) The shortness of the Mo-P bonds in the two compounds is associated with the strong \(\pi\)-acceptor properties of the fluorophosphine ligand.\(^{18}\) The addition of water to a solution of the complex results in the slow hydrolysis of the P-F bond.\(^{16}\)

Recent work has also demonstrated the conversion of coordinated phosphites into coordinated fluorophosphines.\(^{19}\) Thus, molybdenum(0) complexes of the type \(\text{fac}-[\text{Mo(CO)}_3(\text{bipy})\{\text{P(OR)F}\}]\) (where \(\text{bipy} = 2,2'\)-bipyridine; \(\text{R} = \text{Me, Et or i-Pr}\)) react with 2 equivalents of BF\(_3\).OEt\(_2\) to afford the fluorophosphine compounds \(\text{fac}-[\text{Mo(CO)}_3(\text{bipy})\{\text{P(OR)F}\}]\). In a similar reaction, treatment of \(\text{fac}-[\text{Mo(CO)}_3(\text{bipy})\{\text{P(OMe)F}\}][\text{with 2 equivalents of BCl}_3\) led to the geometrically rearranged product \(\text{mer}-[\text{Mo(CO)}_3(\text{bipy})\{\text{P(OMe)Cl}\}]\). This compound, in turn, reacts with excess sodium methoxide to regenerate the phosphite starting material of meridional configuration at molybdenum.

A series of coordinated secondary halogenophosphine compounds of the type \([\text{W(CO)}_5(\text{PHXPh})]\) and \([\text{W(CO)}_5(\text{PH}_2\text{X})]\) (where \(\text{X} = \text{Cl, Br, or I}\) have been isolated,\(^{20}\) which react with arsenic trifluoride to give the corresponding fluorophosphine complexes:\(^{21}\)

\[
\begin{align*}
[\text{W(CO)}_5(\text{PH}_2\text{Cl})] & \xrightarrow{\text{AsF}_3} [\text{W(CO)}_5(\text{PH}_2\text{F})] \\
[\text{W(CO)}_5(\text{PHCl})] & \xrightarrow{\text{AsF}_3} [\text{W(CO)}_5(\text{PHF}_2)]
\end{align*}
\]
The mixed halogenophosphine compound \([\text{W(CO)}_5(\text{PCIFH})]\) was also isolated as a distillable oil.

In contrast to the extensive coordination chemistry of trifluorophosphine and its derivatives, the coordination chemistry of fluoroarsines is limited. Indeed, the first transition metal derivative of trifluoroarsine, viz. \([(\eta^5-\text{C}_5\text{H}_5)\text{Mn(AsF}_3)(\text{CO})_2]\), was isolated in 1971.\(^{22}\) To that work, however, some compounds of the type \([\text{Mo(AsCl}_3)_n(\text{CO})_{6-n}]\) \((n = 1-3)\) had been prepared.\(^{23,24}\) As with coordinated trifluorophosphine, coordinated trifluoroarsine readily undergoes solvolysis; for example, with ethanol the following reaction takes place:

\[
[(\eta^5-\text{C}_5\text{H}_5)\text{Mn(AsF}_3)(\text{CO})_2] \xrightarrow{\text{EtOH, } 20 \, ^\circ\text{C}} [(\eta^5-\text{C}_5\text{H}_5)\text{Mn(AsF}_2\text{OC}_2\text{H}_5)(\text{CO})_2] + \text{HF}
\]

The analogous PF\(_3\) complex does not react with ethanol under these conditions.

The coordination chemistry of halogenophosphines other than fluorophosphines is limited. For example, the first iron-phosphorus trichloride complex to be structurally authenticated was \((R^*,R^*)-\pm-[\eta^5-\text{C}_5\text{H}_5]_1,2-\text{C}_6\text{H}_4(\text{PMePh})_2(\text{PCl})_3]\text{Cl} \cdot 2\text{MeCN}\) in 1989.\(^{25}\) As with trifluorophosphine metal complexes, chlorophosphine complexes undergo rapid solvolysis in protic solvents.\(^{26}\) Boiling of an acetone solution of the halogenophosphine compound \(\text{cis-[PtCl}_2(\text{PR}_2\text{Cl})(\text{ER}_3)]}\) (where \(E = \text{P or As}; R = R' = \text{alkyl or phenyl}\)) with aqueous hydrohalic acid for 5 min. produces the corresponding hydroxyphosphine complex:

\[
\text{cis-[PtCl}_2(\text{PPh}_2\text{Cl})(\text{ER}_3)] \xrightarrow{\text{HX}_{\text{aq}}} \text{cis-[PtX}_2(\text{PPh}_2\text{OH})(\text{ER}_3)]}
\]

Sodium alkoxides convert the chlorophosphine complex into the corresponding alkoxy derivatives:
The reaction of dichlorophenylphosphine with the compounds \([\text{Cp}_2\text{M(CO)}\text{H}]\)

(where \(\text{M} = \text{Nb} \text{ or Ta}\)) gave the halogenophosphine complexes

\([\text{Cp}_2\text{M(CO)}\text{(PCIHPh)}]\)\text{Cl}.\text{27} In basic media these complexes are converted into the neutral compounds \([\text{Cp}_2\text{M(CO)}\text{-(PH(O)Ph)}]\):

\[
\text{[Cp}_2\text{M(CO)H]} + \text{PCI}_2\text{Ph} \rightarrow \text{Cp}_2\text{M}^+ \text{Cl}^- \quad \text{OH}^- \rightarrow \text{Cp}_2\text{M}^{+}
\]

In a similar reaction, but beginning with \((\pm)-[\text{Cp}^*\text{CpTa(CO)}\text{H}]\) (where \(\text{Cp}^* = \text{C}_5\text{Me}_5\)), two diastereomers of the chlorophosphine complex were obtained with 60:40 diastereoselectivity. Treatment of this mixture with sodium hydroxide gave diastereomeric phosphoryl complexes that could be separated by chromatography at low temperature, thus demonstrating the stability of the chiral tantalum stereocentre in the complexes.

A convenient route to chloro- and bromo-phosphine transition metal complexes involves the halogenation of terminal phosphido-metal complexes.\text{28,29} Terminal phosphido-metal complexes can be generated by deprotonation of primary or secondary phosphine complexes.\text{30} Structural evidence suggests that, depending upon substituents, phosphido groups exist in one of two binding modes.\text{31-35} The terminal phosphido group can be pyramidal and nucleophilic (M-PR\(_2\)), with a relatively long M-P bond and a small M-P-R bond angle (<114\(^\circ\)) (a), or planar and electrophilic (M = PR\(_2\)), with a short M-P bond and large M-P-R bond angle (approx. 130\(^\circ\)) (b).
The dependence of the reactivity of phosphido-metal compounds upon geometry (nucleophilic for pyramidal; electrophilic for planar) has aroused considerable interest.\(^{30-35}\) For example, it has been reported that the terminal phenylphosphido-complex [Os(PHPh)Cl(CO)\(_2\)(PPh\(_3\))\(_2\)] exhibits amphoteric behaviour.\(^{30}\) An X-ray crystal structure analysis of this compound revealed a long Os-P bond (2.523 (7) Å) and an Os-P-C bond angle of 113.4 (6)\(^{\circ}\), which indicated pyramidal stereochemistry at phosphorus. The nucleophilic behaviour of the complex was demonstrated by conversion into the corresponding secondary phosphine complex upon treatment with iodomethane:

\[
\text{Ph}_3\text{P} \quad \text{OC} \quad \text{Cl} \quad \text{Me} \quad \text{I}^- \quad \text{Os} \quad \text{Me} \quad \text{P} \quad \text{H} \quad \text{Ph} \quad \text{Ph}_3\text{P} \quad \text{OC} \quad \text{Ph}_3\text{P} \quad \text{Ph}
\]

The phosphido-osmium complex, however, also reacts with nucleophiles, as demonstrated by methoxide addition to yield the zerovalent complex [Os(CO)\(_2\)-(PH(OMe)Ph)(PPh\(_3\))\(_2\)]. This behaviour can be rationalized in terms of methoxide addition to the planar form of the phenylphosphido complex:

\[
\text{Ph}_3\text{P} \quad \text{OC} \quad \text{Cl} \quad \text{MeOH} \quad \text{Os} \quad \text{Me} \quad \text{P} \quad \text{H} \quad \text{Ph} \quad \text{Ph}_3\text{P} \quad \text{OC} \quad \text{Ph}_3\text{P} \quad \text{Ph}
\]

\[
\text{Ph}_3\text{P} \quad \text{OC} \quad \text{P} \quad \text{H} \quad \text{Ph} \quad \text{Ph}_3\text{P} \quad \text{OC} \quad \text{Ph}_3\text{P} \quad \text{Ph}
\]

\[
\text{Ph}_3\text{P} \quad \text{OC} \quad \text{Cl} \quad \text{OMe}^- \quad \text{Os} \quad \text{P} \quad \text{H} \quad \text{Ph} \quad \text{Ph}_3\text{P} \quad \text{OC} \quad \text{Ph}_3\text{P} \quad \text{Ph}
\]
The halogenophosphido-iron complex \([(\eta^5-C_5Me_5)Fe(CO)_2(P(Bu-t)Cl)]\) can be obtained from the reaction between equimolar quantities of \(t-BuPCl_2\) and \(\text{Na}[(C_5Me_5)Fe(CO)_2]\) in methylcyclohexane at -78 °C.\(^{36}\) Despite the electronegative substituent, the reactivity at phosphorus is high with the compound \((\pm)-[(\eta^5-C_5Me_5)Fe(CO)_2(P(Bu-t)ClMe)]I\) being isolated, presumably as a diastereomeric mixture, from its reaction with iodomethane:

\[
\text{Mel} \quad \text{I} \quad \text{Re} \quad \text{Me} \quad \text{I} \quad P-\text{Bu-t} \quad \text{Me} \quad \text{Ph} \quad \text{Ph}
\]

Similarly, a rhenium chlorophosphine complex has been generated from a phosphido intermediate as ca 1:1 mixture of diastereomers, chiral at phosphorus.\(^{29}\) The diastereomers, however, were not separated.

The number of coordinated halogenoarsine complexes reported in the literature is few;\(^{37,38,39}\) however, an example is shown below:\(^{26}\)

\[
[\text{Pt}_2\text{X}_4(\text{ER}'_3)_2] + 2\text{AsR}_2\text{Cl} \quad \text{MeI} \quad 2 \text{cis-[PtCl}_2(\text{AsClR}_2)(\text{ER}'_3)]
\]

\((E = \text{P or As}; R = R' = \text{alkyl or phenyl})\)
The arsenic-halogen bonds in the monochloroarsineplatinum(II) complexes are hydrolysed by weak bases: \(^{26}\)

\[
\text{cis-}[\text{PtCl}_2(\text{AsClPh}_2)(\text{ER}_3)] \xrightarrow{\text{alkali}} \text{[Pt}_2\text{Cl}_2(\text{Ph}_2\text{AsO})_2(\text{ER}_3)_2] \\
\xrightarrow{\text{HCl}} \text{cis-}[\text{PtCl}_2(\text{AsPh}_2\text{OH})(\text{ER}_3)]
\]

Sodium alkoxides convert chloroarsine complexes into the corresponding alkoxo complexes as follows:

\[
\text{cis-}[\text{PtCl}_2(\text{AsClR}_2)(\text{ER'}_3)] \xrightarrow{\text{NaOR}^* \atop 20^\circ\text{C}} \text{cis-}[\text{PtCl}_2(\text{AsOR'}R_2)(\text{ER'}_3)]
\]

A potential route to halogenoarsine complexes is via the halogenation of terminal arsenido-metal compounds, which contain pyramidal and electronegative M-AsR₂ or planar and electropositive M = AsR₂ arsenido groups.\(^{40,41}\) The nucleophilicity of the pyramidal arsenido-metal group in such compounds has been demonstrated by their conversion into arsine complexes with electrophiles: \(^{42}\)

\[
\begin{array}{c}
\text{OC} \\
\text{M} \\
\text{AsMe}_2 \\
\text{OC} \\
\end{array} + RX \rightarrow \begin{array}{c}
\text{OC} \\
\text{M}^+ \\
\text{AsMe}_2R \\
\text{OC} \\
\end{array}
\]

\((M = \text{Cr, Mo, W})\)

Pyramidal arsenido-metal complexes containing sterically demanding substituents on arsenic can be converted into planar arsenido-metal derivatives: \(^{43}\)
The planar arsenidometal complexes readily react with nucleophiles, for example, with Me$_3$P or t-BuNC, to generate trans-tungsten(II) complexes with complete stereoselectivity:

\[ \text{(M} = \text{W, Mo)} \]

To date, the stereochemistry of substitution of halogen in coordinated halogenophosphine and -arsine complexes has not been investigated. Indeed, the only stereochemical studies of coordinated-phosphines and -arsines have involved the stereospecific generation and subsequent alkylation of phosphido-iron and arsenido-iron groups in chiral complexes of the type \((R^*,R^*)-(\pm)-[({\eta}^5-C_5H_5)(1,2-C_6H_4-(PMePh)_2)FeER_2]\). This work led to the preparation of coordinated secondary and tertiary phosphines and arsines, chiral at phosphorus or arsenic, with complete stereoselectivity. For example, coordinated secondary phosphines and arsines of the type \([(R^*,R^*)-(\pm)-[({\eta}^5-C_5H_5)(1,2-C_6H_4(PMePh)_2)Fe(EHMePh)]PF_6\) react with KOBu-t at below -60 °C (E = As) or -95 °C (E = P) to generate tertiary phosphido- or arsenido-iron derivatives chiral at phosphorus or arsenic with complete retention of configuration at phosphorus or arsenic. Alkylation of these nucleophilic intermediates, at the same temperatures, also proceeds with complete retention of configuration at
phosphorus or arsenic to generate the kinetic products \([(R^*,R^*),(S^*)]- (+)-(r,5-C_5H_5)\{(1,2-C_6H_4(PMePh)_2)Fe(EMeRPh)\}PF_6\) with >99% diastereoselectivity.

\[\begin{array}{c}
\text{Ph} \hspace{1cm} \text{Me} \hspace{1cm} \text{PF}_6^- \\
\text{Me} \hspace{1cm} \text{Ph} \hspace{1cm} \text{Fe}^+ \hspace{1cm} \text{Ph} \\
\text{P} \hspace{1cm} \text{E} \hspace{1cm} \text{H} \\
(R^*,R^*),(R^*) \hspace{1cm} (R^*,R^*),(S^*)
\end{array}\]

\[\begin{array}{c}
\text{Ph} \hspace{1cm} \text{Me} \hspace{1cm} \text{PF}_6^- \\
\text{Me} \hspace{1cm} \text{Ph} \hspace{1cm} \text{Fe}^+ \hspace{1cm} \text{Ph} \\
\text{P} \hspace{1cm} \text{E} \hspace{1cm} \text{R} \\
(R^*,R^*),(R^*) \hspace{1cm} (R^*,R^*),(S^*)
\end{array}\]

(The apparent inversion that takes place in the reaction is consistent with the rules of Cahn et al. for the specification of absolute configuration.\(^{45}\)) These results will be elaborated upon in later sections of the thesis.

In this work, the chiral pseudo-tetrahedral auxiliary \([(R^*,R^*),(R^*)]-(+)-(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2)Fe\}^+\) has been used as a stereochemical probe of reactions at arsenic or phosphorus in halogeno-arsine and -phosphine complexes of the type \([(R^*,R^*),(R^*)]-(+)-(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2)Fe(ER_1R_2)\}PF_6\]. Moreover, it was envisaged that use of the optically active form of the iron(II) auxiliary could lead to the resolution of halogeno-arsines and -phosphines chiral at phosphorus or arsenic upon fractional crystallization of the diastereomeric complexes. This in turn could provide potential routes to resolved halogeno-arsines and -phosphines if stereospecific displacements from the metal could be effected.

The studies of Mislow and coworkers have established that simple trialkylphosphines possess pyramidal inversion barriers of >120 kJ mol\(^{-1}\), and that electronegative (and π-donor) substituents (for example, oxygen, nitrogen or halogen) on phosphorus significantly raise the barriers to inversion (Figure 1).\(^{46,47}\) These observations were rationalised by the suggestion that an electronegative group (X) attached to the phosphorus atom withdraws electrons along the P-X δ-bond, increasing
the \( p \)-character of the atomic orbital on phosphorus involved in the bonding to \( X \) and concomitantly raising the \( s \)-character of the orbital containing the lone-pair on the phosphorus atom. Since the orbital containing the lone-pair has essentially pure \( p \)-character in the transition state, the rehybridization is increased, which leads to an increase in the inversion barrier. The opposite effect is expected when \( X \) is a relatively electropositive substituent. For example, an inversion barrier of 50 kJ mol\(^{-1}\) has been estimated for PhP[SiH(CH\(_3\)]\(_2\).\(^{46}\)

**Figure 1.** Phosphine pyramidal inversion barriers vs electronegativity

The observed trends in pyramidal inversion barriers for phosphines are paralleled within the arsine series with electronegative substituents on arsenic increasing barrier heights.\(^{48}\)

**Figure 2.** Arsine pyramidal inversion barriers vs electronegativity
In principle therefore, the resolution of a phosphine or an arsine containing an electronegative substituent, such as a halogen, should be possible if the molecule is kinetically inert. It has been shown, however, that halogeno substituents undergo facile intermolecular exchange in certain halogeno-arsines and -phosphines. For example, a mixture of PCl₃ and PBr₃ redistributes to an equilibrium mixture of bromochlorophosphines in 1-1.5 h. The products of the redistribution were too unstable to be isolated but they were characterized by Raman and NMR spectroscopic studies.

\[
\text{PBr}_3 + \text{PCl}_3 \rightleftharpoons \text{PClBr}_2 + \text{PCl}_2\text{Br}
\]

The lability of the phosphorus-halogen bond is significantly lower in fluorophosphines, however, and redistribution products can sometimes be isolated:

\[
\text{PF}_3 + \text{PCl}_3 \rightarrow \text{PF}_2\text{Cl} + \text{PFCl}_2
\]

Halogen redistribution reactions have also been observed for certain halogenoarsenic(V) compounds. For example, Me₃AsF₂, when mixed with Me₃AsCl₂, affords Me₃AsFCI. The fate of the iron stereocentre in the auxiliary \((R^*,R^*)-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe]^+\) during substitution processes at iron is also to be examined in this work. Optically active complexes, chiral at the metal, have previously been employed to investigate stereochemical changes during organic reactions.

Brunners’ resolution of \((\pm)-[(\eta^5-C_5H_5)\text{Mn(CO)(NO)(PPh}_3)]\text{PF}_6,\) in which the metal atom is the stereogenic centre, provided the impetus for the resolution of many other chiral organo-transition metal compounds. The original manganese complex was resolved by the fractional crystallization of a pair of menthoxy esters as shown below:
The resolution was completed by the removal of the resolving agent from the pure diastereomers with anhydrous HCl in toluene, followed by treatment of the reaction mixture with hexafluorophosphate, to give the optically active enantiomers of the chiral manganese hexafluorophosphate complex:
Similar procedures have been employed for the resolution of many other chiral transition metal complexes. The stereochemistry at the metal centres in these complexes has been monitored during insertion, reductive elimination, and metal-carbon bond-cleavage reactions. For example, Gladysz and coworkers have demonstrated that metal-carbon bond cleavage by protic and halogen electrophiles proceeds with predominant retention of absolute configuration at rhenium in the complex (+)-[(η⁵-H₅)ReCH₃(NO)(PPh₃)]:

![Diagram](image_url)

\[ S- (+) \]

\[ X = \text{Cl}, S- (+); \text{Br}, R- (+); \text{I}, R- (+); \text{O} \text{SO}_2\text{CF}_3, R- (+); \text{OCOCF}_3, R- (+); \text{OCHO}, R- (+) \]

To account for these and similar observations, a square-pyramidal intermediate arising from the addition of the electrophile to the metal atom has been suggested for the reaction. Slow rearrangement of this intermediate would account for the racemization observed (Scheme I).
A second method of establishing stereochemical stability at a stereogenic centre involves the use of diastereomeric complexes, with a stereogenic centre located on a coordinated ligand. Unlike the first method, which requires a procedure for the elucidation of the optical purity of the reactant and the product, diastereomeric purities can be determined by NMR spectroscopic analysis.

Consiglio and coworkers have employed chiral bis(tertiary phosphine) ligands in stereochemical investigations of pseudo-tetrahedral ruthenium(II) complexes. For example, stereochemical studies of nucleophilic substitution of halide in the diastereomers shown below have been undertaken.
Alkylation of either diastereomer of the complex proceeded with retention of configuration at the metal:

In related work, optically active unidentate tertiary phosphines have been employed for stereochemical studies at iron. A survey of the literature on the stereochemical pathways of organometallic reactions reveals that most proceed with retention of configuration at the metal stereocentre. Racemization (or epimerization) is sometimes observed, but inversion of configuration at the metal is rare. With this knowledge, chiral transition metal auxiliaries have been effectively employed for stereochemical control in a variety of diastereo- and enantio-
selective\textsuperscript{77-79} organic transformations. For example, enantiomers of the complex (±)-
\[\{(\eta^5-C_5H_5)Fe(COCH_3)(CO)(PPh_3)\}\] have been used in stereoselective aldol and imine
condensations and tandem Michael additions.

Thus, treatment of the iron-acetyl complex with \textit{n}-butyllithium generates the

\begin{align*}
\text{Ph}_3\text{P} \quad \text{Fe}^+ \quad \text{CO} \quad \text{CH}_3 \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \q
Scheme II

Reagents: (i) n-BuLi; (ii) RX; (iii) R'X; (iv) Br₂, H₂O

In the present work, the stereochemistry of substitution of acetonitrile in the diastereomers 

(R*,R*)-(±)- and (R*,S*)-syn/anti-[\(\eta^5\)-C₅H₅]₁₂C₆H₄(PMePh₂)₉Fe(NCMe)]PF₆ has been investigated.
Chapter 2

Reactivity of \((R^*,R^*)\)- and \((R^*,S^*)\)-syn/anti-\([\eta^5\text{C}_5\text{H}_5]^{-}\{1,2\text{-}\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe(NCMe)}\}]\text{PF}_6
Compounds of the type (+)-[(η⁵-C₅H₅)Fe(CO)(PPh₃)R] (where R = alkyl or acyl), chiral at iron, have been employed for diastereo- and enantio-selective organic syntheses and for probing stereochemical changes at iron during substitution reactions. 81 The electronic and steric influence of the (+)-[(η⁵-C₅H₅)Fe(CO)(PR₃)] group, for example, facilitates highly stereoselective reactions of an iron-acyl group (for an illustration see Scheme IX). In other work, the stereochemical fate of the metal centre during insertion and cleavage reactions of iron-carbon bonds has been investigated. 52-55 Sulphur dioxide, for example, inserts into the Fe-C bond with retention of configuration in the reaction shown below: 82-87

\[ \text{Fe} \quad \text{CH}_2 \text{C}_\text{O} \quad \text{PPh}_3 \]

\[ \text{SO}_2 \rightarrow \]

\[ \text{Fe} \quad \text{SO}_2 \quad \text{CH}_2 \text{C}_\text{O} \quad \text{PPh}_3 \]

Despite the extensive use of complexes chiral at iron for stereochemical studies, less use has been made of compounds containing chiral bis(tertiary phosphines). For
example, Tröchel and Molzahn\textsuperscript{88} have prepared the achiral complex \([(\eta^5\text{-}C_5\text{H}_5)-(\text{dppe})\text{Fe}(\text{NCMe})]\text{PF}_6\) [where dppe = 1,2-bis(diphenylphosphino)ethane] and used it for the preparation of a number of derivatives by substitution of the coordinated acetonitrile with anionic ligands. In a similar vein, Astruc and coworkers\textsuperscript{89} have developed the chemistry of this complex, as well as that of the related compounds \([(\eta^5\text{-}C_5\text{Me}_5)-(\text{dppe})\text{Fe}(\text{NCMe})]\text{PF}_6\textsuperscript{90} and \([(\eta^5\text{-}C_5\text{H}_5)-(\text{dppm})\text{Fe}(\text{NCMe})]\text{PF}_6\textsuperscript{91} where dppm = 1,2-bis(diphenylphosphino)methane].\textsuperscript{91} For example, substitution of the acetonitrile ligand by carbon monoxide in the dppm derivative proceeds at room temperature to give the carbonyl derivative:\textsuperscript{91}

\[
\begin{array}{c}
\text{Fe}^+ \\
\text{PF}_6^- \\
\text{Ph}_2\text{P} \\
\text{PPh}_2 \\
\text{NCMe}
\end{array}
\text{CO (5-10 atm)} \text{ 20 °C}
\begin{array}{c}
\text{Fe}^+ \\
\text{PF}_6^- \\
\text{Ph}_2\text{P} \\
\text{PPh}_2 \\
\text{CO}
\end{array}
\]

The use of such complexes for stereochemical studies, however, has been limited by the tendency for one end of the bis(tertiary phosphine) to dissociate during substitution.\textsuperscript{92-97} In an attempt to circumvent this problem, Brunner et al\textsuperscript{98} have made use of a norbornene-based bis(tertiary phosphine), but the syn and anti diastereomers of the iron complex could not be separated:

\[
\begin{array}{c}
\text{Fe}^+ \\
\text{PF}_6^- \\
\text{Ph}_2\text{P} \\
\text{PPh}_2 \\
\text{CO}
\end{array}
\text{syn}
\begin{array}{c}
\text{Fe}^+ \\
\text{PF}_6^- \\
\text{Ph}_2\text{P} \\
\text{PPh}_2 \\
\text{CO}
\end{array}
\text{anti}
\]

In the present work the \(R^*\text{-}R^*\text{ and } R^*\text{-}S^*\text{ diastereomers of the bis(tertiary phosphine) 1,2-phenylenebis(methylphenylphosphine), chiral at phosphorus,} \)
have been employed in order to establish the stereochemistry of reactions at iron in complexes of the type \((R^*,R^*)-\) and \((R^*,S^*)-\)\-[(\(\eta^5\)-C\(_5\)H\(_5\))\{1,2-C\(_6\)H\(_4\)(PMePh\(_2\))\}FeR]\) and [(\(\eta^5\)-C\(_5\)H\(_5\))\{1,2-C\(_6\)H\(_4\)(PMePh\(_2\))\}FeL]\PF\(_6\).

2.2 Stereochemical Considerations

NMR spectroscopy is a powerful analytical technique for the determination of diastereomeric purity. Whereas diastereomers have different NMR spectra, enantiomers do not. Thus, the integration of an NMR spectrum can be used to determine the stereoselectivity of a reaction involving diastereomers.

Racemic complexes of the type \((R^*,R^*)-(\pm)-[(\eta^5\)-C\(_5\)H\(_5\))\{1,2-C\(_6\)H\(_4\)(PMePh\(_2\))\}FeR]\) contain diastereotopic PMe groups, and P nuclei, as indicated in the diagram below.
Accordingly, the $^1$H NMR spectrum of a complex of this type will exhibit a pair of PMe resonances (doublets, due to coupling of the protons to phosphorus) and, in the $^{31}$P($^1$H) NMR spectrum of the complex, the phosphorus nuclei will resonate as an AB spin system.

The meso or $R^*,S^*$ diastereomer of 1,2-$C_6H_4$(PMePh)$_2$ possesses constitutionally equivalent donor stereocentres of opposite helicity. In the chelating conformation ($R^*,S^*$)-1,2-$C_6H_4$(PMePh)$_2$ therefore possesses a plane of symmetry perpendicular to the 1,2-phenylene ring and complexes of the type ($R^*,S^*$)-[$(η^5-C_5H_5)$-\{1,2-$C_6H_4$(PMePh)$_2$\}FeR] will exist as syn and anti diastereomers. If the syn and anti diastereomers of a particular complex of this type can be separated and each of the diastereomers separately reacted with an appropriate reagent, stereochemical retention or inversion at iron during the course of the reaction can be monitored by NMR spectroscopy.

\[ \text{syn} \]
\[ \text{anti} \]

2.3 Results and Discussion

2.3.1 Synthesis and Reactivity of ($R^*,R^*$)- and ($R^*,S^*$)-syn/anti-\[$(η^5-C_5H_5)$\{1,2-$C_6H_4$(PMePh)$_2$\}Fe(NCMe)]PF$_6$

The diastereomers and enantiomers of 1,2-phenylenebis(methylphenylphosphine) were obtained by the published method. The brick-red complex ($R^*,R^*$)-\[(±)-[$(η^5-C_5H_5)$\{1,2-$C_6H_4$(PMePh)$_2$\}Fe(NCMe)]PF$_6$\], ($R^*,R^*$)-1, was isolated in 96%
yield as an air-stable solid by UV irradiation of a mixture \([(\eta^5-C_5H_5)Fe(CO)_2Br]\) and \((R^*,R^*)-(\pm)-1,2-C_6H_4(PMePh)_2\) in acetonitrile, followed by conversion of the intermediate bromide salt into the corresponding hexafluorophosphate salt with aqueous NH_4PF_6.\(^{88}\)

\[
\begin{align*}
\text{[R-(R*,R*)]-1} \\
\text{[S-(R*,R*)]-1}
\end{align*}
\]

The \(^1\)H NMR spectrum of \((R^*,R^*)\)-1 in [\(^2\)H_2]dichloromethane at 20 °C contains a pair of bis(tertiary phosphine) PMe resonances separated by ca 0.2 ppm, which is characteristic of all \(R^*,R^*\) complexes of this type (Table III). The \(\eta^5-C_5H_5\) resonance at \(\delta 4.15\) is also typical of \(R^*,R^*\) diastereomers.

The meso diastereomer \((R^*,S^*)-(\pm)\-\((\eta^5-C_5H_5)\,1,2-C_6H_4(PMePh)_2\)Fe-(NCMe))PF_6, \((R^*,S^*)-1\), was prepared with use of \((R^*,S^*)\)-1,2-C_6H_4(PMePh)_2 by a similar method.

\[
\begin{align*}
\text{[R-(R*,S*)]-syn-1} \\
\text{[R-(R*,S*)]-anti-1}
\end{align*}
\]
The $^1$H and $^{31}$P($^1$H) NMR spectra in $^{[2}$H$_2]$dichloromethane at 20 °C of the product isolated in 59% yield from the reaction with the $R^*,S^*$ ligand, however, were consistent with the presence of a single diastereomer with singlet resonances being observed at δ 2.28, δ 1.10, and δ 4.49 for the $\text{PMe}_3$, $\text{NCMe}$, and $\eta^5$-$\text{C}_5\text{H}_5$ protons, respectively, and a singlet resonance for the phosphorus nuclei at δ 87.0. The $^1$H NMR spectrum of the residue obtained after removal of the solvent from the mother liquor indicated the presence of two diastereomers in the ratio 3:1 (Table IV). The minor peaks corresponded to those of the initial diastereomer isolated, but the minor diastereomer could not be isolated in a pure form. The isolated major diastereomer was assigned the syn stereochemistry on the basis of the shielding pattern in the $^1$H NMR spectrum. The assignment was subsequently confirmed by an X-ray crystal structure analysis. The complex belongs to the orthorhombic space group $Pbca$. Table I lists most important distances and angles in the complex. The cation, as illustrated in Figure 3, has the syn stereochemistry. The Fe-N bond length of 1.910 (5) Å is comparable to that reported for similar compounds. For example, an Fe-N bond length of 1.881 (5) Å was found in $[(\eta^5\text{C}_5\text{H}_5)\text{dppe}\text{Fe(NCMe)}]BF_4$.101
Figure 3. Molecular structure of the cation of (R*,S*)-syn-1 showing the atom labelling scheme for non-hydrogen atoms.
Table I. Selected Bond Distances (Å) and Angles (°) of (R*,S*)-syn-1 with Estimated Standard Deviations in Parentheses

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<th>Bond Pair</th>
<th>Distance (Å)</th>
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</table>
$^1$H NMR experiments have shown that pure ($R^*,S^*$)-syn -1 does not undergo epimerization at iron over one month at 20 °C in [2H$_2$]dichloromethane or [2H$_3$]acetonitrile. Furthermore, exchange between [2H$_3$]acetonitrile and coordinated acetonitrile was not observed over the same period under similar conditions.

Rearrangement into an equilibrium mixture of syn and anti diastereomers, however, was observed when the pure syn diastereomer was heated for 2 h in boiling methanol, with syn:anti = 3:1 at equilibrium. The half-life for the rearrangement was established by $^1$H NMR spectroscopy to be ca 50 min at 50 °C in [2H$_3$]acetonitrile. Exchange of the coordinated acetonitrile with the deutrated solvent was also observed in this experiment, with a similar $t_{1/2}$. These data are consistent with dissociation of the acetonitrile ligand during rearrangement at iron.

Treatment of ($R^*,R^*$)-1 with methylmagnesium bromide in tetrahydrofuran at 20 °C gave dark-red crystalline ($R^*,R^*$)-(±)-[(η$^5$-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}FeMe], ($R^*,R^*$)-2, in ca 75% yield. This method, however, is not particularly reliable and yields for reactions with some Grignard reagents were as low as 40%. Two additional products were identified by $^1$H NMR spectroscopy of the crude reaction mixture resulting from the Grignard reactions: the cyanomethyl complex ($R^*,R^*$)-(±)-[(η$^5$-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}Fe(CH$_2$CN)] (ca 40%), and the halogeno derivatives ($R^*,R^*$)-(±)-[(η$^5$-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}FeX] (where X = Cl, Br or I) (ca 20%) (see Scheme III). The mixtures were separated by liquid chromatography. Relevant $^1$H NMR data are summarized in Table III.
A similar result was obtained when (R*,S*)-syn-1 was reacted with methylmagnesium bromide, with only one diastereomer of the methyl and cyanomethyl and halogeno derivatives being observed. Reactions of an anti:syn = 2:1 mixture of (R*,S*)-1 led to the production of the same two product diastereomers as obtained from the pure syn material. In [2H2]toluene the R*,S* iron-methyl complex exhibits PMe, FeMe, and \( \eta^5 \)-C5H5 resonances at \( \delta \) 1.74, 0.57, and 3.80, respectively. Furthermore, the spectrum is essentially unchanged over the temperature range -90 to 100 °C. Indeed, heating of a sample of the pure (R*,S*)-Fe-Me complex at 100 °C for 24 h did not cause epimerization at iron (Table IV). On the basis of the \(^1\)H NMR data, methylation of (R*,S*)-syn-1 affords a single diastereomer, which has been assigned
the syn stereochemistry. The minor products of the reaction also appear to have retained
the syn stereochemistry. An X-ray structure analysis of the iron-methyl derivative is
currently underway in order to confirm the stereochemical assignment.

Stereochemical investigations of tetrahedral nickel nitrosyl complexes containing
\((R^*,S^*)\)-1,2-\(\text{C}_6\text{H}_4\)(PMePh)\(_2\) also revealed retention of configuration at the metal during
substitution reactions.\(^{103}\) Neutral compounds of the type \((R^*,S^*)\)-[NiX(NO)\(\{\text{1,2-}
\text{C}_6\text{H}_4\text{(PMePh)}\}_2\}] exist as single diastereomers of anti stereochemistry in the solid state
and in solution, although derivatives of the type \((R^*,S^*)\)-[NiL(NO)\(\{\text{1,2-}
\text{C}_6\text{H}_4\text{-(PMePh)}\}_2\}]\text{PF}_6 (where L = PR\(_3\)) can be isolated as syn/anti
mixtures.

\[
\text{NO} \quad \text{syn} \quad \text{NO} \quad \text{anti}
\]

Consiglio and coworkers\(^{70(c)}\) and Cesaretti et al\(^{105}\) in stereochemical studies
of chiral half-sandwich ruthenium complexes have shown that substitution of
coordinated acetonitrile proceeds with predominant retention of configuration at
ruthenium. For example, treatment of \((R\text{-menthyl, } R\text{Ru})-[(\eta^5\text{-C}_5\text{H}_5\text{Men})\text{Ru(CO)}\]
\((\text{PPh}_3)\text{(NCCD}_3\text{)}])\text{BF}_4\) with sodium iodide gave the iodo derivative of the same
configuration at ruthenium, diastereomerically pure.\(^{105}\) No conclusion could be drawn
on the pathway of this reaction, however, since the substitution was not performed on
the other diastereomer of the complex.
The formation of the cyanomethyl derivative can be rationalized in terms of deprotonation of the acetonitrile ligand by the Grignard reagent, followed by intramolecular linkage isomerism of the cyanomethyl carbanion. Methane was evolved during the reaction. The small quantities of halogeno-iron by-products observed in the reactions presumably arose from halide displacement of acetonitrile.

The reaction of either (SRu,Rc)- or (RRu,Rc)-[(T15-C5H5)(prophos)Ru(NCMe)]PF6 [where prophos = (R)-1,2-propanebis(diphenylphosphine)] with methylmagnesium bromide yields the corresponding methyl compound [(η⁵-C₅H₅)-(prophos)RuMe] in 3-5% yield, amongst other unidentified products. In related work, et al. have shown that treatment of [(η⁵-C₅Me₅)(PMe₃)Fe(acac)] (where acac = acetylacetonate-O,O) with t-butylmagnesium chloride or benzylmagnesium chloride in the presence of trimethylphosphine affords in high yield [(η⁵-C₅Me₅)-(PMe₃)FeCl]. Similarly, treatment of [(η⁵-C₅Me₅)(PMe₃)Fe(acac)] with 1 equiv. of C₃H₅MgBr and trimethylphosphine gave a 39% yield of violet [(η⁵-C₅Me₅)-(PMe₃)₂FeBr].

The ¹H NMR spectra of both (R*,R*)- and (R*,S*)-syn-2 in dry [²H₈]toluene exhibit sharp triplets at δ -0.85 and δ -0.57 for the respective FeMe groups. No changes in the ¹H NMR spectra were observed when the samples were heated at 100 °C for 24 h. The addition of traces of water to the NMR samples, however, resulted in immediate collapse of the FeMe resonances in both cases without broadening of the other signals in the spectra. Both (R*,R*)- and (R*,S*)-2 can be recovered unchanged from the wet solutions. Consistent with rapid proton exchange between the Fe-Me group and water, the addition of [²H₂]water to a solution of (R*,R*)-2 in dichloromethane resulted in complete deuteration of the Fe-Me group. There does not appear to be a precedent in
the literature for the unusually high acidity of the iron-methyl protons in \((R^*,R^*)-2\), but it may be noteworthy that the authors of papers concerning related complexes state that \(^1\text{H} \text{NMR spectra were recorded in dry [}^2\text{H}_8\text{]toluene.}^{96,107,108}\) No such phenomenon was observed for the cyanomethyl compounds.

A single crystal X-ray analysis of \((R^*,R^*)-2\) revealed no unusual features; crystals of the complex belong to the monoclinic space group \(P2_1/n\). Table II gives selected bond distances and angles in the complex. The geometry of \((R^*,R^*)-2\) is shown in Figure 4, which also shows the atomic numbering scheme employed. The crystal structure revealed an iron-carbon bond length of 2.053 (2) \(\text{Å}\), which is comparable to the lengths of similar bonds in other \(\text{Fe-Me}\) compounds.\(^{70(b),109-112}\)
Figure 4. A view of the $S$ enantiomer of $(R^*, R^*)$-2 showing the atom labelling scheme for non-hydrogen atoms.
Table II. Selected Bond Distances (Å) and Angles (°) of \((R^*, R^*)-2\)
with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-P(1)</td>
<td>2.1335(6)</td>
<td>Fe-P(2)</td>
<td>2.1327(5)</td>
</tr>
<tr>
<td>Fe-C(4)</td>
<td>2.053(2)</td>
<td>Fe-C(51)</td>
<td>2.093(2)</td>
</tr>
<tr>
<td>Fe-C(52)</td>
<td>2.084(2)</td>
<td>Fe-C(53)</td>
<td>2.082(2)</td>
</tr>
<tr>
<td>Fe-C(54)</td>
<td>2.092(2)</td>
<td>Fe-C(55)</td>
<td>2.082(2)</td>
</tr>
<tr>
<td>P(1)-C(1)</td>
<td>1.837(2)</td>
<td>P(1)-C(11)</td>
<td>1.840(2)</td>
</tr>
<tr>
<td>P(1)-C(31)</td>
<td>1.835(2)</td>
<td>P(2)-C(2)</td>
<td>1.828(2)</td>
</tr>
<tr>
<td>P(2)-C(21)</td>
<td>1.849(2)</td>
<td>P(2)-C(32)</td>
<td>1.840(2)</td>
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<td>Fe-Cp</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>P(1)-Fe-P(2)</td>
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<td>P(1)-Fe-C(4)</td>
<td>88.07(7)</td>
</tr>
<tr>
<td>P(1)-Fe-Cp</td>
<td>128.5</td>
<td>P(2)-Fe-C(4)</td>
<td>87.61(7)</td>
</tr>
<tr>
<td>P(2)-Fe-Cp</td>
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<td>C(4)-Fe-Cp</td>
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</tr>
<tr>
<td>Fe-P(1)-C(1)</td>
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<td>Fe-P(1)-C(1)</td>
<td>119.47(6)</td>
</tr>
<tr>
<td>Fe-P(1)-C(31)</td>
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<td>C(1)-P(1)-C(11)</td>
<td>100.93(1)</td>
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<tr>
<td>C(1)-P(1)-C(31)</td>
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<td>C(11)-P(1)-C(31)</td>
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<tr>
<td>Fe-P(2)-C(32)</td>
<td>109.78(6)</td>
<td>C(2)-P(2)-C(21)</td>
<td>101.35(1)</td>
</tr>
<tr>
<td>C(2)-P(2)-C(32)</td>
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<td>C(21)-P(2)-C(32)</td>
<td>100.66(8)</td>
</tr>
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<td>P(1)-C(11)-C(12)</td>
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<td>P(1)-C(11)-C(16)</td>
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<tr>
<td>P(2)-C(21)-C(22)</td>
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<td>P(2)-C(21)-C(26)</td>
<td>118.89(1)</td>
</tr>
<tr>
<td>P(1)-C(31)-C(32)</td>
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<td>P(1)-C(31)-C(36)</td>
<td>125.43(1)</td>
</tr>
<tr>
<td>P(2)-C(32)-C(31)</td>
<td>115.57(1)</td>
<td>P(2)-C(32)-C(33)</td>
<td>125.25(1)</td>
</tr>
</tbody>
</table>

Footnote: Cp is the centroid of the cyclopentadienyl ring (0.5267, 0.2512, 0.3345).
Attempts to insert CO or SO₂ into the Fe-C bond of \((R^*,R^*)-2\) were unsuccessful, but the reaction of \((R^*,R^*)-2\) with stannous chloride in boiling methanol / ethyl acetate\(^{113}\) over 18 h gave an almost quantitative yield of \((R^*,R^*)-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}FeSnCl_2Me], (R^*,R^*)-3\). The \(^1H\) NMR spectrum of the tin derivative in \([2H_2]\)dichloromethane exhibits a sharp singlet at \(\delta 1.53\) for the SnMe resonance. No exchange of the tin-methyl protons was observed when water was added to the \(^1H\) NMR sample.

\[\text{(R^*,R^*)-2} \xrightarrow{\text{SnCl}_2} \text{(R^*,R^*)-3}\]

Treatment of \((R^*,R^*)-1\) with lithium aluminium hydride in tetrahydrofuran at 20 °C gave \((R^*,R^*)-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}FeH], (R^*,R^*)-4\), in 45% yield, as air-sensitive orange crystals. The \(^1H\) NMR spectrum of the hydride in \([2H_8]\)toluene contains an FeH resonance at \(\delta -16.37\) (\(2J_{\text{PH}} = 69.9\) Hz). The resonance was not observed when the \(^1H\) NMR spectrum was recorded in \([2H_2]\)dichloromethane. Presumably exchange between hydride and chloride ions takes place in dichloromethane as has been reported previously for similar compounds.\(^{107,114}\) Treatment of \((R^*,R^*)-4\) with triphenylcarbenium hexafluorophosphate in acetonitrile regenerated the original complex.
The achiral analogue (R*,S*)-(+)-(T\textsubscript{5}-C\textsubscript{5}H\textsubscript{5})\{1,2-C\textsubscript{6}H\textsubscript{4}(PMePh)\textsubscript{2}\}FeH, (R*,S*)-4, was isolated in 41% yields as an air-sensitive solid by treatment of pure (R*,R*)-syn-l or (R*,S*)-anti/syn-l with lithium aluminium hydride in tetrahydrofuran. The \textsuperscript{1}H NMR spectrum in [\textsuperscript{2}H\textsubscript{5}]toluene of (R*,S*)-4 displays a single set of resonances for the PMe, FeMe, and T\textsubscript{5}-C\textsubscript{5}H\textsubscript{5} protons at \(\delta\) 1.90, \(\delta\) -16.62, and \(\delta\) 4.05, respectively. No evidence of the other diastereomer was obtained. An X-ray crystal structure analysis is required in order to establish the stereochemistry of the R*,S* hydride.

Previous work in our group has shown that the acetonitrile ligand in (R*,R*)-1 is readily substituted by primary, secondary, or tertiary phosphines to give the corresponding phosphine complexes.\textsuperscript{44} Thus, (R*,S*)-syn-l reacts with PMePh\textsubscript{2} in boiling methanol to give a ca 90% yield of (R*,S*)-(±)-(\(\eta\textsuperscript{5}-C\textsubscript{5}H\textsubscript{5}\))\{1,2-C\textsubscript{6}H\textsubscript{4}(PMePh)\textsubscript{2}\}Fe(PMePh\textsubscript{2})PF\textsubscript{6}, (R*,S*)-5. The \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra of the product in [\textsuperscript{2}H\textsubscript{2}]dichloromethane reveal partial inversion of configuration at iron during acetonitrile substitution, with syn:anti = 4:1 in the product. The diastereomers can be separated by fractional crystallization: the major diastereomer crystallizes from acetone-diethyl ether and the more soluble minor diastereomer from dichloromethane-petroleum ether. Relevant \textsuperscript{1}H NMR data for the two complexes can be found in Table IV.

The pure diastereomers of (R*,S*)-5 were shown by \textsuperscript{1}H NMR spectroscopy to be stable to inversion at iron when heated in boiling dichloromethane.
2.3.2 Synthesis and Reactivity of \((R^*,R^*)\)-(+)\-\(\mu\)-N₂\(\{(\eta^5-C₅H₅)\{1,2\-C₆H₄(PMePh)₂\}Fe\}\₂\)(PF₆)₂, \((R^*,R^*)\)-6

The dinitrogen complex \((R^*,R^*)\)-6 was prepared from the carbonyl \((R^*,R^*)\)-(+)\-\(\mu\)-N₂\(\{(\eta^5-C₅H₅)\{1,2\-C₆H₄(PMePh)₂\}Fe\}\₂\)(PF₆), \((R^*,R^*)\)-7, according to the literature method for related compounds (see Scheme IV).¹¹⁵
Thus, \((R^*,R^*)\)-7 was prepared by heating a mixture of \([(\eta^5-C_5H_5)Fe(CO)_2Cl]\) and \((R^*,R^*)\)-(±)-1,2-C_6H_4(PMePh)_2 in boiling methanol for 18 h. The progress of the reaction was monitored by IR spectroscopy (Figure 5). Upon completion of the
reaction, the reaction mixture was cooled to room temperature and treated with aqueous NH₄PF₆; cooling of the solution to -30 °C gave a 70% yield of \((R^*,R^*)\)-7 as air-stable yellow crystals.

The dinitrogen complex \((R^*,R^*)\)-6 was obtained as an orange solid in 99% yield by UV irradiation over 15 h of a solution of \((R^*,R^*)\)-7 in acetone at -30 °C, followed by reaction of the intermediate acetone complex in tetrahydrofuran with dinitrogen for a further 3 h (Scheme IV). The complex \((R^*,R^*)\)-6 has been assigned an end-on bridging dinitrogen structure, as proposed for related compounds. The \(v(N_2)\) IR absorption in \((R^*,R^*)\)-6 occurs at 2045 cm\(^{-1}\).

Dissolution of \((R^*,R^*)\)-6 in acetone, followed by the addition of diethyl ether and cooling of the solution to -30 °C, regenerates air-stable black crystals of \((R^*,R^*)\)-(±)-\([\eta^5-C_5H_5]\{1,2-C_6H_4(PMePh)_2\}Fe(OCMe_2)]PF_6, \((R^*,R^*)\)-8, in 72% yield. The \(v(CO)\) absorption in \((R^*,R^*)\)-8 occurs at 1654 cm\(^{-1}\), consistent with oxygen coordination of acetone to a positively charged metal ion.
The reactivity of the dinitrogen complex was further investigated through a number of reactions, as depicted in Scheme V. For example, treatment of \((R^*,R^*)-6\) with methylmagnesium bromide in tetrahydrofuran at 20 °C produces the iron-methyl complex \((R^*,R^*)-2\) exclusively in 75% yield; heating \((R^*,R^*)-6\) in boiling acetonitrile affords \((R^*,R^*)-1\); and, treatment of \((R^*,R^*)-6\) [or \((R^*,R^*)-1\)] with \((\pm)-\text{PHMePh}\) in
boiling methanol gives the secondary phosphine derivatives \([((R^*,R^*),(R^*)))/\]

\([(R^*,R^*),(S^*)]-(\pm)-(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe(PHMePh)\}PF_6, (R^*,R^*)-9, in
ca 86% yield. The secondary phosphine complex was isolated as an equimolar mixture
of two diastereomers that can be separated by fractional crystallization from suitable
solvents.\(^{44}\)

\[
\begin{align*}
((R^*,R^*)(R^*)-9^* \\
(R^*,R^*)(S^*)-9^*
\end{align*}
\]

* one enantiomer of each diastereomer depicted
Table III. Selected $^1$H NMR Chemical Shift Data for $(R^*,R^*)$-1-7

<table>
<thead>
<tr>
<th>Compound</th>
<th>L or R</th>
<th>$\delta(\eta^5$-$C_5H_5$)</th>
<th>$1,2$-$C_6H_4$(PMePh)$_2$</th>
<th>L or R</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(R^<em>,R^</em>)$-1</td>
<td>NCMe</td>
<td>4.15</td>
<td>2.07</td>
<td>2.32</td>
</tr>
<tr>
<td>$(R^<em>,R^</em>)$-2</td>
<td>Me</td>
<td>3.87</td>
<td>1.75</td>
<td>1.87</td>
</tr>
<tr>
<td>$(R^<em>,R^</em>)$</td>
<td>CH$_2$CN</td>
<td>3.90</td>
<td>2.03</td>
<td>2.15</td>
</tr>
<tr>
<td>$(R^<em>,R^</em>)$-3</td>
<td>SnCl$_2$Me</td>
<td>4.21</td>
<td>2.10</td>
<td>2.48</td>
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<tr>
<td>$(R^<em>,R^</em>)$-4</td>
<td>H</td>
<td>3.96</td>
<td>1.79</td>
<td>1.87</td>
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<tr>
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<tr>
<td>$(R^<em>,R^</em>)$-7</td>
<td>CO</td>
<td>4.70</td>
<td>2.23</td>
<td>2.38</td>
</tr>
</tbody>
</table>
Table IV. Selected $^1$H NMR Chemical Shift Data for (R*,S*)-1 - 7

<table>
<thead>
<tr>
<th>compound</th>
<th>L or R</th>
<th>$\delta$($\eta^5$-C$_5$H$_5$)</th>
<th>1,2-C$_6$H$_4$(PMePh)$_2$</th>
<th>L or R</th>
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</thead>
<tbody>
<tr>
<td>(R*,S*)-syn-1</td>
<td>NCMe</td>
<td>4.49</td>
<td>2.28</td>
<td>1.10</td>
</tr>
<tr>
<td>(R*,S*)-anti-1</td>
<td>NCMe</td>
<td>3.89</td>
<td>2.11</td>
<td>2.22</td>
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<tr>
<td>(R*,S*)-2</td>
<td>Me</td>
<td>3.80</td>
<td>1.74</td>
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</tr>
<tr>
<td>(R*,S*)</td>
<td>CH$_2$CN</td>
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<td>1.60</td>
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<td>(R*,S*)-4</td>
<td>H</td>
<td>4.05</td>
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</tr>
<tr>
<td>(R*,S*)-syn-5</td>
<td>PMePh$_2$</td>
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<td>2.09</td>
<td>1.20</td>
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<tr>
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<tr>
<td>(R*,S*)-anti-7</td>
<td>CO</td>
<td>4.47</td>
<td>2.20</td>
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</table>
Reactions were carried out under a positive pressure of argon using the Schlenk technique. Solvents were dried by following the usual literature procedures and were freshly distilled under argon prior to use. $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded on a Varian VXR-300 spectrometer or a Bruker CXP-200 spectrometer at 20 °C in $[^2$H$_2$]dichloromethane, unless stated otherwise. Spectra were referenced internally with respect to residual protonated solvent resonances ($^1$H) relative to SiMe$_4$ ($\delta = 0$) or 85% H$_3$PO$_4$ ($^{31}$P{$^1$H}). IR spectra were recorded with use of a Perkin-Elmer 683 Model spectrophotometer. Optical rotations were measured at 20 °C on the specified solutions in a 1-dm cell with a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by staff within the Research School of Chemistry. Petroleum ether used had bp 40-60 °C. The X-ray diffraction data for $(R^*,S^*)$-[(η5C5H5){1,2-C4H6(PMePh)$_2$}-Fe(NCMe)]PF$_6$ were collected on a Nicolet XRD P3 diffractometer equipped with MoKα by Dr W. T. Robinson of the University of Canterbury, New Zealand. The molecular structure was determined by Dr A. C. Willis of the Research School of Chemistry. The X-ray diffraction data for $(R^*,R^*)$-[(η5C5H5){1,2-C4H6-(PMePh)$_2$}FeMe] were collected on a Picker FACS-I diffractometer equipped with MoKα radiation by Dr A. C. Willis, who also determined the molecular structure. 1,2-Phenylenebis(methylphenylphosphine) was prepared, separated into its diastereomers, and resolved by the published methods.100 Bromodicarbonyl(η5-cyclopentadienyl)iron(II) and dicarbonylchloro(η5-cyclopentadienyl)iron(II) were also prepared by reported methods.120

$(R^*,R^*)$-($\pm$)-Acetonitrile(η5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ($(R^*,R^*)$-1)
A suspension of [(η⁵-C₅H₅)Fe(CO)₂Br] (2.0 g, 7.8 mmol) and (R*,R*)-1,2-C₆H₄(PMePh)₂ (2.52 g, 7.8 mmol) in acetonitrile (80 mL) was irradiated for 50 min with a Hanovia 125W UV lamp. The resulting brown solution was reduced in volume (to ca 10 mL) and treated with aqueous NH₄PF₆ (12.5%, 20 mL). Diethyl ether (30 mL) was added to the reaction mixture, which was then stirred for ca 12 h. The brick-red product was collected, washed with diethyl ether, and dried: mp 238-240 °C dec; 4.7 g (95%). Anal. Calcd for C₂₇H₂₃FifeNP₃: C, 51.5; H, 4.5; N, 2.2; P, 14.8. Found: C, 51.8; H, 4.6; N, 2.1; P, 14.6. ¹H NMR: δ 1.68 (t, 3 H, JPH = 1.3 Hz, MeCN), 2.07 (d of d, 3 H, JPH = 8.7 Hz, ²JPH = 2.2 Hz, PMe), 2.32 (d of d, 3 H, JPH = 8.1 Hz, ³JPH = 1.8 Hz, PMe), 4.15 (t, 5 H, ⁴JPH = 1.6 Hz, η⁵-C₅H₅), 7.22-7.65 (m, 14 H, aromatics). ³¹P{¹H} NMR: δ 86.8, 87.5 (AB m, 2 P, ²²JAB = 47.0 Hz).

(R*,S*)-syn-Acetonitrile(η⁵-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ((R*,S*)-syn-1)

This compound was obtained from [(η⁵-C₅H₅)Fe(CO)₂Br] and (R*,S*)-1,2-C₆H₄(PMePh)₂ in acetonitrile by the method described for the corresponding R*,R* diastereomer, but with a reaction time of 40 min: mp 194-195 °C dec; 2.87 g (59%). Anal. Calcd for C₂₇H₂₈F₆FeNP₃: C, 51.5; H, 4.5; N, 2.2; P, 14.8. Found: C, 51.3; H, 4.5; N, 2.3; P, 14.4. ¹H NMR: δ 1.10 (t, 3 H, ⁵JPH = 1.3 Hz, MeCN), 2.28 (t, 6 H, ²JPH = 4.7 Hz, ²PMe), 4.49 (t, 5 H, ³JPH = 1.5 Hz, η⁵-C₅H₅), 7.16-7.84 (m, 14 H, aromatics). ³¹P{¹H} NMR: δ 87.0 (s, 2 P).

(R*,S*)-anti/syn-Acetonitrile(η⁵-cyclopentadienyl)[1,2-phenylenebis-(methylphenylphosphine)]iron(II) Hexafluorophosphate ((R*,S*)-anti/syn-1)
The mother liquor from the isolation of \((R^*,S^*)\)-syn-1 was evaporated to dryness. The \(^1\text{H}\) NMR spectrum showed a 3:1 mixture of diastereomers. \(^1\text{H}\) NMR (major): \(\delta\) 2.11 (t, 6 H, \(2J_{PH} = 5.1\) Hz, 2 PMe), 2.22 (t, 3 H, \(5J_{PH} = 1.2\) Hz, NCMe), 3.89 (t, 5 H, \(3J_{PH} = 1.7\) Hz, \(\eta^5\)-C5H5), 7.33-7.66 (m, 14 H, aromatics). \(^31\text{P}\{^1\text{H}\}\) NMR: \(\delta\) 86.9 ppm (s). \(^1\text{H}\) and \(^31\text{P}\{^1\text{H}\}\) NMR (minor): identical with those of \((R^*,S^*)\)-syn-1.

\((R^*,R^*)\)-\((\eta^5\text{-Cyclopentadienyl})\text{methyl[1,2-phenylenebis(methylphenylphosphine)]iron(II)}\) ((\(R^*,R^*)\)-2)

**Method 1:** To a solution of \((R^*,R^*)\)-6 (1.5 g, 1.25 mmol) in tetrahydrofuran (200 mL) at 20 °C was added methylmagnesium bromide (10 mL, 1.25 M in diethyl ether, 12.5 mmol). After 12 h the solvent was evaporated off and the residue was extracted with diethyl ether (200 mL) and the extract washed with aqueous NH4PF6. The organic layer was separated off and dried over MgSO4. The dried extract was concentrated to ca 5 mL and the residue was chromatographed on basic alumina (Activity I) with diethyl ether as eluent. The eluate, after drying over MgSO4 and slow evaporation, yielded dark-red crystals of the product: mp 140 °C; 0.65 g (57%).

Anal. Calcd for C26H28FeP2: C, 68.1; H, 6.2; P, 13.5. Found: C, 68.1; H, 6.2; P, 13.3. \(^1\text{H}\) NMR ([\(^2\text{H}_8\)]toluene): \(\delta\) -0.85 (t, 3 H, \(3J_{PH} = 7.5\) Hz, FeMe), 1.75 (d, 3 H, \(2J_{PH} = 9.2\) Hz, PMe), 1.87 (d, 3 H, \(2J_{PH} = 7.8\) Hz, PMe), 3.87 (t, 5 H, \(3J_{PH} = 1.3\) Hz, \(\eta^5\)-C5H5), 6.94-7.31 (m, 14 H, aromatics).

**Method 2:** To a solution of \((R^*,R^*)\)-1 (3.0 g, 4.77 mmol) in tetrahydrofuran (125 mL) at 20 °C was added methylmagnesium bromide (10 mL, 4.7 M in diethyl ether, 47 mmol). After 12 h, the solvent was evaporated off and the residue was extracted into diethyl ether (150 mL) and washed with aqueous NH4Br to destroy excess Grignard reagent. The organic layer was separated, dried over MgSO4, and the volume
was reduced to 5 mL. The residue was then chromatographed on basic alumina (Activity I) with diethyl ether as eluent. The eluate, after drying over MgSO₄, and slow evaporation yielded dark-red crystals of the product: yield 40-75%. ¹H NMR ([²H₈]toluene): identical to that of (R*,R*)-2.

(R*,R*)-(±)-Cyanomethyl(η⁵-Cyclopentadienyl)[1,2-phenylenebis-(methylphenylphosphine)]iron(II)

This compound was isolated as a by-product in the preparation of (R*,R*)-2 using method 2: yield 0-40%. Anal. Calcd for C₂₇H₂₇FeNP₂: C, 67.1; H, 5.6; N, 2.9; P, 12.8 Found: C, 66.8; H, 5.7; N, 2.6; P, 12.5. ¹H NMR ([²H₈]toluene): δ -1.03 (m, 1 H, FeCHH'CN), -0.41 (m, 1 H, FeCHH'CN), 2.03 (d of d, 3 H, 2J_PH = 9.4 Hz, 2J_HH = 1.3 Hz, PMe), 2.15 (d of d, 3 H, 2J_PH = 8.3 Hz, 2J_HH = 1.2 Hz, PMe), 3.90 (t, 5 H, 3J_PH = 1.5 Hz, η⁵-C₅H₅), 6.89-7.25 (m, 14 H, aromatics). IR ν(CN) 2175 cm⁻¹.

(R*,R*)-(±)-Bromo(η⁵-Cyclopentadienyl)[1,2-phenylenebis-(methylphenylphosphine)]iron(II)

This compound was isolated as a by-product in the preparation of (R*,R*)-2 using method 2: yield 0-20%. Anal. Calcd for C₂₅H₂₅FeBrP₂: C, 57.4; H, 4.8; P, 11.7. Found: C, 57.0; H, 5.1; P, 11.7. ¹H NMR ([²H₈]toluene): 2.57 (t, 6 H, 2J_PH = 8.8 Hz, 2PMe), 3.89 (s, 5 H, η⁵-C₅H₅), 7.02-7.34 (m, 14 H, aromatics).

(R*,S*)-syn-(η⁵-Cyclopentadienyl)methyl[1,2-phenylenebis(methylphenylphosphine)]iron(II) ((R*,S*)-2)

This compound was obtained from either (R*,S*)-syn-1 or (R*,S*)-anti/syn-1 and methylmagnesium bromide in tetrahydrofuran using method 2 described for (R*,R*)-2: mp 148-149 °C; yield 40-64%. Anal. Calcd for C₂₆H₂₈FeP₂: C, 68.1; H,
6.2; P, 13.5. Found: C, 68.1; H, 6.4; P, 13.4. $^1$H NMR: $\delta$ -0.57 (t, 3 H, $^3J_{PH} = 7.6$ Hz, FeMe), 1.74 (t, 6 H, $^2J_{PH} = 4.7$ Hz, 2 PMe), 3.80 (t, 5 H, $^3J_{PH} = 1.2$ Hz, $\eta^5$-C$_5$H$_5$), 6.91-7.27 (m, 14 H, aromatics).

(R*,S*)-syn-Cyanomethyl($\eta^5$-Cyclopentadienyl)[1,2-phenylenebis-(methylphenylphosphine)]iron(II)

This compound was isolated as a by-product in the preparation of (R*,S*)-2:
yield 0-40%. Anal. Calcd for C$_{27}$H$_{27}$FeNP$_2$: C, 67.1; H, 5.6; N, 2.9; P, 12.8. Found: C, 66.9; H, 5.6; N, 2.4; P, 12.7. $^1$H NMR ([$^2$H$_8$]toluene): $\delta$ -0.75 (t, 1 H, $^3J_{PH} = 7.2$ Hz, FeCHH'CN), -0.18 (t, 1 H, $^3J_{PH} = 7.3$ Hz, FeCHH'CN), 1.66 (t, 6 H, $^2J_{PH} = 4.62$ Hz, PMe), 3.74 (t, 5 H, $^3J_{PH} = 1.5$ Hz, $\eta^5$-C$_5$H$_5$), 6.85-7.35 (m, 14 H, aromatics).

(R*,S*)-syn-Bromo($\eta^5$-Cyclopentadienyl)[1,2-phenylenebis-(methylphenylphosphine)]iron(II)

This compound was isolated as a by-product in the preparation of (R*,S*)-2:
yield 0-20%. Anal. Calcd for C$_{25}$H$_{25}$FeBrP$_2$: C, 57.4; H, 4.8; P, 11.7. Found: C, 56.8; H, 5.2; P, 11.9. $^1$H NMR ([$^2$H$_8$]toluene): 2.39 (t, 6 H, $^2J_{PH} = 7.2$ Hz, 2 PMe), 3.82 (s, 5 H, $\eta^5$-C$_5$H$_5$), 6.85-7.25 (m, 14 H, aromatics).

(R*,R*)-(±)-($\eta^5$-Cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]dichloromethylstannatoiron(II) Hemidichloromethane Solvate

$((R^*,R^*)\cdot0.5\text{CH}_2\text{Cl}_2)$

A mixture of (R*,R*)-2 (0.5 g, 1.1 mmol) and tin(II) chloride dihydrate (1 g, 4.4 mmol) in methanol (25 mL) / ethyl acetate (2.5 mL) was boiled under reflux for ca 18 h. The orange product was recrystallized from methanol / dichloromethane to give
orange needles of the hemidichloromethane solvate: mp 230-232 °C; 0.71 g (99%).

Anal. Calcd for C_{26.5}H_{29}Cl_{3}FeP_{2}Sn: C, 46.0; H, 4.2; P, 9.0; Cl, 15.4. Found: C, 45.3; H, 3.8; P, 9.0; Cl, 15.6. \(^1\)H NMR: \(\delta\) 1.53 (s, 3 H, SnCl_{2}Me), 2.10 (d, 3 H, \(\text{J}_{PH} = 8.1\) Hz, PMe), 2.48 (d, 3 H, \(\text{J}_{PH} = 8.5\) Hz, PMe), 4.21 (t, 5 H, \(\text{J}_{PH} = 1.9\) Hz, \(\eta^5\)-C_{5}H_{5}), 7.03-7.78 (m, 14 H, aromatics).

\((R^*,R^*)-(\pm)-(\eta^5\text{-Cyclopentadienyl})\text{hydrido[1,2-phenylenebis(methyl-phenylphosphine)]iron(II)}\) \((\text{[(R^*,R^*)-4]}\)

To a solution of \((R^*,R^*)-4\) (2.0 g, 3.2 mmol) in tetrahydrofuran (100 mL) at 20 °C was added lithium aluminium hydride (0.2 g, 5 mmol) and the reaction mixture was stirred for ca 12 h. The excess reducing agent was destroyed by the slow addition of methanol. The solvent was evaporated off and the residue was extracted with n-hexane (ca 2 L). Slow evaporation of the extract yielded the product as air-sensitive orange crystals: 0.63 g (45%). Anal. Calcd for C_{25}H_{26}FeP_{2}: C, 67.6; H, 5.9; P, 13.9. Found: C, 67.2; H, 6.1; P, 13.7. \(^1\)H NMR ([\(\text{H}_8\)]toluene): \(\delta\) -16.37 (d of d, 1 H, \(\text{J}_{PH} = 69.9\) Hz, FeH), 1.79 (d, 3 H, \(\text{J}_{PH} = 6.9\) Hz, PMe), 1.87 (d, 3 H, \(\text{J}_{PH} = 8.5\) Hz, PMe), 3.96 (s, 5 H, \(\eta^5\)-C_{5}H_{5}), 6.65-7.66 (m, 14 H, aromatics).

The reaction of \((R^*,R^*)-4\) with triphenylcarbenium hexafluorophosphate in acetonitrile at 0 °C gave \((R^*,R^*)-1\) in high yield.

\((R^*,S^*)-\text{syn-(\eta^5\text{-Cyclopentadienyl})hydrido[1,2-phenylenebis(methyl-phenylphosphine)]iron(II)}\) \((\text{[(R^*,S^*)-4]}\)

This compound was obtained from either \((R^*,S^*)-\text{syn-1}\) or \((R^*,S^*)-\text{anti/syn-1}\) and lithium aluminium hydride in tetrahydrofuran at 20 °C by the procedure described for \((R^*,R^*)-4\): 0.57 g (41%). Anal. Calcd for C_{25}H_{26}FeP_{2}: C, 67.6; H, 5.9; P, 13.9.

Found: C, 67.2; H, 5.7; P, 13.6. \(^1\)H NMR ([\(\text{H}_8\)]toluene): \(\delta\) -16.62 (t, 1 H, \(\text{J}_{PH} =\)
75.8 Hz, FeH), 1.90 (t, 6 H, $^{2}J_{PH} = 4.2$ Hz, 2 PMe), 4.05 (s, 5 H, $^{15}$C$_{5}$H$_{5}$), 6.90-7.34 (m, 14 H, aromatics).

$(R^*,S^*)$-syn-(Cyclopentadienyl)(methyldiphenylphosphine)[1,2-phenylenebis(methyldiphenylphosphine)]iron(II) Hexafluorophosphate

$(R^*,S^*)$-syn-5

A mixture of $(R^*,S^*)$-syn-1 (0.4 g, 0.65 mmol) and methyldiphenylphosphine (0.13 g, 0.65 mmol) in methanol (50 mL) was heated under reflux for 2 h. The yellow solution was then reduced in volume to ca 10 mL and diluted with diethyl ether to yield the product as the major component of a 4:1 mixture of itself with the corresponding $(R^*,S^*)$-anti-5 diastereomer. Fractional crystallization of the mixture from acetone (5 mL) by the slow addition of diethyl ether gave pure $(R^*,S^*)$-syn-5 as yellow needles: mp 215-218 °C dec; 0.3 g (73%). Anal. Calcd for C$_{38}$H$_{38}$F$_{6}$FeP$_{4}$: C, 57.9; H, 4.9; P, 15.7. Found: C, 57.7; H, 4.8; P, 15.7. $^{1}$H NMR: $\delta$ 1.20 (d, 3 H, $^{2}J_{PH} = 6.8$ Hz, PMePh$_{2}$), 2.09 (t, 6 H, $^{2}J_{PH} = 4.6$ Hz, 2 PMe), 4.49 (q, 5 H, $^{3}J_{PH} = 1.8$ Hz, $^{15}$C$_{5}$H$_{5}$), 7.24-7.64 (m, 24 H, aromatics). $^{31}$P($^{1}$H) NMR: $\delta$ 48.7 (d, 2 P, $J_{AX}$, bis(tertiary phosphine)), 76.1 (t, 1 P, $J_{AX}$ = PMePh$_{2}$).

$(R^*,S^*)$-anti-(Cyclopentadienyl)(methyldiphenylphosphine)[1,2-phenylenebis(methyldiphenylphosphine)]iron(II) Hexafluorophosphate

$(R^*,S^*)$-anti-5

The mother liquor from the isolation of $(R^*,S^*)$-syn-5 was evaporated to dryness, and the residue was recrystallized from dichloromethane-petroleum ether mixture giving yellow needles of the anti diastereomer: 0.06 g (15%). Anal. Calcd for C$_{38}$H$_{38}$F$_{6}$FeP$_{4}$: C, 57.9; H, 4.9; P, 15.7. Found: C, 57.4; H, 4.7; P, 15.7. $^{1}$H NMR: $\delta$ 1.39 (t, 3 H, $^{2}J_{PH} = 3.8$ Hz, PMePh$_{2}$), 2.05 (t, 6 H, $^{2}J_{PH} = 4.3$ Hz, 2 PMe), 4.15 (q, 5 H, $^{3}J_{PH} = 1.7$ Hz, $^{15}$C$_{5}$H$_{5}$), 6.25-7.98 (m, 24 H,
aromatics). $^{31}$P $^1$H NMR: $\delta$ 49.6 (d, 2 P, $J_{AX}$, bis(tertiary phosphine)), 78.1 (t, 1 P, $J_{AX}$ = PMePh$_2$).

$(R^*,R^*)$-(±)-Carbonyl($\eta^5$-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ($(R^*,R^*)$-7)

A mixture of $[(T15-C5H5)Fe(CO)2Cl]$ (1.0 g, 4.7 mmol) and $(R^*,R^*)$-1,2-C$_6$H$_4$(PMePh)$_2$ (1.6 g, 4.9 mmol) was ground together and transferred to a Schlenk flask. Tetrahydrofuran (10 mL) was added and the suspension was warmed to 50 °C. After ca 15 min, the reaction mixture became yellow. The solvent was evaporated off, and the residue was extracted with methanol and heated under reflux for ca 18 h. The progress of the reaction was monitored by solution IR spectroscopy in dichloromethane by the growth in the product $\nu$(CO) absorption at 1980 cm$^{-1}$ and concomitant decreases in the intensities of the $\nu$(CO) bands at 2050 and 2018 cm$^{-1}$ of $[(T15-C5H5)Fe(CO)2Cl]$. Upon completion of the reaction, NH$_4$PF$_6$ (0.9 g) in methanol (5 mL) was added dropwise. The yellow product precipitated immediately, and was collected, washed with cold methanol and dried in a vacuum. Additional product was obtained from the filtrate when it was cooled to -30 °C for 12 h: mp 248-252 °C; 2.03 g (70%). Anal. Calcd for C$_{26}$H$_{25}$F$_6$FeOP$_3$: C, 50.6; H, 4.1; P, 15.1. Found: C, 49.7; H, 4.0; P, 15.4.

$^1$H NMR: $\delta$ 2.23 (d, 3 H, $J$PM = 9.3 Hz, PMe), 2.38 (d, 3 H, $J$PM = 9.9 Hz, PMe), 4.70 (s, 5 H, $\eta^5$-C$_5$H$_5$), 7.15-7.76 (m, 14 H, aromatics).

$(R^*,S^*)$-Carbonyl($\eta^5$-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ($(R^*,S^*)$-7)

This compound was isolated as an equimolar mixture of syn and anti diastereomers from $[(\eta^5$-C$_5$H$_5$)Fe(CO)$_2$Cl]$ and $(R^*,S^*)$-1,2-C$_6$H$_4$(PMePh)$_2$ by the method described for $(R^*,R^*)$-7: mp 218-220 °C dec; 1.2 g (42%). Anal. Calcd for C$_{26}$H$_{25}$F$_6$FeOP$_3$: C, 50.6; H, 4.1; P, 15.1. Found: C, 50.1; H, 3.9; P, 15.4. IR
(nujol): ν(CO) 1960, 1945 cm⁻¹. ¹H NMR ((R*,S*)-syn-7): δ 2.34 (t, 6 H, 2JPH = 5.3 Hz, 2 PMe), 4.94 (t, 5 H, 3JPH = 1.6 Hz, η⁵-C₅H₅), 7.30-7.84 (m, 14 H, aromatics). ¹H NMR ((R*,S*)-anti-7): δ 2.20 (t, 6 H, 2JPH = 5.0 Hz, 2 PMe), 4.47 (t, 5 H, 3JPH = 1.6 Hz, η⁵-C₅H₅), 7.30-7.84 (m, 14 H, aromatics).

(R*,R*)-µ-Dinitrogenbis[(η⁵-Cyclopentadienyl){1,2-phenylenebis-(methylphenylphosphine)}iron(II)] (Hexafluorophosphate) (R*,R*)-6

A solution of (R*,R*)-7 (6 g, 9.74 mmol) in acetone (450 mL) was cooled to -30 °C under a stream of dinitrogen, and then irradiated for ca 15 h with a Hanovia 125W UV lamp. The reaction mixture was allowed to warm to room temperature. The solvent was evaporated off and the black residue was extracted with tetrahydrofuran (200 mL) and dinitrogen was bubbled through the extract for ca 3 h. The resulting orange product was collected, washed with a cold solution of 1:1 tetrahydrofuran / diethyl ether, and dried: 5.8 g (99%). Anal. Calcd for C₅₀H₅₀F₁₂Fe₂N₂P₆: C, 49.9; H, 4.2; N, 2.3. Found: C, 50.0; H, 4.3; N, 2.0. IR (KBr disc): ν(N₂) 2045 cm⁻¹. ¹H NMR: δ 1.85 (m, 12 H, 4 PMe), 3.75 (s, 10 H, η⁵-C₅H₅), 7.22-7.90 (m, 28 H, aromatics).

A solution of (R*,R*)-6 in acetonitrile was heated under reflux for 2 h to give (R*,R*)-1 in high yield.

(R*,R*)-(±)-Acetone(η⁵-cyclopentadienyl){1,2-phenylenebis(methylphenylphosphine)}iron(II) Hexafluorophosphate ((R*,R*)-8)

The dinitrogen compound (R*,R*)-6 (0.1 g, 0.08 mmol) was dissolved in acetone. A black solution resulted immediately with concomitant evolution of dinitrogen. Dilution of the solution with diethyl ether (1 mL) and cooling to -30 °C afforded black crystals of the product: mp 195-199 °C dec; 0.08 g (75%). Anal. Calcd for C₂₈H₃₁F₆FeOP₃: C, 52.1; H, 4.8; P, 13.9. Found: C, 52.3; H, 4.8; P, 13.9. IR (nujol): 1654 cm⁻¹ ν(CO).
[(R*,R*),(R*)]-(-)-(η⁵-Cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate

Hemidichloromethane Solvate [(R*,R*),(R*)]-9·0.5CH₂Cl₂

To a suspension of (R*,R*)-6 (0.17 g, 1.41 mmol) in methanol (50 mL) was added (+)-PITh₁ePh (0.25 g, 2.0 mmol) and the reaction mixture was heated under reflux for 12 h. The reaction mixture was concentrated to ca 10 ml and then diluted with diethyl ether to give the product as an equimolar mixture of [(R*,R*),(R*)]- and [(R*,R*),(S*)]-9. Fractional crystallization of the mixture from dichloromethane by the slow addition of petroleum ether gave the pure (R*,R*),(R*) diastereomer as yellow needles of the hemidichloromethane solvate: mp 238-248 °C; 0.4g (47%). Anal. Calcd for C₃₂.₅H₃₅ClF₆FeP₄: C, 51.7; H, 4.7; P, 16.4. Found: C, 52.1 H, 4.8; P, 16.1.

³¹P{¹H} NMR: δ 35.6, 79.8, 83.0 (ABX m, 3 P, 12_JAB₁ = 43.2 Hz, 12_JAX₁ = 58.7 Hz, 12_JBX₁ = 54.1 Hz).

[(R*,R*),(S*)]-(-)-(η⁵-Cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate

Monoacetone Solvate ([(R*,R*),(S*)]-3·Me₂CO)

The mother liquor from the isolation of [(R*,R*),(R*)]-9 was evaporated to dryness and the residue was recrystallized from acetone-diethyl ether to give yellow needles of [(R*,R*),(S*)]-2: mp 138-140 °C; 1.0g (41%). Anal. Calcd for C₃₅H₄₀F₆FeOP₄: C, 54.6; H, 5.6; P, 16.1. Found: C, 54.3; H, 5.4; P, 16.2. ¹H NMR: δ 1.55 (d of d, 3 H, 2_JPH = 8.8 Hz; 3_JHH = 6.1 Hz, PHMePh), 2.12 (s, 6 H, Me₂CO), 2.20 (d, 3 H, 2_JPH = 9.0 Hz, PMe), 2.32 (d, 3 H, 2_JPH = 8.3 Hz, PMe), 4.36
(q, 5H, \(3J_{PH} = 2.0\) Hz, \(\eta^5\)-C\(_5\)H\(_5\)), 4.83 (d of m, 1 H, \(1J_{PH} = 333\) Hz, PHMePh), 6.80-7.75 (m, 19 H, aromatics). \(^{31}\)P\(^{1}\)H NMR: \(\delta\) 31.1, 81.0, 81.7 (ABX m, 3 P, \(|^{2}J_{AB}| = 42.8\) Hz, \(|^{2}J_{AX}| = 55.6\) Hz, \(|^{2}J_{BX}| = 56.1\) Hz).
Chapter Three

Synthesis and Reactivity of Coordinated Halogenophosphines

Although the method of metal complexes of secondary phosphine, it has only recently been demonstrated that a feasible method for the resolution of secondary phosphine is a combination of optical rotation and fractional crystallization. Indeed, it was shown that diastereomERICALLY pure inversion at the phosphorus atom can be stereospecifically achieved. Reactions of these chiral phosphine ligands with retention of configuration at phosphorus. However, inversion is 95% of the hydroxylation. As an extension of this work, a diastereomERICALLY pure halogenophosphine has been isolated. The \( \text{C}_2 \text{H}_4 \text{P}(\text{CF}_3 \text{CH} \text{=CH}_2) \text{P} \) has been employed as a visible probe for the resolution of secondary phosphines.
3.1 Introduction

Although the method of metal complexation has been used for the resolution of tertiary phosphine, it has only recently been demonstrated that metal complexation is a feasible method for the resolution of secondary phosphines, stereogenic at phosphorus. Indeed, it was shown that diastereomERICally pure coordinated secondary phosphines could be deprotonated at -95 °C to generate chiral tertiary phosphido-iron complexes stereospecifically. Alkylation of these chiral phosphido-iron complexes at -95 °C proceeds with retention of configuration at phosphorus (Scheme VI). Because of the relatively low barrier to inversion (ca 60 kJ mol⁻¹) of the tertiary phosphido-iron group, alkylations above -95 °C gave thermodynamic mixtures of the chiral tertiary phosphine products with diastereoselectivities reflecting stereospecific alkylations of the equilibrium concentrations of the intermediates.

As an extension of this work, the stereochemistry of nucleophilic reactions of coordinated halogenophosphines has been investigated. As well, the chiral auxiliary [(η⁵-C₅H₅){1,2-CH₄(PMePh)₂}Fe]⁺ has been employed to establish if metal complexation is a viable procedure for the resolution of coordinated halogenophosphines.
Scheme VI*

*One enantiomer of each racemate is depicted
3.2 Results and Discussion

3.2.1 Synthesis of Halogenophosphine Transition Metal Complexes

The complex $(R^* R^*)-(\pm)-\left(\eta^5-C_5H_5\right)\left\{1,2-C_6H_4(PMePh)\right\}Fe(NCMe)\right\}PF_6$, $(R^* R^*)-1$, was prepared in a ca 90% yield as previously described and was employed as the precursor of the compounds $(R^* R^*)-(\pm)-\left(\eta^5-C_5H_5\right)\left\{1,2-C_6H_4(PMePh)\right\}FeL\right\}PF_6$ by substitution of the acetonitrile ligand with $L$. In a similar manner, optically pure $[R-(R^* R^*)]+589-\left(\eta^5-C_5H_5\right)\left\{1,2-C_6H_4(PMePh)\right\}Fe(NCMe)\right\}PF_6$, $R-(R^* R^*)-1$, $[\alpha]D +421^o (CH_2Cl_2)$, was obtained by UV irradiation of $[\eta^5-C_5H_5]Fe(CO)_2 Br$ with $[S-(R^* R^*)]-(\pm)-1,2-C_6H_4(PMePh)_2$ in acetonitrile and treatment of the intermediate bromide salt with NH$_4$PF$_6$.

The reaction of $(R^* R^*)-1$ with a large excess of $(\pm)$-PCI$MePh$ in boiling dichloromethane afforded $[(R^*)]_{(R^* R^*)}[/(S^*)]_{(R^* R^*)}-(\pm)-\left(\eta^5-C_5H_5\right)\left\{1,2-C_6H_4(PMePh)\right\}Fe(PCI MePh)\right\}PF_6$, $[(R^*)]_{(R^* R^*)}[/(S^*)]_{(R^* R^*)}-10$, in 88% yield (Scheme VII). The chlorophosphine complex was isolated as a 3:1 mixture of the two diastereomers that could be separated by fractional crystallization. The major diastereomer crystallizes from dichloromethane-petroleum ether as a monodichloromethane solvate. The more soluble diastereomer was obtained pure from acetone-diethyl ether, as the monoacetone solvate. Both diastereomers are stable to the atmosphere in the solid state and in solution.
3.2.2 X-ray Crystal Structure of [(R*),(R*,R*)]-10·CH2Cl2

The major diastereomer of the chlorophosphine complex crystallizes in the monoclinic space group P21/n. In this space group both enantiomers of the chiral cation are present. Table V lists selected distances and angles in the complex. The geometry of the cation is illustrated in Figure 6, which also shows the atomic numbering scheme employed. The chlorophosphine-P stereocentre in the structure is pyramidal with a relatively long Fe-P bond length (2.158 (2) Å) and small Fe-P-Cl bond angle (111.1°). The three chiral phosphorus stereocentres in each cation have the same helicity: accordingly, the diastereomer takes the stereochemical descriptor (R*,R*),(R*).
Figure 6. A view of cation of $[(R^*),(R^*,R^*)]-10$ showing the labelling scheme of the non-hydrogen atoms. The $R$ enantiomer of the cation is depicted.
Table V. Selected Bond Distances (Å) and Angles (°) of 

\[(R^*),(R^*,R^*)\]-10

with Estimated Standard Deviations in Parentheses

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The $^1$H NMR spectrum of diastereomerically pure $(R^*,R^*)$-10 in $[^2\text{H}_2]$dichloromethane exhibits the bis(tertiary phosphine) PMe resonances as a pair of doublets at $\delta$ 2.12 and $\delta$ 2.33; for the corresponding $(S^*),(R^*,R^*)$-10 diastereomer PMe resonances are located at $\delta$ 2.12 and $\delta$ 2.15. The unidentate phosphine PMe resonances appears as doublet at $\delta$ 1.38 and $\delta$ 2.34 for the $(R^*),(R^*,R^*)$ and $(R^*,R^*),(S^*)$ diastereomers, respectively. The $^{31}$P($^1$H) NMR spectrum in $[^2\text{H}_2]$dichloromethane reveals the splitting pattern of an ABX spin system, the AB part referring to the $^{31}$P nuclei of the bis(tertiary phosphate) ligand. A downfield resonance was observed for the chlorophosphine ligand at ca 170 ppm in the $^{31}$P($^1$H) NMR spectrum. No evidence of phosphorus-halogen exchange was found in the NMR spectra of the pure diastereomers in $[^2\text{H}_3]$acetonitrile. Relevant NMR data for the chlorophosphine complex are listed in Tables VI and VII.

The enantiomers of the chiral auxiliary $(R^*,R^*)$-(-$\pm$)-[(η⁵-C₅H₅){1,2-C₆H₄(PMePh₂)}Fe]+ appear to be excellent resolving agents for chiral secondary halogenophosphines. Thus, optically pure [R-(R*,R*)]-1 reacts with an excess of $(\pm)$-PClMePh in boiling dichloromethane to give a 3:1 diastereomeric mixture of [R-[(R*),(R*,R*)]$/[R-[(S*),(R*,R*)]]$-(+)$\delta89$-[(η⁵-C₅H₅){1,2-C₆H₄(PMePh₂)}Fe-(PClMePh)]PF$_6$, [R-[(R*),(R*,R*)]]$/[R-[(S*),(R*,R*)]]$-10, in 98% yield. Fractional crystallization of the mixture from acetone-diethyl ether produces optically pure [R-$\delta (R^*,R^*),(S^*)]$-2, [$\alpha$]$D^\circ +261^\circ$ (CH$_2$Cl$_2$). This complex represents the first example of a resolved unidentate halogenophosphine ligand coordinated to a transition metal. The more soluble R-[(S*),(R*,R*)] diastereomer could not be obtained pure.
3.2.3 Alternative Approaches to the Synthesis of Halogenophosphine Transition Metal Complexes

Another strategy for the preparation of secondary halogenophosphine-iron(II) compounds involves the use of secondary phosphine-iron(II) complexes. Deprotonation of such complexes affords tertiary phosphido-iron(II) species that could be expected to yield the corresponding halogenophosphine derivatives upon halogenation. The main thrust of this approach was the possibility of generating the coordinated halogenophosphine in a stereospecific manner. A similar route to halogenophosphine complexes has recently been reported. Thus, Malisch and coworkers have demonstrated that phosphido-tungsten complexes, upon treatment with bromine, give coordinated bromophosphine complexes:

\[
\text{Me}_2\text{P} \ldots \text{Ph}_2 \xrightarrow{\text{Br}_2} \text{Me}_2\text{P} \ldots \text{PBr}_2 \text{Ph}_2
\]

The acetonitrile complex \((R^*,R^*)\)-1 reacts with chiral secondary phosphines \((\pm)\)-PHMePh and \((\pm)\)-PHEtPh in boiling methanol to give high yields of the corresponding secondary phosphine derivatives \([(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6, [(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-9, and [(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-11, as air-stable solids. The complexes are generated as equimolar mixtures of \((R^*,R^*),(R^*)\) and \((R^*,R^*),(S^*)\) diastereomers that can be separated by fractional crystallization from suitable solvents; the \(^1\text{H}\) and \(^31\text{P}\{^1\text{H}\}\) NMR data for the complexes are presented in Tables VI and VII.
Treatment of the diastereomERICally pure secondary phOSPhine complexes with KOBu-t in tetrahydrofuran at -95 °C produced the corresponding tertiary phosphido-iron(II) intermediates \([(R^*,R^*),(R^*)]-\) and \([(R^*,R^*)(S^*)]-(-)-(\eta^5-C_5H_5)(1,2-C_6H_4(PMePh)_2)Fe(PRPh)]\) (where \(R = \text{Me or Et}\)). Whereas protonation or alkylation of the phosphido-iron intermediates in tetrahydrofuran at the deprotonation temperature (-95 °C) proceeded in a stereospecific manner, treatment with bromine under the same conditions followed by the addition of \(\text{NH}_4\text{PF}_6\), afforded the corresponding bromophosphine complexes as diastereomERIC mixtures (Scheme VIII). Fractional crystallizations of the mixtures from suitable solvents gave the air-stable bromophosphine diastereomers of each complex. No evidence of rearrangement was observed for either the chloro- or bromophosphine complexes over a period of one month according to \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopic analysis of dichloromethane solutions of the complexes at various intervals.

The low temperature deprotonation and subsequent bromination of the primary phosphine complex \((R^*,R^*)-(-)-(\eta^5-C_5H_5)(1,2-C_6H_4(PMePh)_2)Fe(PH_2Ph)]PF_6\), \((R^*,R^*)-14\), prepared in 95% yield from \((R^*,R^*)-1\) with \(\text{PH}_2\text{Ph}\) in boiling methanol, gave a mixture of products that could not be identified.
Scheme VIII

The reaction of \((R^*,R^*)-1\) with \((\pm)-\text{PHMePh}\) was carried out in two steps:

1. Treatment with KOBu-t, \(< -90^\circ C\)
2. Reaction with \(\text{Br}_2 / \text{thf}, < -90^\circ C\)

The chemical reactions and products are as follows:

- \((R^*,R^*),(R^*)\) to \((R^*,R^*),(S^*)\)
- \((R^*,R^*),(S^*)\) to \((S^*),(R^*,R^*)\)
- \((S^*),(R^*,R^*)\) to \((R^*),(R^*,R^*)\)

The yield of the complex \((R^*),(R^*,R^*)\) is 70%.

The corresponding molar ratio is as follows:

- \(R = \text{Me}\) : 1 : 7
- \(R = \text{Et}\) : 1 : 9
The reaction of \((R^*,R^*)-1\) with excess \(\text{PCl}_2\text{Ph}\) in boiling dichloromethane gave an 84% yield of the complex \((R^*,R^*)-(\pm)-\{(\eta^5-\text{C}_5\text{H}_5)\{1,2\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PCl}_2\text{Ph})\}\text{PF}_6\), \((R^*,R^*)-12\), which is air-stable in the solid state and in solution.

3.2.4 Stereoselective Reactions of Coordinated Halogenophosphine Complexes

3.2.4.1 Reactions with Carbon Nucleophiles

Treatment of the diastereomerically pure chlorophosphine complex \([(R^*),(R^*,R^*)]-10\) in tetrahydrofuran with ethylmagnesium bromide at ca 20 °C afforded the corresponding tertiary phosphine complex \([(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-(-\pm)-\{(\eta^5-\text{C}_5\text{H}_5)\{1,2\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PEtMePh})\}\text{PF}_6\), \([((R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-15\), with \((R^*,R^*),(R^*):(R^*,R^*),(S^*) = 1:3\), according to \(\text{H}^1\) and \(\text{P}^31\{\text{H}^1\}\) NMR spectroscopy (Scheme IX). Thus, the alkylation proceeds with predominant retention of absolute configuration at the unidentate phosphorus stereocentre.

In a similar reaction, treatment of \([(R^*),(R^*,R^*)]-10\) in tetrahydrofuran with benzylmagnesium bromide at 20 °C generated the tertiary phosphine complex \([(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-(-\pm)-\{(\eta^5-\text{C}_5\text{H}_5)\{1,2\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PBnMePh})\}\text{PF}_6\), \([((R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-16\), with \((R^*,R^*),(R^*):(R^*,R^*),(S^*) = 1:8\). Again,
substitution of the chloro group of the coordinated chlorophosphine has proceeded with predominant retention of configuration of the phosphorus stereocentre (Scheme IX). The ratio of diastereomers of tertiary phosphine products was not altered by changing the reaction temperature. Fractional crystallization of the mixtures from suitable solvents gave the pure diastereomers. Treatment of \([(S^*),(R^*,R^*)]-10\) with Grignard reagents under similar conditions gave predominantly \((R^*,R^*)\) diastereomers of the corresponding tertiary phosphine complexes.

**Scheme IX**

\[(R^*),(R^*,R^*)\]-10

\[(R^*)\]-15 or -16

\[(R^*,R^*)\]-15 or -16

\((R^*,R^*),(S^*)\) : \((R^*,R^*),(R^*)\)

\(R = \text{Et}\) 
3 : 1

\(R = \text{Bn}\) 
8 : 1
The stereochemical identity of the tertiary phosphine complexes was based upon data for the alkylation of the phosphido-iron compound, \((\pm)-[(\eta^5-C_5H_5)(1,2-C_6H_4-(PMePh)_2)Fe(PMePh)]\), which was prepared in situ from \([(R^*,R^*),(R^*)]-9\) in tetrahydrofuran by treatment with KOBu-t at -95 °C. Quenching of the intermediate phosphido-iron(II) complex with ethyl iodide or benzyl bromide at the same temperature gave stereocemically homogeneous samples of the \((R^*,R^*),(S^*)\) diastereomers of the respective tertiary phosphine complexes according to \(^1H (300 MHz)\) or \(^{31}P(^1H) (121 MHz)\) NMR spectroscopy. Pure \([(R^*,R^*),(S^*)]-9\) was converted into pure \([(R^*,R^*),(R^*)]-15\) or \([(R^*,R^*),(R^*)]-16\) under the same reaction conditions. Thus, the absolute configuration of the chiral phosphido-iron phosphorus stereocentre was retained during the alkylation of both diastereomers of the intermediate phosphido-iron complex and hence the reaction is stereospecific.

\[
\begin{align*}
&(R^*,R^*),(R^*)-9 \\
& \xrightarrow{1. \text{KOBu-t, -95 °C}} (R^*,R^*)-9 \\
& \xrightarrow{2. \text{RX, -95 °C}} (R^*,R^*),(R^*)-15 \text{ or -16}
\end{align*}
\]

\[
\begin{align*}
&(R^*,R^*),(S^*)-9 \\
& \xrightarrow{1. \text{KOBu-t, -95 °C}} (R^*,R^*)-9 \\
& \xrightarrow{2. \text{RX, -95 °C}} (R^*,R^*),(R^*)-15 \text{ or -16}
\end{align*}
\]

\(R = \text{Et or Bn}\)
To account for the observation of predominant retention of configuration at phosphorus during alkylations of the chlorophosphine iron complexes with Grignard reagents, transition states involving four-membered rings have been postulated, as depicted below:

Similar observations have been made by Quin and coworkers\textsuperscript{122-124} in studies of the nucleophilic displacement of chloride ion in 7-chlorophosphanorbornene (7-chloro-PNB). Treatment of 7-chloro-PNB with PhMgBr proceeds with complete retention of configuration at phosphorus.

The mechanism proposed for this reaction involves a phosphoramidate intermediate that underwent pseudorotation via a trigonal bipyramidal transition state (Berry pseudorotation\textsuperscript{125} or turnstile rotation\textsuperscript{126}). The preference for an equatorial disposition of the lone pair on the phosphorus atom was an important factor in determining the stereochemical pathway.
Attempts to stereoselectively substitute one of the diastereotopic chloro groups in (R*,R*)-12 with one equivalent of a Grignard reagent (methyl-, ethyl-, or t-butyl-magnesium bromide) or reducing agent (sodium borohydride) at low temperatures gave mixtures of products that could not be identified.

3.2.4.2 Reactions with Oxygen Nucleophiles

Treatment of diastereomerically pure [(R*),(R*,R*)]-10 with thallium(I) phenoxide in boiling tetrahydrofuran gave the corresponding phenylphosphite complex

\[ [(R*),(R*,R*)]/[(S*),(R*,R*)] \text{-}(\pm)\cdot[(\eta^5\text{C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})\text{Fe}(\text{PMe(OPh)}\text{Ph})\}]\cdot\text{PF}_6, \]

in 58% yield, \[ [(R*),(R*,R*)]/[(S*),(R*,R*)] = 1:6. \] The major diastereomer was assigned the \((S*),(R*,R*)\) stereochemistry on the basis of \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopic evidence in relation to the data obtained for the corresponding chlorophosphine complex. Thus, this reaction proceeds with predominant inversion of chirality at phosphorus (Scheme X).

Treatment of [(R*),(R*,R*)]-10 with a solution of freshly prepared sodium phenoxide in tetrahydrofuran at room temperature also afforded the phenylphosphite complex, but with a lower stereoselectivity, viz: \((R*),(R*,R*):(S*),(R*,R*) = 1:3. \) In both cases, therefore, substitution by phenoxide ion proceeds with predominant inversion of configuration at the phosphorus stereocentre. The complexes \([S*),(R*,R*)\] and \([R*),(R*,R*)\]-17 are stable to the atmosphere in the solid state and in solution. Under similar conditions \([S*),(R*,R*)\]-10 is converted into \([R*),(R*,R*)]/[S*),(R*,R*)]-17 with \((R*),(R*,R*):(S*),(R*,R*) = 2:1 \) (Scheme X).
The $S_N2$ mechanism accounts for the inversion of the phosphorus stereocentre during substitution of chloride ion by phenoxide ion. In classical situations the stereochemical change requires attack of the nucleophile opposite to the leaving group. With very large substituents on the phosphorus centre, such as the present chiral iron auxiliary, the situation will be less clear, which could account for the partial loss of selectivity in the phenoxide ion substitution reactions. Similar observations have been made for substitution at silicon by phenoxide nucleophiles, where inversion took place when optically active $\text{(+)-1-NpSiMePh(SPh)}$ was treated with sodium phenoxide to produce $\text{(+)-1-NpSiMePh(OPh)}$.\textsuperscript{127}

Scheme X

\begin{equation}
\text{Scheme X}
\end{equation}

\begin{align*}
\text{Scheme X} & \quad 1. \text{TIOPh} / \Delta \\
& \quad \text{or} \\
& \quad 2. \text{NaOPh}
\end{align*}

\begin{align*}
\text{[(S*),(R*,R*)]-17} & \quad \text{[(R*),(R*,R*)]-17} \\
\text{(S*),(R*,R*)} : \text{(R*),(R*,R*)} & = 6 : 1 \\
\text{TIOPh} & \quad 3 : 1 \\
\text{NaOPh} & \quad 3 : 1
\end{align*}

Treatment of a solution of either $\text{[(R*),(R*,R*)]-10}$ or $\text{[(S*),(R*,R*)]-10}$ in tetrahydrofuran with freshly prepared sodium methoxide at $20 \, ^\circ\text{C}$ yielded an equilibrium
mixture of diastereomers of the methoxylphosphine complex \([(R^*)(R^*,R^*)]/\[(S^*),(R^*,R^*)\]-(-\[\eta^5-C_5H_5\]1,2-C_6H_4(PMePh)_2)Fe(PMe(OMe)Ph)]PF_6,\[(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-18, with (R^*),(R^*,R^*):{(S^*)}(R^*,R^*) = 13:1. The same ratio of methylphosphite diastereomers was observed regardless of which diastereomer of the starting complex was employed, thus establishing that the reaction proceeded under thermodynamic control. The ratio of products did not alter over one month in [\(^2\text{H}_2\)]dichloromethane.

The same equilibrium mixture of the methoxyphosphine complex can also be generated by treating the acetonitrile complex \((R^*),(R^*)-1\) with \((\pm)\text{PClMePh}\) in boiling methanol. In this reaction, however, substitution of the chloro group presumably takes place prior to coordination of the phosphine ligand to the iron, as chlorophosphine complexes are kinetically stable in boiling methanol. Indeed, halogenophosphines are
known to react with alcohols to form phosphites. A similar result was observed for PhPCl2, in boiling methanol the reaction of \((R*,R*)-1\) with PhPCl2 led to the production of a high yield of \((R*,R*)-12\). The attempted substitution of the chloro atom in \([(R*),(R*,R*)-10\] or \([(S*),(R*,R*)-11\] by treatment with thallium(I) hydroxide or sodium hydroxide was unsuccessful.

### 3.2.4.3 Diastereoselective Reductions

Treatment of a solution of \([(R*),(R*,R*)-10\] in tetrahydrofuran at room temperature with sodium borohydride produced the corresponding secondary phosphine complex \([(R*,R*),(R*)]/[(R*,R*),(S*)]-9\] as a \((R*,R*),(R*)\):(R*,R*),(S*) = 3:1 diastereomeric mixture. Thus, hydride ion substitution of the chloro atom in this complex proceeds with predominant retention of configuration at the phosphorus stereocentre. A concerted mechanism, similar to that proposed for the substitution reactions involving Grignard reagents, can be visualized for the borohydride reaction.
No exchange of the chlorine in \([(R^\ast),(R^\ast,R^\ast)]-10\) was observed with either sodium iodide in acetone or benzoyl fluoride in tetrahydrofuran. These reagents did, however, cause slow epimerization of the unidentate phosphorus stereocentre.

### 3.2.5 NMR Spectra of Complexes

Compounds 9 - 18 were characterized by \(^1\)H and \(^{31}\)P(\(^1\)H) NMR spectroscopy; selected data for the compounds are given in Tables VI and VII. The relative absolute configurations of the chiral \(P\)-stereocentres were assigned with knowledge of the solid state structures of \([(R^\ast),(R^\ast,R^\ast)]-10\) and \([(R^\ast,R^\ast),(R^\ast)]-9\).
3.2.5.1 $^1$H NMR Spectra

The non-equivalent PMe groups of the bis(tertiary phosphine) ligand in compounds 9 - 18 resonate as doublets of doublets, with average $^2J_{PH}$ values of ca 9.0 Hz. The bis(tertiary phosphine) PMe resonances in the $(R^*)_2(R^*)$ diastereomers of the phosphine complexes containing electronegative substituents (Cl, OPh, or OMe) are separated by ca 0.22 ppm; the chemical shift differences of the PMe resonances for the $(S^*)_2(R^*)_2$ diastereomers are separated by ca 0.4 ppm. Similarly, for the secondary and tertiary phosphine complexes, the PMe resonances for the bis(tertiary phosphine) are separated by ca 0.4 - 0.6 ppm in the $(R^*,R^*)_2(R^*)$ diastereomers and ca 0.2 ppm in the $(R^*,R^*)_2(S^*)$ diastereomers.

In complexes containing methyl-substituted unidentate phosphines, the PMe resonances occur generally as doublets with $^2J_{PH}$ ca 5.7 - 9.5 Hz. These resonances appear between 0.46 - 1.38 ppm for the $(R^*,R^*)_2(R^*)$ diastereomers and in the region 1.06 - 2.34 ppm for the $(R^*,R^*)_2(R^*)$ diastereomers. Similarities are also observed in chemical shift values for the PCH$_2$Me groups in the complexes 11 and 15: for the $(R^*,R^*)_2(R^*)$ diastereomers the resonances occur between 0.46 - 0.47 ppm, and, for the $(R^*,R^*)_2(S^*)$ diastereomers, the resonances lie between 0.62 - 0.69 ppm.
Table VI. Selected $^1$H NMR Chemical Shift Data for [(R*,R*),(R*)]- [(R*,R*),(S*)]- 9 - 18

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<tr>
<th>compound</th>
<th>L</th>
<th>$\delta(\eta^5-C_5H_5)$</th>
<th>1,2-C$_6$H$_4$(PMePh)$_2$</th>
<th>L$_e$</th>
<th>$\delta(PMe)$</th>
<th>$\delta(PMe)$</th>
<th>$\delta(PH)$</th>
<th>$\delta(PMe)$</th>
<th>$\delta(PCH_2Me)$</th>
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<td>(R*,R*),(R*)-9</td>
<td>PHMePh</td>
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<td>0.64</td>
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<td>(R*,R*),(S*)-9</td>
<td>PHMePh</td>
<td>4.36</td>
<td>2.20 2.32</td>
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<td>(R*,R*),(R*)-10</td>
<td>PClMePh</td>
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<td>2.12 2.33</td>
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<td>(R*,R*),(S*)-10</td>
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<td>2.15 2.52</td>
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3.2.5.2 $^{31}$P($^1$H) NMR Spectra

In the $^{31}$P($^1$H) NMR spectra, compounds 2-11 exhibit the splitting pattern of ABX spin systems (Table VII). Downfield $^{31}$P($^1$H) NMR chemical shifts were observed for unidentate phosphine ligands with electronegative substituents (156 - 200 ppm). Similar observations have been reported for halogeno-phosphine and -phosphido transition metal complexes, as well as for iron-phosphonate complexes. For compounds 9 - 18, $^{2}J_{AB}$ coupling constants of ca 43 Hz were observed. For complexes without electronegative substituents on the unidentate phosphine ligand, $|^{2}J_{AX}|$ values of 53 - 59 Hz and $|^{2}J_{BX}|$ values of between 50 - 56 Hz were calculated. For compounds with electronegative substituents on the unidentate phosphine, $|^{2}J_{AX}| = 56 - 78$ Hz and $|^{2}J_{BX}| = 52 - 80$ Hz. All calculations were checked by NMR simulation experiments with the Davins programme. The recorded and simulated $^{31}$P($^1$H) NMR spectra of compounds 10 and 11 are shown in Figures 7-8 and are typical of the spectra obtained for complexes of the type [(S*),(R*,R*)]- and [(R*),(R*,R*)]-[(η⁵-C₅H₅){1,2-C₆H₄(PMePh)₂}Fe(PXR'R')]PF₆ and [(R*,R*),(S*)]- and [(R*,R*),(R*)]-[(η⁵-C₅H₅){1,2-C₆H₄(PMePh)₂}Fe(PRR'R'')]PF₆.
Table VII. Selected $^{31}$P{$^1$H} NMR Spectroscopic Data for [(R*,R*),(R*)]- [(R*,R*),(S*)]- 9 - 18

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<td>78.9</td>
<td>42.6</td>
<td>56.3</td>
<td>50.4</td>
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<tr>
<td>$(R^<em>,R^</em>),(S^*)$-16</td>
<td>PBnMePh</td>
<td>42.4</td>
<td>77.2</td>
<td>79.6</td>
<td>42.6</td>
<td>54.8</td>
<td>50.7</td>
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<tr>
<td>$(R^<em>,R^</em>),(R^*)$-17</td>
<td>PMe(OPh)Ph</td>
<td>80.3</td>
<td>81.0</td>
<td>176.9</td>
<td>43.5</td>
<td>77.4</td>
<td>62.7</td>
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<tr>
<td>$(R^<em>,R^</em>),(S^*)$-17</td>
<td>PMe(OPh)Ph</td>
<td>78.7</td>
<td>79.1</td>
<td>176.9</td>
<td>42.5</td>
<td>75.8</td>
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<tr>
<td>$(R^<em>,R^</em>),(R^*)$-18</td>
<td>PMe(OMe)Ph</td>
<td>81.5</td>
<td>82.2</td>
<td>171.2</td>
<td>44.4</td>
<td>59.5</td>
<td>77.2</td>
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<tr>
<td>$(R^<em>,R^</em>),(S^*)$-18</td>
<td>PMe(OMe)Ph</td>
<td>79.9</td>
<td>80.1</td>
<td>171.2</td>
<td>43.3</td>
<td>70.5</td>
<td>74.4</td>
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</table>
Figure 7a. $^{31}P\{^1H\}$ NMR spectrum of $[(R^*),(R^*,R^*)]_{-10}$: (i), recorded; (ii), simulated; (iii), expansion of the AB part of the spectrum.
Figure 7b. $^{31}\text{P}^{[\text{H}]}$ NMR spectrum of $[(R^*),(R^*,R^*)]-10$ : (i), recorded; (ii), simulated.
Figure 8a. $^{31}\text{P}^{[1\text{H}]}$ NMR spectrum of $[(R^*,R^*),(R^*)]$-11: (i), recorded; (ii), simulated.
3.3 Experimental

The preparation and experimental methods are described in Section 2.3.1. Optical rotations were determined in chloroform, M(1H) NMR spectra were recorded in [D$_6$]DMSO and referenced to SiMe$_4$ (0.0 ppm) or externally using 85% H$_3$PO$_4$. All signals were deduced on a Varian NMR-P1 double resonance.

Figure 8b. $^{31}$P{¹H} NMR spectrum of [(R*,R*),(S*)]-11: (i), recorded; (ii), simulated.
3.3 Experimental

The instrumentation and experimental methods employed in this work were similar to those described in Section 2.3.1. Optical rotations were measured at 20 °C on the solutions specified in 1-dm cell with use of a Perkin-Elmer Model 241 polarimeter. $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded in $[^2$H$_2]$dichloromethane unless stated otherwise. Spectra were referenced internally using the residual protio solvent resonance ($^1$H) relative to SiMe$_4$ ($\delta = 0.0$ ppm) or externally using 85% H$_3$PO$_4$ ($^{31}$P{$^1$H}). The X-ray diffraction data were collected on a Nicolet XRD P3 diffractometer equipped with MoK$\alpha$ by Dr W. Robinson of the University of Canterbury, New Zealand. The molecular structure was determined by Dr A. C. Willis of the Research School of Chemistry.

The compounds (±)-PMePh(SiMe$_3$) and (±)-PClMePh prepared by published procedures.$^{135,136}$

(±)-Methylphenylphosphine

Ammonia (2 L) was condensed onto triphenylphosphine (300 g) and sodium foil (52.6 g, 2 equiv.) was slowly added to the mixture with stirring. The resulting bright red solution of Na[PPh$_2$] was treated with methyl bromide until the colour of the phosphide ion was discharged (1 h). Additional sodium foil (50 g, 2 equiv.) was then added to the mixture to generate a solution of Na[PMePh]. After stirring for 3 h the mixture was treated with deoxygenated water (300 mL) and the ammonia was allowed to evaporate off. More water (500 mL) was then added to the reaction mixture and the product was extracted into dichloromethane (3 x 400 mL). The organic layer was separated, dried over MgSO$_4$, filtered and evaporated to dryness. The product distilled as a colourless oil: bp 83-85 °C (2 mmHg); 105 g (97%).
(±)-Trimethylsilylmethylphenylphosphine

To a stirred solution of methylphenylphosphine (23.4 g) in tetrahydrofuran (250 mL) was slowly added 1 equiv. of sodium foil (4.33 g). After 15 min stirring at room temperature, the reaction mixture was heated under reflux for a further 45 min. Unreacted sodium metal was removed by filtration and chlorotrimethylsilane (23.9 mL, 1 equiv.) was added dropwise. Upon completion of the addition, the reaction mixture was heated under reflux for 30 min, the solvent evaporated off under reduced pressure, and the residue extracted into diethyl ether. After filtration (to remove some sodium chloride) the extract was distilled; the product distilled as a colourless oil: bp 78-89 °C (1.2 mmHg): 19.3 g (52%).

(±)-Chloromethylphenylphosphine

Trimethylsilylmethylphosphine (19.3 g) in dichloromethane (100 mL) was added dropwise to a stirred solution of hexachloroethane (23.3 g, 1 equiv.) in dichloromethane (150 mL). The reaction mixture warmed to boiling point during the addition and was maintained at this temperature for a further 30 min. The solvent and excess C2Cl4 were distilled off under reduced pressure and the residual oil was distilled with use of a Vigreaux column to afford the product as a colourless oil: bp 50 °C (0.2 mmHg); 13.9 g (89%).

\[ \text{[R-(R*,R*)]-(+)-589-(Acetonitrile)(η^5-cyclopentadienyl)[1,2-phenylenebis-(methylphenylphosphine)]iron(II) Hexafluorophosphate (R-(R*,R*)-1} \]

This compound was obtained from \([\text{η}^5-\text{C}_5\text{H}_5]\text{Fe(CO)}_2\text{Br}\) and \([\text{S-(R*,R*)}]-(+)-1,2-\text{C}_6\text{H}_4(\text{PMePh})_2\) in acetonitrile by the method described for the corresponding racemate, but with a reaction time of 30 min. The brick-red precipitate of the desired product was collected and recrystallized from hot methanol: red prisms, mp 230-231 °C dec, 4.6 g (94
[(R*),(R*,R*)]-(±)-(Chloromethylphenylphosphine)(η⁵-cyclopentadienyl)-[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Dichloromethane Solvate [(R*),(R*,R*)]-10·CH₂Cl₂

A mixture of (R*, R*)-1 (2.0 g, 3.2 mmol) and (+)-PCIMePh (9.8 g, 62 mmol) in dichloromethane (30 mL) was heated under reflux for 12 h. The resulting orange solution was then diluted with diethyl ether to give the orange air-stable product as an (R*),(R*,R*):(S*),(R*,R*) = 3:1 mixture of diastereomers. Fractional crystallization of the mixture from dichloromethane (10 mL) by the slow addition of petroleum ether (bp 40-60 °C) gave the pure (R*),(R*,R*) diastereomer as orange needles of the monodichloromethane solvate: mp 169-170 °C; 1.8 g (69%). Anal. Calcd for C₃₃H₃₅Cl₃F₆FeP₄: C, 47.7; H, 4.2; P, 15.6; Cl, 12.7. ¹H NMR: δ 1.38 (d, 3 H, 2fPH = 5.7 Hz, PCIMePh), 1.54 (s, CH₂Cl₂), 2.12(d, 3 H, 2fPH + 4fPH₂ = 9.0 Hz, PMe), 2.33 (d, 3 H, 2fPH + 4fPH₂ = 10.1 Hz, PMe), 4.31 (q, 5 H, 3fPH = 1.8 Hz, T₅-C₅H₅), 7.10-7.73 (m, 19 H, aromatics). ³¹P{¹H} NMR: δ 78.5, 78.7, 168.7 (ABX m, 3 P, 2fAB₂ = 43.8 Hz, 2fAX₂ = 67.2 Hz, 2fBX₂ = 51.7 Hz).

[(S*),(R*,R*)]-(±)-(Chloromethylphenylphosphine)(η⁵-cyclopentadienyl)-[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Monoacetone Solvate [(S*),(R*,R*)]-10·Me₂CO

The mother liquor from the isolation of [(R*),(R*,R*)]-10 was evaporated to dryness and the residue was recrystallized from acetone-diethyl ether to give orange needles of [(S*),(R*,R*)]-10: mp 162-164 °C; 0.4 g (15%). Anal. Calcd for C₃₅H₃₉ClF₆FeOP₄:
C, 52.2; H, 4.9; P, 15.4; Cl, 4.4. Found: C, 52.0; H, 4.8; P, 15.1; Cl, 4.3. $^1$H NMR: \( \delta 2.12 \) (s, 6 H, Me$_2$CO), 2.15 (d, 3 H, \( ^2J_{PH} = 8.4 \) Hz, PMe), 2.34 (d, 3 H, \( ^2J_{PH} = 5.5 \) Hz, PClMePh), 2.52 (d, 3 H, \( ^2J_{PH} = 9.2 \) Hz, PMe), 4.40 (q, 5 H, \( ^3J_{PH} = 1.8 \) Hz, \( \eta^5\)-C$_5$H$_5$), 6.97-8.02 (m, 19 H, aromatics). $^{31}$P\{\(^1\)H\} NMR: \( \delta 77.5, 79.1, 169.6 \) (ABX m, 3 P, \( ^1J_{AB} = 42.6 \) Hz, \( ^2J_{AX} = 66.3 \) Hz, \( ^2J_{BX} = 65.0 \) Hz).

\[[R-[(S^{*}),(R^{*}),(R^{*})]]-(+)-(\text{Chloromethylphenylphosphine})(\eta^5-\text{cyclopentadienyl})[1,2-\text{phenylenebis(methylphenylphosphine)})\text{iron(II)}\]

Hexafluorophosphate Monoaceticone Solvate \((R-[(S^{*}),(R^{*},R^{*})]-10\cdot\text{Me}_2\text{CO})\)

Reaction of \([R-(R^{*},R^{*})]-1\) with \((\pm)-\text{PClMePh},\) according to 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: mp 219-220 °C; 0.25 g (10%); [\(\alpha\)]D + 261° (c 0.03, CH$_2$Cl$_2$). Anal. Calcd for C$_{35}$H$_{39}$ClF$_6$FeOP$_4$: C, 52.2; H, 4.9; P, 15.4; Cl, 4.4. Found: C, 52.1; H, 4.9; P, 15.1; Cl, 4.3. $^1$H and $^{31}$P\{\(^1\)H\} NMR: identical with those of the corresponding racemate.

\([R^{*},R^{*}),(R^{*})]\cdot(\pm)-(\eta^5-\text{Cyclopentadienyl})(\text{methylphenylphosphine})[1,2-\text{phenylenebis(methylphenylphosphine)})\text{iron(II)}\]

Hexafluorophosphate Hemidichloromethane Solvate \(([(R^{*},R^{*}),(R^{*})]-9\cdot0.5\text{CH}_2\text{Cl}_2)\) (Method 1)

A mixture of \((R^{*},R^{*})-1\) (2.0 g, 3.2 mmol) and \((\pm)-\text{PHMePh}\) (0.4 g, 3.2 mmol) in methanol (50 mL) was heated under reflux for 2 h. The yellow solution was then reduced in volume to ca 10 mL and diluted with diethyl ether to give an equimolar mixture of \([(R^{*},R^{*}),(R^{*})]\)- and \([(R^{*},R^{*}),(S^{*})]-9\). Fractional crystallization of the mixture from dichloromethane-petroleum ether gave pure \((R^{*},R^{*}),(R^{*})\)-9 as a hemidichloromethane solvate: mp 238-248 °C; 1.1 g (45%). Anal. Calcd for C$_{32.5}$H$_{35}$ClF$_6$FeP$_4$: C, 51.7; H, 4.7; P, 16.4. Found: C, 51.9; H, 4.7; P, 16.1. $^1$H NMR: \( \delta 0.64 \) (d of d, 3 H, \( ^2J_{PH} = 2.12 \) Hz, \( ^2J_{PH} = 8.4 \) Hz, PMe), 2.15 (d, 3 H, \( ^2J_{PH} = 5.5 \) Hz, PClMePh), 2.34 (d, 3 H, \( ^2J_{PH} = 9.2 \) Hz, PMe), 4.40 (q, 5 H, \( ^3J_{PH} = 1.8 \) Hz, \( \eta^5\)-C$_5$H$_5$), 6.97-8.02 (m, 19 H, aromatics). $^{31}$P\{\(^1\)H\} NMR: \( \delta 77.5, 79.1, 169.6 \) (ABX m, 3 P, \( ^1J_{AB} = 42.6 \) Hz, \( ^2J_{AX} = 66.3 \) Hz, \( ^2J_{BX} = 65.0 \) Hz).
9.5 Hz, $^3J_{HH} = 6.1$ Hz, PHMePh), 1.60 (d, 3 H, $^2J_{PH} = 9.0$ Hz, PMe), 2.23 (d, 3 H, $^2J_{PH} = 8.3$ Hz, PMe), 4.39 (q, 5 H, $^3J_{PH} = 2.0$ Hz, $^1$C$_5$H$_5$), 4.65 (d of m, 1 H, $^1J_{PH} = 333$ Hz, PHMePh), 6.75-8.00 (m, 19 H, aromatics). $^{31}$P{1H} NMR: $\delta$ 35.6, 79.8, 83.0 (ABX m, 3 P, $|^2J_{AB}| = 43.2$ Hz, $|^2J_{AX}| = 58.7$Hz, $|^2J_{BX}| = 54.1$ Hz).

$[(R^*,R^*),(S^*)]-(-)-(\eta^5$-Cyclopentadienyl)(methylphenylphosphine)[$1,2$-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Monoacetone Solvate ($[(R^*,R^*),(S^*)]-9\cdot$Me$_2$CO) (Method 1)

The mother liquor from the isolation of $[(R^*,R^*),(R^*)]-9$ was evaporated to dryness and the residue was recrystallized from acetone-diethyl ether to give yellow needles of $[(R^*,R^*),(S^*)]-9$: mp 138-140 °C; 1.0 g (41%). Anal. Calcd for C$_{35}$H$_{40}$F$_6$FeOP$_4$: C, 54.6; H, 5.6; P, 16.1. Found: C, 54.3; H, 5.4; P, 16.2. $^1$H NMR: $\delta$ 1.55 (d of d, 3 H, $^2J_{PH} = 8.8$ Hz; $^3J_{HH} = 6.1$ Hz, PHMePh), 2.12 (s, 6 H, Me$_2$CO), 2.20 (d, 3 H, $^2J_{PH} = 9.0$ Hz, PMe), 2.32 (d, 3 H, $^2J_{PH} = 8.3$ Hz, PMe), 4.36 (q, 5 H, $^3J_{PH} = 2.0$ Hz, $^1$C$_5$H$_5$), 4.83 (d of m, 1 H, $^1J_{PH} = 333$ Hz, PHMePh), 6.80-7.75 (m, 19 H, aromatics). $^{31}$P{1H} NMR: $\delta$ 31.1, 81.0, 81.7 (ABX m, 3 P, $|^2J_{AB}| = 42.8$ Hz, $|^2J_{AX}| = 55.6$ Hz, $|^2J_{BX}| = 56.1$ Hz).

$[(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]-(-)-(\eta^5$-Cyclopentadienyl)(methylphenylphosphine)[$1,2$-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ($[(R^*,R^*),(R^*)]/[(R^*,R^*),(S^*)]]-9$) (Method 2)

A solution of $[(R^*),(R^*,R^*)]-10$ (0.05 g, 0.06 mmol) in tetrahydrofuran (30 mL) was treated with sodium borohydride (0.012 g, 0.3 mmol) at room temperature. After 12 h, the solvent was evaporated from the reaction mixture and the residue was extracted into dichloromethane and washed with aqueous NH$_4$PF$_6$. After drying over MgSO$_4$ and evaporation of the solvent, the product was obtained as an $(R^*,R^*),(R^*)/(R^*,R^*),(S^*) = 3:1$ mixture of diastereomers.
[(R*,R*),(R*)]-(-)-(η⁵-Cyclopentadienyl)(ethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate

Hemidichloromethane Solvate ([(R*,R*),(R*)]-11·0.5CH₂Cl₂)

Compound (R*-R*)-1 was reacted with (±)-PHEtPh in methanol (50 mL) to give an equimolar mixture of [(R*,R*),(R*)] and [(R*,R*),(S*)]-11; fractional crystallization of the mixture from dichloromethane-petroleum ether gave pure [(R*,R*),(R*)]-11 as a dichloromethane solvate: mp 191-193 °C; yield 40%. Anal. Calcd for C₃₃,5H₃₇ClF₆FeP₄: C, 52.3; H, 4.9; P, 16.1. Found: C, 52.3; H, 4.9; P, 15.8. ¹H NMR: δ 0.47 (m, 4 H, PCH₂H'Me), 1.26 (m, 1 H, PCH₂H'Me), 1.56 (d, 3 H, ²Jₚₜ = 9.2 Hz, PMe), 2.20 (d, 3 H, ³Jₚₜ = 8.5 Hz, PMe), 4.29 (d of t, 1 H, ¹Jₚₜ = 335 Hz, PHEtPh), 4.38 (q, 5 H, ³Jₚₜ = 1.6 Hz, η⁵-C₅H₅), 6.85-8.00 (m, 19 H, aromatics). ³¹P{¹H} NMR: δ 59.4, 81.4, 83.4 (ABX m, 3 P, ³²Jₐₕ = 43.0 Hz, ³²Jₐₓ = 54.1 Hz, ³²Jₜₜ = 53.2 Hz).

[(R*,R*),(S*)]-(-)-(η⁵-Cyclopentadienyl)(ethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate

([(R*,R*),(S*)]-11)

Recrystallization from acetone-diethyl ether of the residue remaining after evaporation of the mother liquor gave yellow needles of [(R*,R*),(S*)]-11: mp 234-236 °C dec.; yield 41%. Anal. Calcd for C₃₃H₃₀F₆FeP₄: C, 54.6; H, 5.0; P, 17.1. Found: C, 54.8; H, 5.1; P, 17.1. ¹H NMR: δ 0.69 (d of t, 3 H, ³Jₚₚ = 15.2 Hz, ²JₚₚH = 7.4 Hz, PCH₂Me), 1.26 (m, 1 H, PCH₂H'Me), 1.58 (m, 1 H, PCH₂H'Me), 2.18 (d, 3 H, ²Jₚₚ = 8.2 Hz, PMe), 2.40 (d, 3 H, ²Jₚₚ = 8.5 Hz, PMe), 4.22 (q, 5 H, ³Jₚₚ = 1.8 Hz, η⁵-C₅H₅), 4.37 (d of m, 1 H, ¹Jₚₚ = 341 Hz, PHEtPh), 7.01-7.87 (m, 19 H, aromatics). ³¹P{¹H} NMR: δ 59.4, 81.4, 83.4 (ABX m, 3 P, ³²Jₐₕ = 43.0 Hz, ³²Jₐₓ = 54.1 Hz, ³²Jₜₜ = 53.2 Hz).
Compound \( (R^*,R^*)-1 \) (2.0 g, 3.2 mmol) reacted with excess \( \text{PCl}_2\text{Ph} \) (11.4 g, 64 mmol) in boiling dichloromethane (30 mL) to give the product as yellow crystals: mp 201 °C; 2.2 g (90%). Anal. Calcd for \( \text{C}_{31}\text{H}_{30}\text{Cl}_6\text{FeP}_4 \): C, 48.5; H, 3.9; P, 16.2; Cl, 9.2. Found: C, 48.0; H 3.9; P, 16.2; Cl, 9.1. \( ^1\text{H} \text{NMR} \): \( \delta \) 2.20 (d, 3 H, \( J_{PH} = 8.6 \) Hz, PMe), 2.57 (d, 3 H, \( J_{PH} = 9.7 \) Hz, PMe), 4.51 (q, 5 H, \( J_{PH} = 1.6 \) Hz, \( \eta^5\text{-C}_5\text{H}_5 \)), 7.18-7.73 (m, 19 H, aromatics). \( ^{31}\text{P} \{^1\text{H}\} \text{NMR} \): \( \delta \) 76.6, 77.9, 205.1 (ABX m, 3 P, \( J_{AB} = 43.3 \) Hz, \( J_{AX} = 55.8 \) Hz, \( J_{BX} = 79.9 \) Hz).

\( (R^*,R^*)-(\pm)-(\eta^5\text{-Cyclopentadienyl})(\text{dimethoxyphenylphosphine})[1,2\text{-phenylenebis(methylphenylphosphine)}]\text{iron(II) Hexafluorophosphate} \)

\( ((R^*,R^*)-13) \)

\( (R^*,R^*)-1 \) reacted with \( \text{PCl}_2\text{Ph} \) in boiling methanol (40 mL) to afford the product as yellow needles: mp 254 °C; 2.1 g (90%). Anal. Calcd for \( \text{C}_{33}\text{H}_{36}\text{Cl}_6\text{FeO}_2\text{P}_4 \): C, 52.3; H, 4.8; P, 16.3. Found: C, 52.3; H, 4.9; P, 16.5. \( ^1\text{H} \text{NMR} \): \( \delta \) 2.05 (d, 3 H, \( J_{PH} = 8.1 \) Hz, PMe), 2.34 (d, 3 H, \( J_{PH} = 9.9 \) Hz, PMe), 3.10 (d, 3 H, \( J_{PH} = 10.7 \) Hz, PPh(OMe)(OMe')), 3.61 (d, 3 H, \( J_{PH} = 10.5 \) Hz, PPh(OMe)(OMe')), 4.02 (s, 5 H, \( \eta^5\text{-C}_5\text{H}_5 \)), (m, 19 H, aromatics). \( ^{31}\text{P} \{^1\text{H}\} \text{NMR} \): \( \delta \) 81.7, 83.8, 156.1 (ABX m, 3 P, \( J_{AB} = 43.3 \) Hz, \( J_{AX} = 77.9 \) Hz, \( J_{BX} = 97.3 \) Hz).

\( (R^*,R^*)-(\pm)-(\eta^5\text{-Cyclopentadienyl})[1,2\text{-phenylenebis(methylphenylphosphine)}]\text{iron(II) Hexafluorophosphate} \)

\( ((R^*,R^*)-14) \)

\( (R^*,R^*)-1 \) reacted with \( \text{PH}_2\text{Ph} \) in boiling methanol (40 mL) to give the product as orange prisms: mp 223 °C dec; 2.0 g (86%). Anal. Calcd for \( \text{C}_{31}\text{H}_{32}\text{FeP}_4 \): C, 53.3;
H, 4.6; P, 17.7. Found: C, 53.5; H 4.6; P, 17.8. $^1$H NMR: $\delta$ 2.22 (d, 3 H, $^2J_{PH} = 8.3$ Hz, PMe), 2.26 (d, 3 H, $^2J_{PH} = 7.6$ Hz, PMe), 4.22 (q, 5 H, $^3J_{PH} = 1.7$ Hz, $\eta^5$-C$_5$H$_5$), 4.65 (d of m, 1 H, $^1J_{PH} = 344$ Hz, PHH'Ph), 5.40 (d of m, 1 H, $^1J_{PH} = 344$ Hz, PHH'Ph), 6.70-7.75 (m, 19 H, aromatics). $^{31}$P($^1$H) NMR: $\delta$ -5.5, 81.4, 83.6 (ABX m, 3 P, $|^2J_{AB}| = 43.6$ Hz, $|^2J_{AX}| = 59.3$ Hz, $|^2J_{BX}| = 54.9$ Hz).

$[(R^*,R^*),(R^*)]$-(-)-(C$_5$-Cyclopentadienyl)(ethylmethylphenylphosphine)@[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate

Hemidichloromethane Solvate ($[(R^*,R^*),(R^*)]$-15·0.5CH$_2$Cl$_2$).

A solution of $[(R^*,R^*),(S^*)]$-9 (0.05 g, 0.13 mmol) in tetrahydrofuran (50 mL) was cooled to -95 °C and treated with KOBu-t (0.060 g, 0.26 mmol). The solution turned deep red; after ca 10 min iodoethane (0.05 mL, 0.65 mmol) was added and the reaction mixture was permitted to warm to room temperature. The solvent was then evaporated off and the residue was dissolved in dichloromethane (50 mL) and washed with aqueous NH$_4$PH$_6$. The organic layer, after drying over MgSO$_4$, was concentrated to ca 5 mL and diluted with diethyl ether. The product crystallized as orange needles: mp 139-141 °C; 0.041 g (81%). Anal. Calcd for C$_{34.5}$H$_{39}$ClF$_6$FeP$_4$: C, 52.9; H, 5.0; P, 15.8.

Found: C, 52.7; H 4.8; P, 16.1. $^1$H NMR: $\delta$ 0.46 (m, 4 H, PCHH'Me), 1.32 (m, 1 H, PCHH'Me), 1.46 (d, 3 H, $^2J_{PH} = 7.7$ Hz, PMeEtPh), 2.07 (d, 3 H, $|^2J_{PH} + |^4J_{PMe}| = 9.5$ Hz, PMe), 2.35 (d, 3 H, $|^2J_{PH} + |^4J_{PH}| = 9.5$ Hz, PMe), 4.10 (q, 5 H, $^3J_{PH} = 1.8$ Hz, $\eta^5$-C$_5$H$_5$), 6.65-8.13 (m, 19 H, aromatics). $^{31}$P($^1$H) NMR: $\delta$ 42.2, 79.1, 79.4 (ABX m, 3 P, $|^2J_{AB}| = 42.7$ Hz, $|^2J_{AX}| = 57.6$ Hz, $|^2J_{BX}| = 50.1$ Hz).
The compound was prepared in the same way as \([(R^*,R^*),(R^*)\]-15. Thus, reaction of \([(R^*,R^*),(R^*)\]-9 with KOBu-t/EtI gave the product as orange needles: mp 158-160 °C; yield 79%. Anal. Calcd for C_{34}H_{38}F_6FeP_4: C, 55.2; H, 5.2; P, 16.7. Found: C, 55.3; H 5.1; P, 16.9. $^1$H NMR: δ 0.62 (d of t, 3 H, $^3$J_{PH} = 14.1 Hz, $^3$J_{HH} = 7.4 Hz, PCHH'Me), 0.64 (d, 3 H, $^2$J_{PH} = 8.0 Hz, PMeEtPh), 1.40 (m, 1 H, CHH'Me), 1.76 (m, 1 H, CHH'Me), 2.09 (d, 3 H, $^2$J_{PH} = 8.0 Hz, PMe), 2.45 (d, 3 H, $^2$J_{PH} = 8.4 Hz, PMe), 4.10 (q, 5 H, $^3$J_{PH} = 1.8 Hz, $\eta^5$-C_5H_5), 6.86-8.12 (m, 19 H, aromatics). $^{31}$P({$^1$H}) NMR: δ 42.4, 78.7, 80.2 (ABX m, 3 P, $^2$J_{AB} = 43.0 Hz, $^2$J_{AX} = 54.7 Hz, $^2$J_{BX} = 52.0 Hz).

A solution of \([(R^*,R^*),(R^*)\]-10 (0.05 g, 0.06 mmol) in tetrahydrofuran (30 mL) was treated with ethylmagnesium bromide (3 mL, 0.22 M in diethyl ether, 0.6 mmol) at room temperature. After 2.5 h methanol (1 mL) was added, to destroy excess Grignard reagent, and the volatiles were removed in vacuo. The residue was dissolved in dichloromethane (50 mL) and the extract was washed with aqueous NH_4PF_6. After drying over MgSO_4, the organic layer was concentrated to ca 2 mL and diluted with diethyl ether. The product was obtained as a \((R^*,R^*),(R^*)\):(R^*,R^*),(S^*) = 1:3 mixture of diastereomers.
Treatment of \([R^*,R^*),(S^*)] \cdot 9\) with KOBu-t/BnBr by the procedure outlined for the preparation of \([(R^*,R^*),(R^*)]-15\) afforded the pure product as orange prisms: mp 259-260 °C; yield 80%. Anal. Calcd for C\(_{39}H\text{I}_4\text{ClF}_6\text{FeP}_4\): C, 56.1; H, 4.9; P, 14.7. Found: C, 56.5; H 4.9; P, 14.3. \(^1\)H NMR: \(\delta\) 1.06 (d, 3 H, \(J_{\text{PH}} = 7.2\) Hz, PBnMePh), 2.02 (d of d, 1 H, \(J_{\text{HH}} = 14.4\) Hz, \(J_{\text{PH}} = 3.2\) Hz, PCHH'Ph), 2.14 (d, 3 H, \(J_{\text{PH}} = 7.7\) Hz, PMe), 2.22 (d, 3 H, \(J_{\text{PH}} = 8.2\) Hz, PMe), 2.86 (d of d, 1 H, \(J_{\text{HH}} = 14.5\) Hz, \(J_{\text{PH}} = 6.8\) Hz, PCHH'Ph), 4.24 (q, 5 H, \(J_{\text{PH}} = 1.8\) Hz, \(\eta^5\)-C\(_5\)H\(_5\)), 6.06-8.16 (m, 24 H, aromatics). \(^3\)P{\(^1\)H} NMR: \(\delta\) 41.1, 77.8, 78.9 (ABX m, 3 P, \(|J_{\text{AB}}| = 42.6\) Hz, \(|J_{\text{AX}}| = 56.3\) Hz, \(|J_{\text{BX}}| = 50.4\) Hz).

Treatment of \([(R^*,R^*),(S^*)]-9\) with KOBu-t/BnBr under identical described for the preparation of \([(R^*,R^*),(R^*)]-16\) gave yellow plates (from dichloromethane-diethyl ether): mp 219-220 °C; yield 85%. Anal. Calcd for C\(_{39}H\text{I}_4\text{ClF}_6\text{FeP}_4\): C, 56.2; H, 4.9; P, 14.7. Found: C, 56.6; H 4.5; P, 15.0. \(^1\)H NMR: \(\delta\) 0.46 (d, 3 H, \(J_{\text{PH}} = 7.4\) Hz, PBnMePh), 2.13 (d, 3 H, \(J_{\text{PH}} = 8.2\) Hz, PMe), 2.58 (d of d, 1 H, \(J_{\text{HH}} = 14.6\) Hz, \(J_{\text{PH}} = 3.1\) Hz, CHH'Ph), 2.61 (d, 3 H, \(J_{\text{PH}} = 8.0\) Hz, PMe), 2.88 (d of d, 1 H, \(J_{\text{HH}} = 14.6\) Hz, \(J_{\text{PH}} = 5.9\) Hz, CHH'Ph), 4.24 (q, 5 H, \(J_{\text{PH}} = 1.8\) Hz, \(\eta^5\)-C\(_5\)H\(_5\)), 6.27-8.13 (m, 24 H, aromatics). \(^3\)P{\(^1\)H} NMR: \(\delta\) 42.4, 77.2, 79.6 (ABX m, 3 P, \(|J_{\text{AB}}| = 42.6\) Hz, \(|J_{\text{AX}}| = 54.8\) Hz, \(|J_{\text{BX}}| = 50.7\) Hz).
[(R*,R*),(R*)]/[(R*,R*),(S*)]-(±)-(Benzylmethylphenyl)(η^5-
cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II)

Hexafluorophosphate  

Reaction of [(R*),(R*,R*)]-10 with benzylmagnesium bromide over 4 h as
described by the preparation of [(R*,R*),(S*)]/[(R*,R*),(R*)]-15 yielded the product as a
(R*,R*),(R*):(R*,R*),(S*) = 1:8 mixture of diastereomers.

[(R*),(R*,R*)]/[(S*),(R*,R*)]-(±)-(η^5-Cyclopentadienyl)-
(methylphenoxyphenyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II)

Hexafluorophosphate  

Method 1: A solution of [(R*),(R*,R*)]-10 (0.05 g, 0.06 mmol) and TlOPh (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 and the residue was extracted with dichloromethane (50
mL) and then washed with aqueous NH_4PF_6. After separating off the organic layer and
drying it over MgSO_4, the solution 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: mp
140-142 °C; 0.035 g (73%). Anal. Calcd for C_{38}H_{39}F_{6}FeP_{4}: C, 56.7; H, 4.7; P, 15.4.
Found: C, 56.1; H 4.6; P, 15.1. 1H NMR (major): δ 2.08 (d, 3 H, 12fPH + 4JpH = 8.6
Hz, PMe), 2.16 (d, 3 H, 2fPH = 6.2 Hz, PMe(OPh)Ph), 2.45 (d, 3 H, 12fPH + 4JpH = 9.9
Hz, PMe), 4.09 (q, 5 H, 3fPH = 1.9 Hz, 115-C_5H_5), 5.80-7.92 (m, 24 H, aromatics).
31p(1H) NMR (major): δ 78.7, 79.1, 176.9 (ABX m, 3 P, 12fAB = 42.5 Hz, 12fAX = 75.8 Hz, 12fBX = 72.2 Hz). 1H NMR (minor): δ 1.13 (d, 3 H, 12fPH = 8.8 Hz,
PMe(OPh)Ph), 2.37 (d, 3 H, 12fPH + 4JpH = 9.7 Hz, PMe), 2.43 (d, 3 H, 12fPH + 4JpH =
10.7 Hz, PMe), 4.17 (q, 5 H, 3fPH = 2.0 Hz, η^5-C_5H_5), 6.15-8.04 (m, 24 H, aromatics).
31p(1H) NMR (minor): δ 80.3, 81.0, 176.9 (ABX m, 3 P, 12fAB = 43.5 Hz, 12fAX =
77.4 Hz, 12fBX = 62.7 Hz).
Method 2: A solution of $[(R^*),(R^*,R^*)]$-10 (0.1 g, 0.12 mmol) in tetrahydrofuran (30 mL) was treated with sodium phenoxide (5 mL, 0.03 M in THF, 0.014 mmol) at room temperature. After 12 h, the solvent was evaporated off and the residue was extracted with dichloromethane (50 mL) and washed with aqueous NH$_4$PF$_6$. The organic layer, after drying over MgSO$_4$, was concentrated to ca 2 mL and diluted with diethyl ether to yield yellow plates of the product with $[(R^*),(R^*,R^*)]:([(S^*),(R^*,R^*)] = 1:3$ (61% yield).

$[(R^*),(R^*,R^*)] / [(S^*),(R^*,R^*]) - (\pm)-(\text{Cyclopentadienyl})(\text{methoxymethyl-phenylphosphine})[1,2-\text{phenylenebis(methylphenylphosphine)}]\text{iron(II) Hexafluorophosphate}$ $[(R^*),(R^*,R^*)] / [(S^*),(R^*,R^*)] - 18$

Method 1: A solution of $[(R^*),(R^*,R^*)]$-10 (0.2 g, 0.24 mmol) in tetrahydrofuran (50 mL) was treated with sodium methoxide (3 mL, 0.09 M; 0.26 mmol) at room temperature. After 3 h, the solvent was evaporated off and the residue was extracted with dichloromethane (100 mL), the extract washed with aqueous NH$_4$PF$_6$, and then dried over MgSO$_4$. Concentration of the solution to ca 5 mL and diluting with diethyl ether gave yellow plates of the product with $(R^*),(R^*,R^*): (S^*),(R^*,R^*) = 13:1$; mp 272 °C; 0.15 g (75%). Anal. Calcd for C$_{33}$H$_{36}$F$_6$FeOP$_4$: C, 53.4; H, 4.9; P, 16.7. Found: C, 53.6; H 5.2; P, 16.7. $^1$H NMR (major): $\delta$ 0.92 (d, 3 H, $^2$J$_{PH} = 6.4$ Hz, PMe(OMe)Ph), 2.13 (d, 3 H, $^2$J$_{PH} + 4$J$_{PH}$ = 8.8 Hz, PMe), 2.32 (d, 3 H, $^2$J$_{PH} + 4$J$_{PH}$ = 10.3 Hz, PMe), 3.16 (d, 3 H, $^3$J$_{PH} = 11.2$ Hz, PMe(OMe)Ph), 4.06 (q, 5 H, $^3$J$_{PH} = 1.8$ Hz, $^\eta^5$-C$_5$H$_5$), 6.79-7.68 (m, 19 H, aromatics). $^{31}$P{$^1$H} NMR (major): $\delta$ 81.5, 82.2, 171.2 (ABX m, 3 P, $^2$J$_{AB}$ = 44.4 Hz, $^2$J$_{AX}$ = 59.5 Hz, $^2$J$_{BX}$ = 77.2 Hz). $^1$H NMR (minor): $\delta$ 2.04 (d, 3 H, $^2$J$_{PH} = 6.5$ Hz, PMe(OMe)Ph), 2.06 (d, 3 H, $^2$J$_{PH} + 4$J$_{PH}$ = 8.6 Hz, PMe), 2.38 (d, 3 H, $^2$J$_{PH} + 4$J$_{PH}$ = 10.1 Hz, PMe), 2.89 (d, 3 H, $^3$J$_{PH} = 11.4$ Hz, PMe(OMe)Ph), 4.04 (q, 5 H, $^3$J$_{PH} = 1.8$ Hz, $^\eta^5$-C$_5$H$_5$), 6.51-7.68 (m, 19 H, aromatics). $^{31}$P{$^1$H} NMR (minor): $\delta$ 79.9, 80.1, 171.2 (ABX m, 3 P, $^2$J$_{AB}$ = 43.3 Hz, $^2$J$_{AX}$ = 70.5 Hz, $^2$J$_{BX}$ = 74.4 Hz).
Method 2: Reaction of \([S^*],(R^*,R^*)\)-10 with sodium methoxide as described for the preparation of \([(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]\)-18 gave the product in 71\% yield as yellow plates with \((R^*),(R^*,R^*):(S^*),(R^*,R^*) = 12:1\).
Chapter Four

Synthesis and Reactivity of Coordinated Halogenoarsines
4.1 Introduction

Recent work in our laboratory has involved the diastereoselective synthesis of a resolved secondary arsine in a chiral iron complex. The resolved secondary arsine complex crystallized from a reaction mixture containing \([R-(R*,R*)]-1\) and \((\pm)\)-AsHMePh in a typical second-order asymmetric transformation, as shown below:

\[
\begin{align*}
\text{[R-[(R*),(R*,R*)]-1]} \\
(\pm)\text{-AsHMePh}
\end{align*}
\]

The optically pure secondary arsine complex was deprotonated with complete stereoselectivity at low temperatures in tetrahydrofuran, generating a chiral tertiary arsenido-iron(II) complex. The inversion barrier of the methylphenylarsenido-iron group in this complex was calculated, on the basis of \(^1\)H NMR spectroscopic measurements, to be ca 91 kJ mol\(^{-1}\), considerably higher than the value of ca 60 kJmol\(^{-1}\) for the
methylphenylphosphido-iron group in an analogous complex. These results are consistent with the higher inversion barriers of tertiary arsines when compared to tertiary phosphines. Ethylation of the arsenido-iron(II) complex at -65 °C afforded the corresponding chiral tertiary arsine complex with complete retention of configuration at arsenic. Displacement of the resolved tertiary arsine from the metal (by treatment with cyanide) completed the asymmetric synthesis of an optically active tertiary arsine from (±)-AsHMePh with use of an optically active organometallic auxiliary.

As an extension of this work, we have investigated here the stereochemistry of reactions of coordinated halogenoarsines.

4.2 Results and Discussion

4.2.1 Synthesis of a Fluoroarsine-Iron(II) Complex

The method of preparation of (±)-AsFMePh is summarized in Scheme XI. Treatment of a solution of (±)-AsBrMePh in acetone with silver fluoride (in the absence of light) gave the chiral fluoroarsine, which was isolated by vacuum distillation as a colourless, air-, moisture-, and light-sensitive oil, bp 52 °C (0.1 mmHg). The fluoroarsine decomposes at room temperature over 24 h into a mixture of unidentified products.
The reaction of the acetonitrile complex \((R^*,R^*)-1\) with an excess of freshly prepared \((\pm)-\text{AsFMePh}\) in boiling dichloromethane, in the absence of light, gave

\[
[(R^*)(R^*,R^*)][(S^*)(R^*,R^*)]-(\pm)-[\eta^5-\text{C}_5\text{H}_5]\{1,2-\text{C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}[(\text{AsFMePh})]\text{PF}_6,
\]

in 98% yield, as a 2.5:1 mixture of diastereomers, according to \(^1\text{H} \text{NMR spectroscopy} \text{ (Scheme XII)}. The major diastereomer crystallizes from dichloromethane-petroleum ether as a \textit{monodichloromethane solvate}. The more soluble minor diastereomer was obtained pure from acetone-diethyl ether as a \textit{monoacetone solvate}. Both diastereomers are stable to the atmosphere in the solid state.
4.2.2 X-ray Crystal Structure of [(R*),(R*,R*)]-19·CH$_2$Cl$_2$

The major diastereomer crystallizes as a monochloromethane solvate in the monoclinic space group $P2_1/n$ as a racemate since both enantiomers of the cation are present in the unit cell. Table VIII gives the most important bond distances and angles in the cation. In Figure IX the geometry of the complex is illustrated, displaying the atomic number scheme used. The structure reveals an Fe-As bond length of 2.235 (1) Å and a Fe-As-F bond angle of 111.1°. All three stereogenic centres in the racemate possess the same relative helicity; accordingly, the cation has the stereochemical descriptor (R*),(R*,R*).
Figure 9. A view of cation of \([(R^*),(R^*,R^*)]\)-19 showing the labelling scheme of the non-hydrogen atoms. The $R$ enantiomer of the cation is depicted.
Table VIII. Selected Bond Distances (Å) and Angles (°) of \([(R^*,R^*),(R^*)]-19\) with Estimated Standard Deviations in Parentheses

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<td>C(51)-C(55)-C(54)</td>
<td>106.8(7)</td>
</tr>
</tbody>
</table>
In Figure 10a the $^1$H NMR spectrum in [2H$_2$]dichloromethane of the original mixture [(R*),(R*,R*)]-19 : [(S*),(R*,R*)]-19 = 2.5 : 1 is shown; Figure 10b shows the $^1$H NMR spectrum of [(R*),(R*,R*)]-19 and Figure 10c the $^1$H NMR spectrum of [(S*),(R*,R*)]-19. The $^1$H NMR spectrum of diastereomerically pure [(R*),(R*,R*)]-19 in [2H$_2$]dichloromethane exhibits bis(tertiary phosphine) PMe resonances as a multiplet at δ 2.22; the corresponding PMe resonances of [(S*),(R*,R*)]-19 appear as a pair of 'filled-in' doublets at δ 2.20 and δ 2.51. The AsMe resonance appears as a doublet at δ 1.11 for the (R*),(R*,R*) diastereomer and as a doublet at δ 2.09 for the (S*),(R*,R*) diastereomer.

Treatment of optically pure [R-(R*,R*)]-1 with an excess of (+)-AsFMePh in boiling dichloromethane in the absence of light gives [R-[(R*),(R*,R*)]]/[[R-[](S*),(R*,R*)]]-(+)-[(115-C$_5$H$_5$){1,2-C$_6$H$_4$(PMePh)$_2$}Fe(AsFMePh)]PF$_6$, [[R-[(R*),(R*,R*)]]/[[R-[(S*),(R*,R*)]]]-19, in 96% yield. The attempted fractional crystallization of the optically active mixture was unsuccessful.
Figure 10b. $^1$H NMR spectrum in $[^2]$H$_2$ dichloromethane of [(R*), (R*, R*)]-19 (insert shows PMe resonances).
Figure 10c. $^1$H NMR spectrum in [2$^2$H$_2$]dichloromethane of [(S$^*$),(R$^*$,R$^*$)]-19 (insert shows PMe resonances).
4.2.3 Stereoselective Reactions of the Coordinated Fluoroarsine Complex

4.2.3.1 Reactions with Carbon Nucleophiles

Treatment of diastereomerically pure \([(R^*),(R^*,R^*)]-19\) in tetrahydrofuran at 20 °C with benzylmagnesium bromide gives the tertiary arsine complex \([(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-[\eta^5-C_5H_5\{1,2-C_6H_4(PMePh)_2\}Fe(AsBnMePh)]PF_6,\n\[(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-20\], with \((R^*),(R^*,R^*):(S^*),(R^*,R^*) = 4:1\). The alkylation of the fluoroarsine complex with the Grignard reagent therefore proceeds with predominant inversion of configuration at the arsenic stereocentre (Scheme XIII).

In a similar reaction, treatment of a solution of \([(R^*),(R^*,R^*)]-19\) in tetrahydrofuran with ethylmagnesium bromide gave \([(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-[\eta^5-C_5H_5\{1,2-C_6H_4(PMePh)_2\}Fe(AsEtMePh)]PF_6,\n\[(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-21\], with \((R^*),(R^*,R^*):(S^*),(R^*,R^*) = 1.5:1\), according to \(^1\)H NMR spectroscopy. The diastereomeric ratio of the products was unaltered over the reaction temperature range, -78 °C to 20 °C. Consistent with these results, the reaction of the diastereomer \([(S^*),(R^*,R^*)]-19\) with Grignard reagents RMgX (where R = Et or Bn) gave predominantly \([(S^*),(R^*,R^*)]\) diastereomers of the corresponding tertiary arsine products.
The identities of the tertiary arsine diastereomers were based upon $^1$H NMR data obtained for the products of the alkylation of the arsenido-iron complex $\{(R^\ast),(R^\ast,R^\ast)\}$-\((+)\)-\([(\eta^5-C_5H_5)(1,2-C_6H_4(PMePh)_2)Fe(AsMePh)]\), which was generated with complete stereoselectivity and retention of configuration at arsenic from $\{(R^\ast),(R^\ast,R^\ast)\}$-\((\pm)\)-\([(\eta^5-C_5H_5)(1,2-C_6H_4(PMePh)_2)Fe(AsHMePh)]PF_6\), $\{(R^\ast),(R^\ast,R^\ast)\}$-\(22\), by treatment with KOBu-$t$ at -65 °C in tetrahydrofuran (Scheme XIV). Quenching of the stereochemically homogeneous arsenido-iron(II) complex with benzyl bromide or ethyl iodide at -65 °C
gave completely pure samples of the \((S^*,(R^*,R^*))\) diastereomers of the respective tertiary arsine complexes, according to \(^1\)H NMR spectroscopy (300 MHz). Similarly, enantiomer \([R-[(R^*),(R^*,R^*)]]-22\), when treated consecutively with KOBu-\(t\) and either benzyl bromide or ethyl iodide in tetrahydrofuran at -65 °C, gave enantiomerically pure \([R-[(S^*),(R^*,R^*)]]-20\), \([\alpha]_D^\circ +365^\circ\) (CH\(_2\)Cl\(_2\)), or \([R-[(S^*),(R^*,R^*)]]-21\), \([\alpha]_D^\circ +380^\circ\) (CH\(_2\)Cl\(_2\)). At temperatures above -65 °C the diastereoselectivity of the alkylation of the intermediate arsenido-iron(II) derivative corresponded to the thermodynamic concentrations of the arsenido-iron diastereomers, that is \((S^*),(R^*,R^*):(R^*),(R^*,R^*) = 3.5:1\) (Scheme XIV).

Treatment of a solution of \([(R^*),(R^*,R^*)]-22\) in tetrahydrofuran at -65 °C with KOBu-\(t\) followed by 1 equivalent of bromine gave the bromoarsine complex \([(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-26\) as a 2:1 mixture of diastereomers that could not be separated by fractional crystallization.

The stereochemistry of substitution of optically active halogenosilicon compounds of the type \((\pm)-(1-Np)Ph(R)SiF\) (where \(R = \text{Me, Et, }i-\text{Pr}\)) and \((\pm)-(1-Np)Fc(H)SiF\) (where \(Fc = \text{ferrocenyI}\)) with carbon nucleophiles has been investigated by Corriu et al.\(^{127}\) In this work it was discovered that alkylation with RMgX (where \(R = \text{Me, Et, }n-\text{Bu, or CH}=\text{CH-CH}_2\)) proceeds predominantly with inversion of configuration at silicon. This observation was rationalised in terms of the influence of the magnesium ion on the reaction pathway.
Scheme XIV

$[(R^*)_2(R^*,R^*)] \cdot 22$

$\mathrm{KOBu-t}$

$\rightarrow > -20°C$

$\leftrightarrow$

$[(R^*)_2(R^*,R^*)]$

$[(S^*)_2(R^*,R^*)]$ [-20 or -21]

$\rightarrow R^+$

$\rightarrow R^*$

$\rightarrow [(S^*)_2(R^*,R^*)] \cdot 20 \text{ or } -21$

$\rightarrow [(R^*)_2(R^*,R^*)] \cdot 20 \text{ or } -21$
4.2.3.2 Reactions with Oxygen Nucleophiles

The fluoroarsine complex is stable in solution under argon in the absence of water with no evidence of decomposition or disproportionation over several weeks. Slow hydrolysis of the As-F bond was observed upon addition of water to the sample, however, with loss of fluoride ion giving the methylphenylarsinous acid derivative

\[ [(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe-(AsMe(OH)Ph)JPF_6, [(S^*),(R^*,R^*)]/[(R^*),(R^*,R^*)]-23. \]  

Similar observations have been made for the hydrolysis of complexes of cis-[PtCl₂(AsClₓPh₂)(ER₃)] (where E = P or As, R = alkyl or phenyl).²⁶ Indeed, the passage of either diastereomer of the fluoroarsine complex through an alumina column activated with 10% water, resulted in the stereospecific hydrolysis of the As-F bonds in the fluoro complexes with complete inversion at arsenic.

Treatment of a solution of \([(R^*),(R^*,R^*)]-19\) in tetrahydrofuran at 20 °C with sodium hydroxide or thallium(I) hydroxide also produced \([(S^*),(R^*,R^*)]-23\) with complete stereoselectivity. Under the same conditions \([(S^*),(R^*,R^*)]-19\) was converted into \([(R^*),(R^*,R^*)]-23\). Thus, fluoride ion substitution by hydroxide ion generates the hydroxyarsine complex with total inversion of configuration at the chiral arsenic stereocentre, presumably by an \(S_N2\) mechanism.
The fluoroarsine complex does not undergo methanolysis in boiling methanol. Treatment of either \([(R^*),(R^*,R^*)]-19\) or \([(S^*),(R^*,R^*)]-19\) with freshly prepared sodium methoxide in tetrahydrofuran at 20 °C, however, gives a 3.5:1 diastereomeric mixture of the methoxyarsine complex \([(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-23\). The diastereomers could not be separated. (Note that the methanolysis products of the chlorophosphine analogue of the arsine complex could not be separated either.) The major diastereomer was assigned the \((R^*),(R^*,R^*)\) stereochemistry on the basis of \(^1\)H NMR spectroscopy (Table IX).

Diastereomerically pure \([(R^*),(R^*,R^*)]-23\), when reacted consecutively with KOBu-t and methyl iodide in tetrahydrofuran at 20 °C, gave the methoxyarsine derivative \([(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-24\), with \((R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 10:1\). Under the same conditions, however, pure \([(S^*),(R^*,R^*)]-23\) was converted into
Treatment of either \([(R^*),(R^*,R^*)]^{-23}\) or \([(S^*),(R^*,R^*)]^{-23}\) with excess thionyl chloride at 20 °C in tetrahydrofuran gave the chloroarsine complex \([(R^*),(R^*,R^*)]^{-24}\) or \([(S^*),(R^*,R^*)]^{-24}\), respectively, as a thermodynamic mixture of diastereomers with \((R^*),(R^*,R^*):(S^*),(R^*,R^*) = 2:1\) (Scheme XV). In a similar reaction, treatment of \([(R^*),(R^*,R^*)]^{-24}\) with thionyl chloride afforded the same mixture of chloroarsine diastereomers.
4.2.3.3 Diastereoselective Reductions

The reaction of a solution of [(R*),(R*,R*)]-19 in tetrahydrofuran at -15 °C with sodium borohydride generated the corresponding secondary arsine complex.
The reduction of the fluoroarsine complex, therefore, proceeds with predominant retention of configuration at the chiral arsenic stereocentre. A concerted mechanism, similar to that proposed for the reaction of halogenophosphine complexes with Grignard reagents can be visualized for the stereoselective reduction:

\[
\begin{align*}
\text{Ph} & \quad \text{F} \\
\text{Me} & \quad \text{As} \\
\text{R} & \quad \text{Ph} \\
\text{Me} & \quad \text{PF}_6^-
\end{align*}
\]

\[\text{[}(R^*),(R^*,R^*)]\text{-22} \quad \text{+} \quad \text{[}(S^*),(R^*,R^*)]\text{-22} \quad \text{NaBH}_4 \quad -15 \degree C / \text{thf} \]

\[\text{[}(R^*),(R^*,R^*)]\text{-19} \quad \text{+} \quad \text{[}(S^*),(R^*,R^*)]\text{-22} \quad \text{PF}_6^-
\]

\[\begin{align*}
\text{Ph} \quad \text{R} \\
\text{Me} \quad \text{As} \\
\text{R} \quad \text{Me} \\
\text{Ph} \quad \text{PF}_6^-
\end{align*}
\]

4.2.4 Synthesis and Reactivity of Bromoarsine Complexes

The acetonitrile complex \((R^*,R^*)\text{-1}\) reacts with an excess of \((\pm)\)-AsBrMePh in boiling dichloromethane to give \(((R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-26, in 88% yield as an inseparable 2:1 mixture of diastereomers. The compound is air-stable in the solid state and in solution. The attempted coordination of \((\pm)\)-AsBrMePh to the iron auxiliary in boiling methanol led to the diastereoselective synthesis of the methoxyarsine derivative
\[ ([R^*],(R^*,R^*)]-(\pm)\)-[\{\eta^5-C_5H_5\}\{1,2-C_6H_4(\text{PMePh}_2)\}Fe-(\text{AsMe(OMe)Ph})\}]PF_6, \]
\[ ([R^*],(R^*,R^*)]-24, \text{ in } 85\% \text{ yield (Scheme XVI). The methoxyarsine complex is air-stable, but it is moisture-sensitive in solution with slow loss of methoxide ion, giving, with complete stereoselectivity, } [(S^*),(R^*,R^*)]-(\pm)-[\{\eta^5-C_5H_5\}\{1,2-C_6H_4(\text{PMePh}_2)\}Fe-(\text{AsMe(OH)Ph})\}]PF_6, [(S^*),(R^*,R^*)]-23, \text{ and methanol. Thus, hydrolysis of the methoxyarsine complex with water proceeds with complete inversion of configuration at the arsenic stereocentre. The methoxyarsine complex can also be generated as an} \]
\[ (R^*),(R^*,R^*):(S^*),(R^*,R^*) = 7:1 \text{ mixture of diastereomers by stirring the bromoarsine complex in methanol for 2 h.} \]

Grignard reagents, RMgX (where R = Et, Bn or i-Pr), react with the \[ [(R^*),(R^*,R^*)]/[(S^*),(R^*,R^*)]-26 \text{ mixture to give the corresponding tertiary arsine complexes. The diastereoselectivities of these reactions at room temperature and below is poor, however.} \]
Scheme XVI

\[
\begin{align*}
\text{(R*,R*)-1} & \quad (\pm)-\text{AsBrMePh} \\
\text{CH}_2\text{Cl}_2/\Delta & \quad \text{MeOH / \Delta} \\
\text{[(R*),(R*,R*)]-26} & \quad \text{[(R*),(R*,R*)]-24} \\
\text{[(S*),(R*,R*)]-26} & 
\end{align*}
\]
4.2.5 NMR Spectra of Complexes

$^1$H NMR spectroscopy has been employed to characterize compounds 19 - 26 with selected data listed in Table IX. The relative absolute configurations of the chiral arsenic stereocentres in the complexes were assigned with knowledge of the solid state structure of $[(R^*)_2(R^*,R^*)]-19$. The non-equivalent PMe resonances of the bis(tertiary phosphine) ligand typically appear as doublets of doublets, or ‘filled in’ doublets ($0 < 2J_{pp} << |2J_{ph} + 4J_{ph}|$), with coupling constants of ca 9.1 Hz. The bis(tertiary phosphine) PMe resonances in the $(R^*),(R^*,R^*)$ diastereomers of complexes with electronegative substituents on the arsenic are separated by ca 0.2 ppm; the chemical shift differences of the PMe resonances of the $(S^*),(R^*,R^*)$ diastereomers are separated by ca 0.3 ppm. Similarly, PMe resonances for the $(R^*),(R^*,R^*)$ diastereomers of coordinated secondary and tertiary arsines are separated by ca 0.1 ppm, whereas for the $(S^*),(R^*,R^*)$ diastereomers the separation is ca 0.4 ppm. The AsMe resonances in $(R^*),(R^*,R^*)$ diastereomers of complexes with electronegative substituents appear in the range 0.8-1.49 ppm; for the corresponding $(S^*),(R^*,R^*)$ diastereomers these resonances occur between 1.69-2.36 ppm. For secondary and tertiary arsine complexes, the AsMe resonances appear between 0.3-0.58 ppm for $(S^*),(R^*,R^*)$ diastereomers and in the range 0.7-1.06 ppm for the corresponding $(R^*),(R^*,R^*)$ diastereomers.
Table IX. Selected $^1$H NMR Chemical Shift Data for [(R$^*$),(R$^*$,R$^*$)]- and [(S$^*$),(R$^*$,R$^*$)]- 19 - 26

<table>
<thead>
<tr>
<th>Compound</th>
<th>L</th>
<th>δ ($\eta^5$-C$_5$H$_5$)</th>
<th>1,2-C$_6$H$_4$(PMePh)$_2$</th>
<th>L</th>
<th>δ (PMe)</th>
<th>δ (PMe)</th>
<th>δ (AsMe)</th>
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<tbody>
<tr>
<td>(R$^<em>$),(R$^</em>$,R$^*$)-19</td>
<td>AsFMePh</td>
<td>4.32</td>
<td>2.22</td>
<td>1.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S$^<em>$),(R$^</em>$,R$^*$)-19</td>
<td>AsFMePh</td>
<td>4.43</td>
<td>2.51 2.20</td>
<td>2.09</td>
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<tr>
<td>(R$^<em>$),(R$^</em>$,R$^*$)-20</td>
<td>AsBnMePh</td>
<td>4.26</td>
<td>2.15 2.16</td>
<td>0.70</td>
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<tr>
<td>(S$^<em>$),(R$^</em>$,R$^*$)-20</td>
<td>AsBnMePh</td>
<td>4.24</td>
<td>2.15 2.51</td>
<td>0.30</td>
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<tr>
<td>(R$^<em>$),(R$^</em>$,R$^*$)-21</td>
<td>AsEtMePh</td>
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<td>2.13 2.28</td>
<td>1.06</td>
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<tr>
<td>(S$^<em>$),(R$^</em>$,R$^*$)-21</td>
<td>AsEtMePh</td>
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<td>2.14 2.42</td>
<td>0.54</td>
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<tr>
<td>(R$^<em>$),(R$^</em>$,R$^*$)-22</td>
<td>AsHMePh</td>
<td>4.33</td>
<td>1.81 2.26</td>
<td>0.58</td>
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<td>(S$^<em>$),(R$^</em>$,R$^*$)-22</td>
<td>AsHMePh</td>
<td>4.30</td>
<td>2.10 2.46</td>
<td>1.47</td>
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<tr>
<td>(R$^<em>$),(R$^</em>$,R$^*$)-23</td>
<td>AsMe(OH)Ph</td>
<td>4.24</td>
<td>2.17 2.41</td>
<td>0.92</td>
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<tr>
<td>(S$^<em>$),(R$^</em>$,R$^*$)-23</td>
<td>AsMe(OH)Ph</td>
<td>4.32</td>
<td>2.21 2.53</td>
<td>1.69</td>
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Table IX (continued)

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<th>Compound</th>
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<th>Y</th>
<th>Z</th>
</tr>
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<tbody>
<tr>
<td>(R*),(R*),(R*)-24</td>
<td>AsMe(OMe)Ph</td>
<td>4.19</td>
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<tr>
<td>(S*),(R*),(R*)-24</td>
<td>AsMe(OMe)Ph</td>
<td>4.18</td>
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<tr>
<td>(R*),(R*),(R*)-25</td>
<td>AsClMePh</td>
<td>4.35</td>
<td>2.19</td>
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<td>(S*),(R*),(R*)-25</td>
<td>AsClMePh</td>
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<td>2.18</td>
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<td>AsBrMePh</td>
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<td>(S*),(R*),(R*)-26</td>
<td>AsBrMePh</td>
<td>4.40</td>
<td>2.17</td>
<td>2.56</td>
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</tbody>
</table>
4.3 Experimental

Unless stated otherwise, the instrumentation and experimental techniques employed in this section were similar to those employed for the work described in Section 3.3.1. Bromomethylphenylarsine was prepared according to a literature procedure.\textsuperscript{138} The X-ray diffraction data were collected on a Nicolet XRD P3 diffractometer equipped with MoK\textalpha by Dr W. T. Robinson of the University of Canterbury, New Zealand. The molecular structure was determined by Dr A. C. Willis of the Research School of Chemistry.

(±)-Fluoromethylphenylarsine

Silver fluoride (5 g, 39 mmol) was added to a solution of AsBrMePh (8.8 g, 36 mmol) in acetone (25 mL) and the reaction mixture was stirred for 12 h in the absence of light. Filtration, to remove silver bromide, followed by evaporation of the filtrate and distillation yielded the product, bp 52\textdegree C (0.1 mmHg); 4.6 g (70%). \textsuperscript{1}H NMR: \(\delta 1.69\) (d, 3 H, 3\textsuperscript{f}FH = 14.3 Hz, AsMe), 7.40-7.70 (M, 5 H, aromatics).

\[([(R^\ast),(R^\ast,R^\ast)]-(±)-[\eta^5-Cyclopentadienyl](fluoromethylphenylarsine)[1,2-phenylenebis(methylphenylphosphine)]iron(II)\] Hexafluorophosphate

Monodichloromethane Solvate \([[(R^\ast),(R^\ast,R^\ast)]-19-CH_2Cl_2]\)

A mixture of \((R^\ast,R^\ast)-1\) (1.0 g, 1.6 mmol) and (±) fluoromethylphenylarsine (4.5 g, 24 mmol) in dichloromethane (30 mL) was heated under reflux for 12 h in the absence of light. Dilution of the orange solution with diethyl ether gave a yellow precipitate of the product as the major component of a 2.5:1 mixture of itself and the corresponding \((S^\ast),(R^\ast,R^\ast)\) diastereomer. Fractional crystallization of the mixture from dichloromethane (10 mL) by the slow addition of petroleum ether (bp 40-60 \textdegree C) gave the pure \((R^\ast),(R^\ast,R^\ast)\)
diastereomer as yellow needles of the monodichloromethane solvate: mp 155-158 °C; 0.87 g (64%). Anal. Calcd for C₃₃H₃₅AsCl₂F₇FeP₃: C, 46.1; H, 4.1; P, 10.8; F, 15.5. Found: C, 45.9; H, 4.1; P, 10.8; F, 15.5. ¹H NMR: δ 1.11 (d, 3 H, JFH = 8.0 Hz, AsMe), 2.22 (m, 6 H, 2xPMe), 4.32 (t, 5 H, JPH = 1.9 Hz, η⁵-C₅H₅), 6.83-7.71 (m, 19 H, aromatics).

[(S*),(R*,R*)]-(-)-(η⁵-Cyclopentadienyl)(fluoromethylphenylarsine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Monoacetone Solvate ([(S*),(R*,R*)]-9-Me₂CO)

The mother liquor from the isolation of [(R*),(R*,R*)]-9 was evaporated to dryness, and the residue was recrystallized from acetone-diethyl ether mixture giving yellow needles of [(S*),(R*,R*)]-9 as a monoacetone solvate: mp 146 °C; 0.21 g (15%). Anal. Calcd for C₃₅H₄₉AsF₇FeOP₃: C, 50.5; H, 4.7; P, 16.0; F, 11.2. Found: C, 50.1; H, 4.6; P, 16.2; F, 11.5. ¹H NMR: δ 2.09 (d, 3 H, JFH = 7.2 Hz, AsMe), 2.12 (s, 6 H, Me₂CO), 2.20 (d, 3 H, 12JPH = 4JPHl = 9.3 Hz, PMe), 2.51 (d, 3 H, 12JPH + 4JPHl = 10.1 Hz, PMe), 4.43 (t, 5 H, JPH = 1.8 Hz, η⁵-C₅H₅), 6.88-7.57 (m, 19 H, aromatics).

[R-[(R*),(R*,R*)]/[(S*),(R*,R*)]]-(+)-(η⁵-Cyclopentadienyl)-(fluoromethylphenylarsine)[1,2-phenylenebis(methylphenylphosphine)]-iron(II) Hexafluorophosphate ([(R*),(R*,R*)]/[(S*),(R*,R*)]-9)

Reaction of [R-(R*,R*)]-1 with (±)-AsFMePh, according to the method described for the corresponding racemate, gave a mixture of optically active diastereomers. ¹H NMR: identical with those of the corresponding racemate.
Method 1: Reaction of \((R^*,R^*)\)-1 with \((\pm)-\text{AsHMePh}\) in methanol over 2 h, as described for the preparation of \([R^*,(R^*,R^*)]\)-19, gave the product as yellow needles: mp 209-210 °C dec; 2.1 g (88%). Anal. Calcd for C\(_{32}\)H\(_{34}\)AsF\(_6\)FeP\(_3\): C, 50.8; H, 4.5; P, 12.3. Found: C, 50.7; H, 4.6; P, 12.9. \(^1\)H NMR: \(\delta\) 0.58 (d, 3 H, \(\eta^5\)-C\(_5\)H\(_5\)), 1.81 (d, 3 H, PMe), 2.26 (d, 3 H, PMe), 3.25 (m, 1 H, AsH), 4.33 (t, 5 H, \(\eta^5\)-C\(_5\)H\(_5\)), 7.05-7.92 (m, 19 H, aromatics).

Reaction of \([R-(R^*,R^*)]-1\) with \((\pm)-\text{AsHMePh}\) in methanol according to the procedure described for the corresponding racemate, gave the pure enantiomer as yellow needles: mp 230-232 °C dec; 2.2 g (90%); \([\alpha]_{D589}^{2319} +319^\circ(\text{c} 0.233, \text{CH}_2\text{Cl}_2)\). Anal. Calcd for C\(_{32}\)H\(_{34}\)AsF\(_6\)FeP\(_3\): C, 50.8; H, 4.5; P, 12.3. Found: C, 50.7; H, 4.4; P, 12.7. \(^1\)H NMR: Identical with that of corresponding racemate.

A solution of \([(R^*),(R^*,R^*)]-19\) (0.05 g, 0.06 mmol) in tetrahydrofuran (30 mL) was cooled to -15 °C and treated with sodium borohydride (0.012 g, 0.32 mmol). After 12 h the solvent was removed from the reaction mixture and the residue was extracted with dichloromethane and the extract was washed with deoxygenated
water. After drying over MgSO₄, the extract was evaporated to dryness leaving the product as an orange solid: mp 172-178 °C; 0.026 g (59%). Anal. Calcd for C₃₂H₃₄AsF₆P₃: C, 50.8; H, 4.5; P, 12.3. Found: C, 50.1; H 4.5; P, 12.5. ¹H NMR (major): identical with that of material [(R*),(R*,R*)]-22 prepared via method 1. ¹H NMR (minor): δ 1.47 (d, 3 H, J₃H₂ = 5.2 Hz, AsMe), 2.10 (d, 3 H, J₃PH = 8.4 Hz, PMe), 2.46 (d, 3 H, J₃PH = 8.8 Hz, PMe), 3.37 (m, 1 H, AsH), 4.30 (t, 5 H, J₃PH = 1.8 Hz, η₅-C₅H₅), 6.95-8.00 (m, 19 H, aromatics). [(R*),(R*,R*)] (major) : (S*),(R*,R*) (minor) = 2 :1.

[(S*),(R*,R*)]-(-)-(Benzylmethylphenylarsine)(η₅-cyclopentadienyl)(1,2-phenylenebis(methylphenylphosphine))iron(II) Hexafluorophosphate

[(R*),(R*,R*)]-20

The complex [(R*),(R*,R*)]-22 (0.2 g, 0.26 mmol) was added to a solution of KOBu-t (0.15 g, 1.34 mmol) in tetrahydrofuran (50 mL) at -65 °C. After ca 10 min benzyl bromide (0.016 mL, 1.34 mmol) was added to the cold solution. The mixture was warmed to room temperature and the solvent was evaporated off. The residue was then extracted into dichloromethane and washed with aqueous NH₄PF₆. After drying over MgSO₄, the extract was concentrated to ca 5 mL. Chromatography of this fraction on basic alumina (Activity I) with dichloromethane as eluent gave the product as a solid, which was recrystallized from dichloromethane-diethyl ether: mp 137 °C; 0.14 g (64%). Anal. Calcd for C₃₉H₄₀AsF₆FeP₃: C, 55.3; H, 4.8; P, 11.0. Found: C, 55.7; H 4.8; P, 10.7. ¹H NMR: δ 0.30 (s, 3 H, AsBnMePh), 2.15 (d, 3 H, J₃PH = 8.1 Hz, PMe), 2.51 (d, 3 H, J₃PH = 8.8 Hz, PMe), 2.55 (d, 1 H, J₃HH = 11.7 Hz, AsCHH'Ph), 2.77 (d, 1 H, J₃HH = 13.0 Hz, AsCHH'Ph), 4.24 (t, 5 H, J₃PH = 1.9 Hz, η₅-C₅H₅), 6.34-7.82 (m, 24 H, aromatics).
[R-[(S*),(R*,R*)]]-20 and [(S*),(R*,R*)]-20

(R5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II)
Hexafluorophosphate  ([R-[(S*),(R*,R*)]]-20)

Reaction of [R-[(R*),(R*,R*)]]-22 with KOBut / benzyl bromide according to the method outlined for the racemic compound [(R*),(R*,R*)]-20 for the corresponding racemate gave the pure enantiomer: mp 141 °C; yield 61%; [α]589+365 °(c 0.200, CH2Cl2). Anal. Calcd for C39H40AsF6FeP3: C, 55.3; H, 4.8; P, 11.0. Found: C, 55.5; H, 4.6; P, 10.8. 1H NMR: identical with that of the corresponding racemate.

[(R*),(R*,R*)]/[(S*),(R*,R*)]-20

(R5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II)
Hexafluorophosphate  ([[(R*),(R*,R*)]/[(S*),(R*,R*)]]-20)

A solution of [(R*),(R*,R*)]-19 (0.05 g, 0.06 mmol) in tetrahydrofuran (30 mL) was treated with benzylmagnesium bromide (3 mL, 0.22 M in diethyl ether, 0.65 mmol) at 20 °C. After 12 h, the solvent was removed and the residue was extracted with dichloromethane, the extract washed with aqueous NH4PF6, and then dried over MgSO4. Concentration to ca 2 mL gave a residue that was chromatographed on basic alumina (Activity I) with dichloromethane as eluant. The eluate, after drying over MgSO4, upon evaporation to dryness gave the product as an (R*),(R*,R*):(S*),(R*,R*) = 4:1 mixture of diastereomers: mp 139 °C dec; 0.03 g (61%). Anal. Calcd for C39H40AsF6FeP3: C, 55.3; H, 4.8; P, 11.0. Found: C, 54.8; H, 4.8; P, 10.9. 1H NMR (major): 0.70 (s, 3 H, AsBnMePh), 2.09 (d, 1 H, JHH = 13.2 Hz, AsCHH1Ph), 2.15 (d, 3 H, J2PH + 4JPHl = 8.6 Hz, PMe), 2.16 (d, 3 H, J2PH + 4JPHl = 9.5 Hz, PMe), 2.66 (d, 1 H, JHH = 13.0 Hz, AsCHH1Ph), 4.26 (t, 5 H, JPH = 1.8 Hz, η5-C5H5), 6.15-8.10 (m, 24 H, aromatics). 1H NMR (minor): identical with that of [(S*),(R*,R*)]-20 prepared from [(R*),(R*,R*)]-22.
[(S*),(R*,R*)];-(-)-(η^5-Cyclopentadienyl)(ethylmethylphosphine) [1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate

\[ \text{[(R*),(R*,R*)]-21} \]

Reaction of \([(R*),(R*,R*)]-22\) with KOBu-t/iodoethane under the conditions outlined for the synthesis of \([(R*),(R*,R*)]-20\) from \([(R*),(R*,R*)]-22\) gave the pure product: mp 199-202 °C; yield 86%. Anal. Calcd for C_{34}H_{38}AsF_{6}FeP_{3}: C, 52.1; H, 4.9; P, 11.9. Found: C, 51.7; H, 4.7; P, 12.7. \(^1\)H NMR: δ 0.54 (s, 3 H, AsMe), 0.72 (t, 3 H, 3J\text{HH} = 7.6 Hz, AsCH₂Me), 1.30 (m, 1 H, AsCHH₁Me), 1.62 (m, 1 H, AsCHH₁Me), 2.14 (d, 3 H, 2J\text{PH} = 8.6 Hz, PMe), 2.42 (d, 3 H, 2J\text{PH} = 9.2 Hz, PMe), 4.17 (t, 5 H, 3J\text{PH} = 1.8 Hz, η^5-C₅H₅), 6.95-7.11 (m, 19 H, aromatics).

\[ R-[(S*),(R*,R*)]]-\text{(+)}_{589}-(\eta^5\text{-Cyclopentadienyl})(\text{ethylmethylphosphine})\text{[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate} \quad \text{[(R-[(S*),(R*,R*)]]-21}} \]

Reaction of \[R-[(R*),(R*,R*)]]-22\) with KOBu-t/iodoethane according to method described for the corresponding racemate gave the pure enantiomer: mp 230-232 °C; yield 87%; [α]_{589} +380 °(c 0.205, CH₂Cl₂). Anal. Calcd for C_{34}H_{38}AsF_{6}FeP_{3}: C, 52.1; H, 4.9; P, 11.9. Found: C, 52.0; H, 4.7; P, 12.1. \(^1\)H NMR: identical with that of the corresponding racemate.

\[ \text{[(R*),(R*,R*)]/[(S*),(R*,R*)]}-\text{(-)}-(\eta^5\text{-Cyclopentadienyl})\text{- (ethylmethylphosphine) [1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate} \quad \text{[(R*),(R*,R*)]/[(S*),(R*,R*)]-21}} \]

Treatment of \[(R*),(R*,R*)]-19\) in tetrahydrofuran with ethylmagnesium bromide under the conditions stated for the preparation of \[(R*),(R*,R*)]/[(S*),(R*,R*)]-20\) from \[(R*),(R*,R*)]-19 gave the product as an \((R*),(R*,R*): (S*),(R*,R*) = 1.5:1\) mixture of
diastereomers: mp 206 °C; yield 59%. Anal. Calcd for C_{34}H_{38}AsF_{6}FeP_{3}: C, 52.1; H, 4.9; P, 11.9. Found: C, 51.7; H 4.9; P, 11.8. $^1$H NMR (major): $\delta$ 0.55 (t, 3 H, AsCH$_2$Me), 0.68 (m, 1 H, AsCHH$^1$Me), 1.06 (s, 3 H, AsMe), 1.21 (m, 1 H, AsCHH$^1$Me), 2.13 (d, 3 H, $^2$J$_{PH}$ = 7.9 Hz, PMe), 2.28 (d, 3 H, $^2$J$_{PH}$ = 8.5 Hz, PMe), 4.19 (t, 5 H, $^3$J$_{PH}$ = 1.7 Hz, $\eta^5$-C$_5$H$_5$), 6.83-8.01 (m, 19 H, aromatics). $^1$H NMR (minor): identical with that of $[(S^*)(R^*,R^*)]$-21 prepared from $[(R^*),(R^*,R^*)]$-22.

Method 1: A solution of $[(R^*),(R^*,R^*)]$-19 (0.05 g, 0.06 mmol) in tetrahydrofuran (30 mL) was treated with NaOH (0.005 g, 0.12 mmol) at 20 °C. After 12 h, the solvent was evaporated off. The residue was extracted with dichloromethane, the extract was washed with aqueous NH$_4$PF$_6$, and then it was dried over MgSO$_4$. Concentration to ca 1 mL and dilution of the solution with diethyl ether gave the product as yellow plates: mp 213 °C; 0.038 g (84%). Anal. Calcd for C$_{32}$H$_{34}$AsF$_6$FeOP$_3$: C, 49.8; H, 4.4; F, 14.8. Found: C, 50.1; H 4.6; F, 14.8. $^1$H NMR: $\delta$ 1.69 (s, 3 H, AsMe), 2.21 (d, 3 H, $^2$J$_{PH}$ + $^4$J$_{PH}$ = 9.0 Hz, PMe), 2.53 (d, 3 H, $^2$J$_{PH}$ + $^4$J$_{PH}$ = 9.8 Hz, PMe), 4.32 (t, 5 H, $^3$J$_{PH}$ = 1.8 Hz, $\eta^5$-C$_5$H$_5$), 7.05-7.78 (m, 19 H, aromatics). IR (nujol): 3575 cm$^{-1}$ (v(OH)).

Method 2: A solution of $[(R^*),(R^*,R^*)]$-19 (0.05 g, 0.06 mmol) in tetrahydrofuran (30 mL) was treated with thallous hydroxide (0.025 g, 0.11 mmol) at 20 °C in the dark. After 12 h the solvent was evaporated off and the residue was extracted with dichloromethane and washed with aqueous NH$_4$PF$_6$. After drying (MgSO$_4$) the solvent was removed to leave the pure product. $^1$H NMR: identical with that of material $[(S^*),(R^*,R^*)]$-23 prepared by method 1.
Method 1: Treatment of \([S^*],(R^* ,R^*)\)-19 with sodium hydroxide by the procedure described for the preparation of \([S^*],(R^* ,R^*)\)-23 by method 1 afforded the product as a yellow precipitate: mp 215 °C; yield 84%. Anal. Calcd for C\(_{32}\)H\(_{34}\)AsF\(_6\)FeOP\(_3\): C, 49.8; H, 4.4; F, 14.8. Found: C, 50.0; H 4.5; F, 14.8. \(^1\)H NMR: \(\delta\) 0.92 (s, 3 H, AsMe), 2.17 (d, 3 H, \(\begin{pmatrix} J_{PH} \end{pmatrix} + 4J_{PH} = 8.9\) Hz, PMe), 2.41 (d, 3 H, \(\begin{pmatrix} J_{PH} \end{pmatrix} + 4J_{PH} = 10.1\) Hz, PMe), 4.24 (t, 5 H, \(\begin{pmatrix} J_{PH} \end{pmatrix} = 1.6\) Hz, \(\eta^5\)-C\(_5\)H\(_5\)), 6.80-8.06 (m, 19 H, aromatics). IR (nujol): 3575 cm\(^{-1}\) (\(\nu\)(OH)).

Method 2: Reaction of \([S^*],(R^* ,R^*)\)-19 with thallous hydroxide by the procedure outlined for the preparation \([S^*],(R^* ,R^*)\)-23 from thallous hydroxide gave the desired product. \(^1\)H NMR: identical with that of material \([S^*],(R^* ,R^*)\)-23 prepared by method 1.

\([R^*],(R^* ,R^*)\)-(±)-\((\eta^5\)-Cyclopentadienyl)(methoxymethylphenylarsine)-[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate (\([R^*],(R^* ,R^*)\)-24)

Reaction of \((R^* ,R^*)\)-1 with (±)-AsBrMePh in boiling methanol (40 mL) as described for compounds \([R^*],(R^* ,R^*)\]-19 and \([R^*],(R^* ,R^*)\]-22 gave a yellow precipitate of the pure product: mp 178-180 °C; yield 94%. Anal. Calcd for C\(_{33}\)H\(_{36}\)AsF\(_6\)FeOP\(_3\): C, 50.4; H, 4.6; P, 11.8. Found: C, 50.9; H, 4.7; P, 11.4. \(^1\)H NMR: \(\delta\) 0.80 (s, 3 H, AsMe), 2.19 (d, 3 H, \(\begin{pmatrix} J_{PH} \end{pmatrix} = 9.0\) Hz, PMe), 2.39 (d, 3 H, \(\begin{pmatrix} J_{PH} \end{pmatrix} + 4J_{PH} = 10.3\) Hz, PMe), 3.09 (s, 3 H, As(OMe)), 4.19 (t, 5 H, \(\begin{pmatrix} J_{PH} \end{pmatrix} = 1.9\) Hz, \(\eta^5\)-C\(_5\)H\(_5\)), 6.95-7.95 (m, 19 H, aromatics).
Method 1: A solution of ([(R*)](R*,R*)]-19 (0.05 g, 0.06 mmol) in tetrahydrofuran (20 mL) was treated with sodium methoxide (3 mL, 0.02 M, 0.07 mmol) at 20 °C. After 3 h, the solvent was removed and the residue was extracted with dichloromethane (50 mL), washed with NH₄PF₆, and dried over MgSO₄. Concentration of the solvent to ca 2 mL, followed by dilution of the concentrate with diethyl ether, gave yellow plates of the product with (R*),(R*,R*):(S*),(R*,R*) = 3.5:1: mp 132-135 °C dec; 0.021 g (48%). Anal. Calcd for C₃₃H₃₆AsF₆FeOP₃: C, 50.4; H, 4.6; P, 11.8. Found: C, 50.7; H, 4.7; P, 11.5. ¹H NMR (major): identical with that of material ([(R*),(R*,R*)]-24 prepared as described above. ¹H NMR (minor): δ 1.85 (s, 3 H, AsMe), 2.11 (d, 3 H, ¹²JPH + ⁴JPH² = 8.8 Hz, PMe), 2.42 (d, 3 H, ¹²JPH + ⁴JPH² = 9.7 Hz, PMe), 2.94 (s, 3 H, As(OMe)), 4.18 (t, 5 H, ¹¹J₅₅-P₅₅ = 1.9 Hz, η⁵-C₅H₅), 6.60-7.95 (m, 19 H, aromatics).

Method 2: Reaction of [(S*),(R*,R*)]-19 with sodium methoxide as described for [(R*),(R*,R*)]-19, gave the product as yellow plates with (R*),(R*,R*): (S*),(R*,R*) = 3.5:1 (41% yield). ¹H NMR: identical with that of material [(R*),(R*,R*)]-24 obtained by method 1.

Method 3: A solution of ([(R*),(R*,R*)]-23 (0.05 g, 0.07 mmol) in tetrahydrofuran (50 mL) was created with KOBu-t (0.016 g, 0.14 mmol) at 20 °C. After ca 30 min 1 equiv. of iodomethane (0.01 g, 0.14 mmol) was added to the reaction mixture. After 12 h the solvent was evaporated off and the residue was extracted with dichloromethane and the extract was washed with aqueous NH₄PF₆. After drying over MgSO₄, the solvent was removed from the extract to leave the product as a yellow powder.
with (R*),(R*,R*):(S*),(R*,R*) = 10:1; 0.031 g (61%). 1H NMR: identical with that of material [(R*),(R*,R*):(S*),(R*,R*)]/[(S*),(R*,R*)]-24 prepared by method 1.

Method 4: Reaction of [(S*),(R*,R*)]-23 with KOBu-t/iodomethane as described in method 3 gave the product with (R*),(R*,R*):(S*),(R*,R*) = 2:1. 1H NMR: identical with that of material [(R*),(R*,R*)]/[(S*),(R*,R*)]-24 prepared by method 1.

\[
[(R*),(R*,R*)]/[(S*),(R*,R*)]-(-\pm)-(\text{Chloromethylphenylarsine})(\eta^5\text{-cyclopentadienyl})[1,2-\text{phenylenebis(methylphenylphosphine)}]\text{iron(II)}
\]

\[
\text{Hexafluorophosphate} \quad \text{[(R*),(R*,R*)]/[(S*),(R*,R*)]-25)}
\]

Method 1: A solution of [(R*),(R*,R*)]-23 (0.05 g, 0.07 mmol) in tetrahydrofuran (30 mL) was treated with thionyl chloride (0.02 mL, 0.28 mmol) at 20 °C. The solvent was evaporated off after 12 h and the residue was extracted with dichloromethane, washed with a solution of NH₄PF₆ in water, and dried over MgSO₄. The extract was then concentrated to ca 2 mL and diluted with diethyl ether to give the product as a mixture with (R*),(R*,R*):(S*),(R*,R*) = 2:1: mp 138 °C; 0.4 g (78%). Anal. Calcd for C₃₂H₃₃AsClF₆FeP₃: C, 48.6; H, 4.2; P, 11.8; C, 4.5. Found: C, 48.1; H 4.2; P, 12.1; Cl, 4.7. 1H NMR (major): 1.33 (S, 3 H, AsClMePh), 2.19 (d, 3 H, \(2J_{PH} = 7.5\) Hz, PMe), 2.43 (d, 3 H, \(2J_{PH} = 9.9\) Hz, PMe), 4.35 (t, 5 H, \(3J_{PH} = 1.8\) Hz, \(\eta^5\text{-C₅H₅})\), 6.95-8.05 (m, 19 H, aromatics). 1H NMR (minor): 2.18 (d, 3 H, \(2J_{PH} = 7.5\) Hz, PMe), 2.25 (s, 3 H, AsClMe Ph), 2.57 (d, 3 H, \(2J_{PH} = 9.9\) Hz, PMe), 4.41 (t, 5 H, \(3J_{PH} = 1.9\) Hz, \(\eta^5\text{-C₅H₅})\), 6.94-7.96 (m, 19 H, aromatics).

Method 2: Reaction of [(S*),(R*,R*)]-23 with thionyl chloride by method 1 gave a product identical with that prepared from the same reaction with [(R*),(R*,R*)]-23.
Method 3: Treatment of a solution of \([(R^*),(R^* ,R^*)]-24\) in tetrahydrofuran (30 mL) with thionyl chloride by method 1 gave the product as mixture of diastereomers with \((R^*),(R^* ,R^*):(S^*),(R^* ,R^*) = 3:1\)

\([(R^*),(R^* ,R^*)]/[(S^*),(R^* ,R^*)]-(-)-(\text{Bromomethylphenylarsine})\)

\((\eta^5\text{-cyclopentadienyl})[[1,2\text{-phenylenebis(methylphenylphosphine)}\text{iron(II)}\text{Hexafluorophosphate} \quad ([(R^*),(R^* ,R^*)]/[(S^*),(R^* ,R^*)]-26)\]

Method 1: Reaction of \((R^* ,R^*)-1\) with \((+)-\text{AsBrMePh}\) in boiling dichloromethane (30 mL) over 12 h, as described for the preparation of \([(R^*),(R^* ,R^*)]-19\), gave the product with \((R^*),(R^* ,R^*):(S^*),(R^* ,R^*) = 2:1\): mp 190-191 °C; yield 91%. Anal. Calcd for C\(_{32}\)H\(_{33}\)AsBrF\(_6\)FeP\(_3\): C, 46.0; H, 4.0; P, 11.1; Br, 9.6. Found: C, 45.4; H, 3.8; P, 11.4; Br, 9.8. 1H NMR (major): \(\delta\) 1.49 (s, 3 H, AsMe), 2.16 (d, 3 H, \(\text{J}_{PH} = 9.0\) Hz, PMe), 2.47 (d, 3 H, \(\text{J}_{PH} = 10.1\) Hz, PMe), 4.36 (t, 5 H, \(\text{J}_{PH} = 1.8\) Hz, \(\eta^5\text{-C}_5\text{H}_5\)), 7.10-7.76 (m, 19 H, aromatics). 1H NMR (minor): \(\delta\) 2.17 (d, 3 H, \(\text{J}_{PH} = 8.4\) Hz, PMe), 2.36 (s, 3 H, AsMe), 2.56 (d, 3 H, \(\text{J}_{PH} = 9.2\) Hz, PMe), 4.40 (t, 5 H, \(\text{J}_{PH} = 1.8\) Hz, \(\eta^5\text{-C}_5\text{H}_5\)), 7.10-7.76 (m, 19 H, aromatics).

Method 2: The complex \([(R^*),(R^* ,R^*)]-22\) (0.1 g, 0.13 mmol) was added to a solution of KOBu-t (0.04 g, 0.36 mmol) in tetrahydrofuran (40 mL) at -65 °C. After ca 20 min 1 equiv. of bromine (0.02 g, 0.13 mmol) in tetrahydrofuran (1 mL) was added to the cold solution. The mixture was warmed to room temperature and the solvent was evaporated off. The residue was extracted with dichloromethane and the extract was washed, first with water, and then with a solution of NH\(_4\)PF\(_6\) (1 g, 6.1 mmol) in water (10 mL). The organic layer was dried (MgSO\(_4\)), filtered, and evaporated to dryness to give the product as a 2:1 mixture of the diastereomers \([(R^*),(R^* ,R^*)]/[(S^*),(R^* ,R^*)]-26\). 1H NMR : identical with that of material \([(R^*),(R^* ,R^*)]/[(S^*),(R^* ,R^*)]-26\) prepared by method 1.
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