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Reactions of coordinated phosphines and arsines. Stereoselective reactions at the fluoroarsine-As stereocentre in the complex [(*R**),(*R**,*R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(AsFMePh)]$PF_6 \cdot CH_2Cl_2$

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Abstract

The reaction of (±)-AsFMePh, freshly prepared from (±)-AsBrMePh and AgF in acetone, with (*R**,*R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(NCMe)]PF_6 in boiling dichloromethane affords a separable mixture of two diastereomeric iron complexes, epimeric at arsenic, *viz.* [(*R**),(*R**,*R**)]-(±)- and [(*S**),(*R**,*R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(AsFMePh)]PF_6, with the diastereomeric ratio (*R**),(*R**,*R**)/(*S**), (*R**,*R**) = 3:1. The major diastereomer of the complex crystallizes as a 1:1-dichloromethane solvate, the crystal structure of which has been determined. The minor (*S**),(*R**,*R**) diastereomer crystallizes from acetone/diethyl ether as a 1:1 acetone solvate. Reactions of the two diastereomers with RMgBr (R = Bn or Et) are stereospecific giving the corresponding tertiary arsenic complexes with predominant inversion of configuration at arsenic. Hydrolysis of either diastereomer of the fluoroarsine complex affords the corresponding hydroxyarsine (arsinous acid) derivative stereospecifically with complete inversion at arsenic.

1. Introduction

Whereas trivalent fluorophosphines, in particular PF_3, are excellent ligands for transition metals in low oxidation states [1], similar fluoroarsines are relatively poor ligands; indeed, [(η^5-C_5H_5)Mn(AsF_3)$(CO)_2$] appears to be the only fluoroarsine derivative of a transition metal described hitherto [2]. In this paper, we report the synthesis and separation of diastereomeric iron(II) complexes of (±)-AsFMePh, epimeric at arsenic, and describe stereoselective reactions of the coordinated fluoroarsine. In a previous article, we described the chemistry of (±)-PClMePh under similar conditions [3].

2. Results

(±)-Bromomethylphenylarsine reacts with silver(I) fluoride in acetone to give (±)-fluoromethylphenylarsine, a colourless air- and light-sensitive oil having b.p. 52°C (0.1 mmHg). The fluoroarsine can be kept for *ca.* 24 h at 20°C without decomposition. When heated in dichloromethane with (*R**,*R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(NCMe)]$PF_6 \cdot CH_2Cl_2$ [4] ((*R**,*R**)-**1**), the arsine gives, by displacement of acetonitrile, the diastereomeric complexes [(*R**),(*R**,*R**)]- and [(*S**),(*R**,*R**)]-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe(AsFMePh)]PF_6 ((*R**),(*R**,*R**)- and (*S**),(*R**,*R**)-**2**) (Scheme 1) [5*]. The product distribution is (*R**),(*R**,*R**)/(*S**), (*R**,*R**) = 2.5:1. The major diastereomer crystallizes as a 1:1-dichloromethane solvate from a solution of the mixture in dichloromethane/petroleum ether (b.p. 60–80°C); the minor

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

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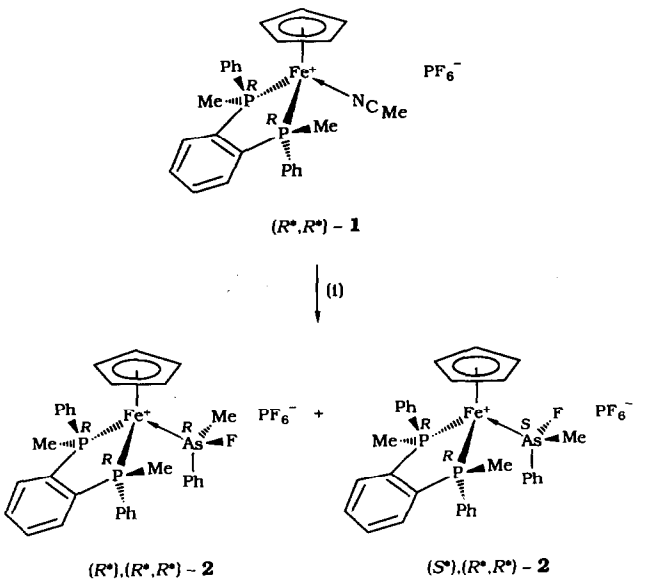


Scheme 1. Reagents and conditions (racemates depicted as enantiomers in each case): (i) (±)-AsFMePh (excess) in boiling dichloromethane (12 h).

diastereomer was recovered as a 1:1-acetone solvate from the filtrate by evaporation and recrystallization of the residue from acetone/diethyl ether. Both isomers are air-stable as solids. (±)-Bromomethylphenylarsine gives a similar pair of complexes with (*R**,*R**)-**1**, *viz.* (*R**),(*R**,*R**)- and (*S**),(*R**,*R**)-**3**, but the (*R**), (*R**,*R**)/(*S**), (*R**,*R**) = 2:1 mixture could not be separated by fractional crystallization. Selected ^{1}H NMR data for the complexes are given in Table 1.

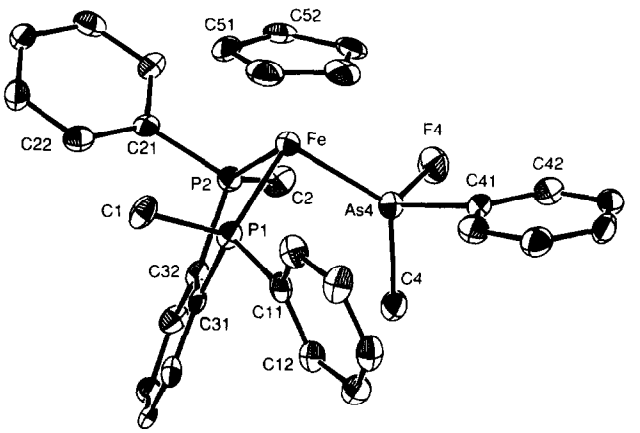


Fig. 1. Molecular structure of cation of (*R**),(*R**,*R**)-**2**·CH_2Cl_2. The *R* enantiomer of the molecule is depicted.

2.1. *X-ray structure of (R*),(R*,R*)-2 · CH_2Cl_2*

The salt (*R**),(*R**,*R**)-**2** · CH_2Cl_2 crystallizes as a racemic compound in the monoclinic space group $P2_1/n$. The structure of the cation of the complex is depicted in Fig. 1. Crystal data for the complex are given in Table 2. Table 3 gives positional parameters, and Table 4 lists the most important distances and angles in the complex. Complete data are available in the supplementary material [7*].

The Fe–As distance is 2.235(1) Å and the As–F distance is 1.775(4) Å; the Fe–As–F angle is 111.1°. The data in other respects are similar to those for related complexes [3,4]. In the structure depicted, each chirotopic stereocentre has the *R* absolute configuration, hence the racemate takes the descriptor (*R**),(*R**,*R**).

TABLE 1. Selected ^{1}H NMR data for complexes [a]

Diastereomer	X	δ(C_5H_5)	1,2-C_6H_4(PMePh)$_2$		AsXMePh
			δ(PMe)	δ(PMe)	δ(AsMe)
(*R**),(*R**,*R**)-**2**	F [b]	4.42 t	2.22 m		1.11 d
(*S**),(*R**,*R**)-**2**	F [c]	4.43 t	2.51 d	2.20 d	2.09 d
(*R**),(*R**,*R**)-**3**	Br [d]	4.36 t	2.16 d	2.47 d	1.49 s
(*S**),(*R**,*R**)-**3**	Br [d]	4.40 t	2.17 d	2.56 d	2.36 s
(*R**),(*R**,*R**)-**4**	Et	4.19 t	2.13 d	2.28 d	1.06 s
(*S**),(*R**,*R**)-**4**	Et	4.17 t	2.14 d	2.42 d	0.54 s
(*R**),(*R**,*R**)-**5**	Bn	4.26 t	2.15 d	2.16 d	0.70 s
(*S**),(*R**,*R**)-**5**	Bn	4.17 t	2.14 d	2.42 d	0.54 s
(*R**),(*R**,*R**)-**6**	OH	4.24 t	2.17 d	2.41 d	0.92 s
(*S**),(*R**,*R**)-**6**	OH	4.32 t	2.21 d	2.53 d	1.69 s
(*R**),(*R**,*R**)-**7**	OMe	4.19 t	2.19 d	2.39 d	0.80 s
(*S**),(*R**,*R**)-**7**	OMe [d]	4.18 t	2.11 d	2.42 d	1.85 s
(*R**),(*R**,*R**)-**8**	Cl [d]	4.35 t	2.19 d	2.43 d	1.33 s
(*S**),(*R**,*R**)-**8**	Cl [d]	4.41 t	2.18 d	2.57 d	2.25 s

[a] Chemical shift values quoted in ppm relative to Me_4Si in $CDCl_2$ at 20°C. [b] Isolated as 1-dichloromethane solvate. [c] Isolated as 1-acetone solvate. [d] Pure diastereomer not isolated.

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

Formula	$C_{32}H_{33}AsF_7FeP_3 \cdot CH_2Cl_2$
FW	859.23
Lattice type	Monoclinic
Space group	$P2_1/n$
Cell dimensions	
a (Å)	13.468(4)
b (Å)	14.552(4)
c (Å)	18.081(5)
β (°)	97.83(2)
V (Å^3)	3510(2)
Z	4
D_c (g cm^{-3})	1.625
Data collection instrument	Nicolet XRD P3
Radiation (graphite monochromatic)	Mo Kα
μ (Mo Kα) (cm^{-1})	17.1
λ (Mo Kα) (Å)	0.71073
Temperature (°C)	−110
Scan method	ω scans
Scan range (ω) (°)	1.4
No. unique data ($2\theta_{max} = 50°$)	6178
No. data used ($I > 3\sigma(I)$)	3600
No. parameters refined	429
R [a]	0.051
R_w [b]	0.057
S [c]	1.51
Largest shift/e.s.d., final cycle	0.2
Largest peak (e Å^{-3})	0.84 (near PF_6^-)

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

2.2. ^1H NMR spectra of 2 and 3

Selected ^{1}H NMR data for solutions of the diastereomers of **2** and **3** in dichloromethane-d_2 are given in Table 1. The assignments are based on the data obtained for $(R^*),(R^*,R^*)$-**2** · CH_2Cl_2, which has been characterized by X-ray diffraction. The non-equivalent P*Me* resonances of the bis(tertiary phosphine) appear as doublets or as "filled-in" doublets ($0 < {}^2J(PP') < |{}^2J(PH) + {}^4J(P'H)|$) with J(PH) *ca.* 9 Hz. For $(R^*),(R^*,R^*)$-**2**, the P*Me* doublets are separated by *ca.* 0.2 ppm; for $(S^*),(R^*,R^*)$-**2**, the separation is *ca.* 0.3 ppm. Similar separations between the P*Me* resonances were observed for the diastereomers of the bromoarsine complex **3** and assignments have been made accordingly (Table 1). Large chemical shift differences were also observed for the As*Me* resonances in the diastereomers of **2** and **3**, *viz.* 1.11–1.49 ppm for the $(R^*),(R^*,R^*)$ complexes and 2.09–2.36 for the $(S^*),(R^*,R^*)$ complexes. In **2**, the value ^3J(HF) *ca.* 8 Hz was observed for both diastereomers. The relative positions of the ^{1}H NMR signals for the diastereomers of **2** and **3** are in accord with those observed for related arsine complexes [8].

2.3. Reactions of $(R^*),(R^*,R^*)$-2 · CH_2Cl_2

2.3.1. With Grignard reagents

A solution of $(R^*),(R^*,R^*)$-**2** · CH_2Cl_2 in tetrahydrofuran at 20°C, when treated with ethylmagnesium bromide in the same solvent, affords the corresponding tertiary arsine complex [(η^5-C_5H_5)Fe{1,2-C_6H_4(PMe-

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

Atom	x	y	z	U_{eq} (Å^2)
Fe	0.10493(7)	0.34004(7)	0.27671(5)	0.0198(5)
P(1)	0.1311(1)	0.4864(1)	0.2597(1)	0.021(1)
P(2)	−0.0362(1)	0.3610(1)	0.2041(1)	0.0197(9)
C(1)	0.2061(5)	0.5160(5)	0.1865(4)	0.030(4)
C(11)	0.1923(5)	0.5517(5)	0.3399(4)	0.023(4)
C(12)	0.1432(5)	0.6102(5)	0.3828(4)	0.025(4)
C(13)	0.1929(6)	0.6513(5)	0.4468(4)	0.029(4)
C(14)	0.2944(6)	0.6325(5)	0.4687(4)	0.031(4)
C(15)	0.3447(6)	0.5751(5)	0.4255(4)	0.033(4)
C(16)	0.2947(5)	0.5351(5)	0.3615(4)	0.028(4)
C(2)	−0.1509(5)	0.3071(5)	0.2265(4)	0.029(4)
C(21)	−0.0358(5)	0.3269(5)	0.1064(4)	0.019(4)
C(22)	0.0046(5)	0.3835(5)	0.0558(4)	0.025(4)
C(23)	0.0102(6)	0.3545(5)	−0.0167(4)	0.034(4)
C(24)	−0.0239(6)	0.2672(5)	−0.0395(4)	0.028(4)
C(25)	−0.0646(5)	0.2112(5)	0.0108(4)	0.028(4)
C(26)	−0.0692(5)	0.2389(5)	0.0834(4)	0.025(4)
C(31)	0.0126(5)	0.5429(5)	0.2268(3)	0.020(4)
C(32)	−0.0660(5)	0.4837(5)	0.1997(4)	0.021(4)
C(33)	−0.1602(5)	0.5189(5)	0.1728(4)	0.026(4)
C(34)	−0.1752(6)	0.6136(5)	0.1710(4)	0.029(4)
C(35)	−0.0978(6)	0.6732(5)	0.1962(4)	0.028(4)
C(36)	−0.0030(6)	0.6372(5)	0.2233(4)	0.027(4)
As(4)	0.03051(6)	0.35259(5)	0.37942(4)	0.0243(4)
F(4)	−0.0515(3)	0.2587(3)	0.3876(2)	0.039(3)
C(4)	−0.0635(5)	0.4469(5)	0.3971(4)	0.031(4)
C(41)	0.1022(6)	0.3422(5)	0.4786(4)	0.028(4)
C(42)	0.0698(6)	0.2853(5)	0.5322(4)	0.036(5)
C(43)	0.1167(6)	0.2894(6)	0.6056(4)	0.037(5)
C(44)	0.1932(6)	0.3505(6)	0.6258(4)	0.036(4)
C(45)	0.2281(6)	0.4055(6)	0.5730(4)	0.037(5)
C(46)	0.1825(6)	0.4002(5)	0.4990(4)	0.034(4)
C(51)	0.1855(5)	0.2706(5)	0.2032(4)	0.029(4)
C(52)	0.1214(5)	0.2084(5)	0.2341(4)	0.029(4)
C(53)	0.1478(6)	0.2082(5)	0.3124(4)	0.031(4)
C(54)	0.2293(6)	0.2694(5)	0.3302(4)	0.036(5)
C(55)	0.2541(6)	0.3085(5)	0.2629(5)	0.039(5)
P(6)	0.5582(2)	0.4656(2)	0.2549(2)	0.051(2)
F(61)	0.4578(4)	0.5098(4)	0.2135(3)	0.078(4)
F(62)	0.4995(5)	0.3755(5)	0.2610(6)	0.168(7)
F(63)	0.5282(5)	0.4993(7)	0.3314(4)	0.131(6)
F(64)	0.6567(4)	0.4203(4)	0.2988(4)	0.095(5)
F(65)	0.6171(5)	0.5576(4)	0.2527(4)	0.107(5)
F(66)	0.5913(4)	0.4352(6)	0.1797(4)	0.139(6)
C(7)	−0.3694(7)	0.4761(8)	−0.0131(6)	0.080(8)
Cl(71)	−0.2630(2)	0.4084(2)	−0.0058(1)	0.056(1)
Cl(72A)	−0.3277(8)	0.5990(4)	−0.0264(4)	0.104(4)
Cl(72B)	−0.369(2)	0.579(1)	0.009(2)	0.095(8)

[a] U_{eq} is one-third of the trace of the orthogonalized U matrix. [b] Occupancy of Cl(72A) = 0.78(2), Cl(72B) = 0.22(2). Isotropic displacement factor for Cl(72B).

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

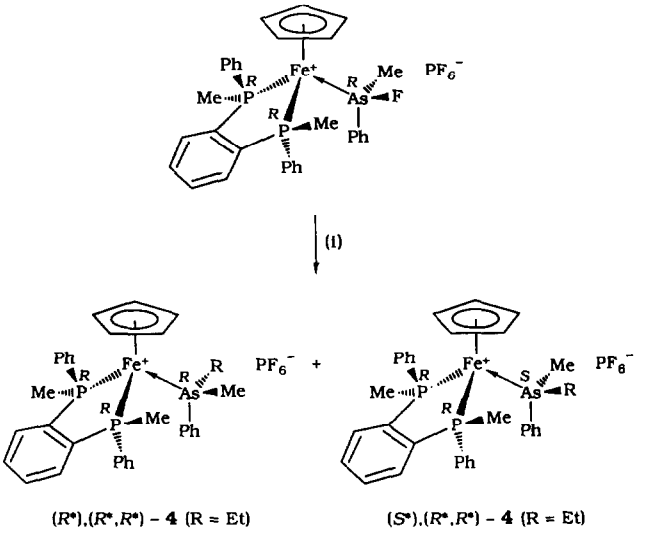
Bond	Distance (Å)	Bonds	Angle (°)
Fe–As(4)	2.235(1)	P(1)–Fe–As(4)	97.84(7)
Fe–P(1)	2.187(2)	P(2)–Fe–As(4)	92.06(7)
Fe–P(2)	2.180(2)	P(1)–Fe–P(2)	85.57(7)
$Fe–C(Cp)_{av}$	2.090(11)	Fe–As(4)–F(4)	111.1(1)
As(4)–F(4)	1.775(4)	Fe–As(4)–C(4)	125.2(2)
As(4)–C(4)	1.923(8)	Fe–As(4)–C(41)	122.9(2)
As(4)–C(41)	1.924(7)	C(4)–As(4)–F(4)	96.0(3)
C(11)–C(12)	1.38(1)	C(41)–As(4)–F(4)	95.8(3)
C(21)–C(22)	1.39(1)	C(4)–As(4)–C(41)	99.2(3)
C(31)–C(32)	1.400(9)		
C(41)–C(42)	1.39(1)		
C(51–C(52)	1.42(1)		

$Ph)_2$}Fe(AsEtMePh)]PF_6 (**4**) with $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 1.5:1$. The reaction with benzylmagnesium bromide yields the (±)-benzylmethylphenylarsine complex **5** with $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 4:1$. Reference samples of $(S^*),(R^*,R^*)$-**4** and **5** were prepared from $[(R^*),(R^*,R^*)]$-[$(\eta^5$-$C_5H_5)$}(1,2-$C_6H_4(PMePh)_2$}Fe(AsHMePh)]PF_6 by treatment with KO^tBu and ethyl- or benzyl-magnesium bromide at −65°C, respectively; these reactions proceed with retention of configuration at arsenic [8]. The diastereoselectivity of the reaction in either case was not improved by carrying out the reaction at −78°C. Thus, alkylations of the fluoroarsine complex with Grignard reagents proceed with predominant inversion of configuration at arsenic [9] (Scheme 2). Reactions of $(S^*),(R^*,R^*)$-**2**·Me_2CO with the Grignard reagents gave the respective tertiary arsine complexes with similar stereoselectivities and inversion at arsenic. The ^1H NMR data for the complexes are given in Table 1.

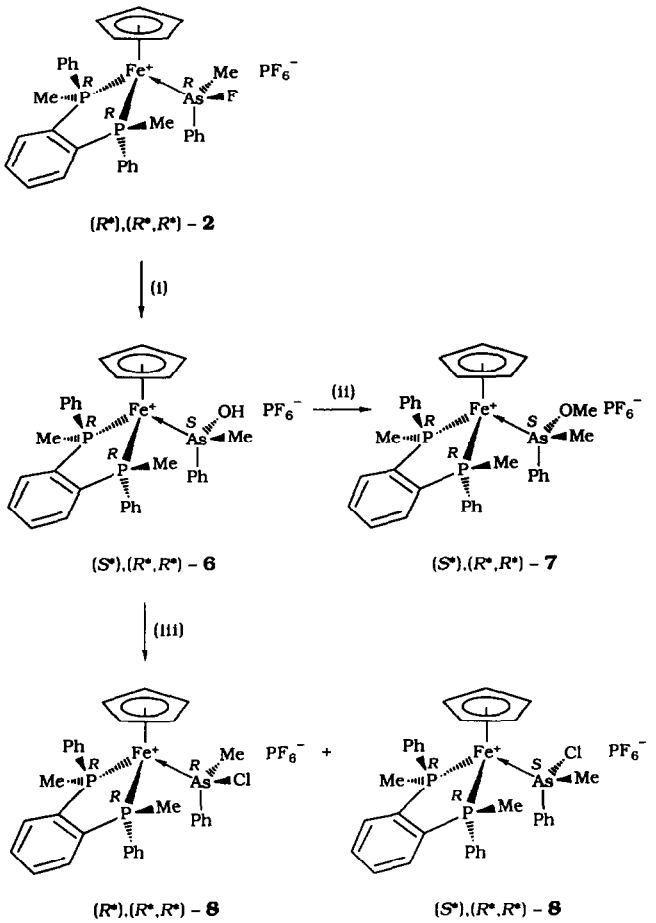
2.3.2. *With water, hydroxide, and alkoxides*

The fluoroarsine complex **2** hydrolyses in solutions containing water or on hydrated alumina columns. The hydrolysis is stereospecific, giving the respective hydroxyarsine derivatives with complete stereoselectivity and inversion at arsenic. Thus, $(R^*),(R^*,R^*)$-**2**·CH_2Cl_2 gives $[(S^*),(R^*,R^*)]$-[$(\eta^5$-$C_5H_5)$}(1,2-C_6H_4)-$(PMePh)_2$}Fe{As(OH)MePh}]PF_6 ($(S^*),(R^*,R^*)$-**6**) and $(S^*),(R^*,R^*)$-**2**·Me_2CO gives $(R^*),(R^*,R^*)$-**6** (Scheme 3). When treated with sodium hydroxide or thallium(I) hydroxide in tetrahydrofuran, the diastereomers of **2** afford similarly the diastereomers of **6** with complete stereoselectivity and inversion at arsenic. Sodium methoxide in tetrahydrofuran at 20°C, however, reacts with either diastereomer of **2** to give in each case an $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 3.5:1$ mixture of the diastereomers of the methoxyarsine complex [$(\eta^5$-$C_5H_5)$}(1,2-$C_6H_4(PMePh)_2$}Fe{As(OMe)MePh}]PF_6 (**7**). The fluoroarsine complex $(R^*),(R^*,R^*)$-**2** is unaffected by boiling methanol, but when reacted with 1 equiv. of NaOMe in tetrahydrofuran it too gave the methoxyarsine complex **7** with $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 3.5:1$. Interestingly, however, if the acetonitrile complex (R^*,R^*)-**1** is reacted with (±)-AsBrMePh in boiling methanol, diastereomerically pure $(R^*),(R^*,R^*)$-**7** crystallizes from the reaction mixture in 94% yield in a typical second-order asymmetric transformation [10]. The inseparable mixture of bromoarsine complex diastereomers $(R^*),(R^*,R^*)/(S^*),(R^*,R^*)$-**3** (see above), when stirred in methanol, also gives the methoxyarsine complex **7**, but with $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 7:1$. Thus, the highly stereoselective synthesis of **7** from (R^*,R^*)-**1** appears to be due to a kinetic effect involving the stereoselective coordination of free (±)-methoxy(methyl)phenylarsine formed from the bromoarsine prior to coordination.

An alternative and highly stereoselective route to $(R^*),(R^*,R^*)$-**7** involves deprotonation of the pure hydroxyarsine complex $(R^*),(R^*,R^*)$-**6** with KO^tBu in tetrahydrofuran and then adding methyl iodide; this reaction gives $(R^*),(R^*,R^*)$-**7** with *ca.* 90% retention of configuration at arsenic. Interestingly, $(S^*),(R^*,R^*)$-**6** under similar conditions affords **7** with considerably reduced stereoselectivity, *viz.* $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 2:1$.



Scheme 2. Reagents and conditions (racemates depicted as enantiomers in each case): (i) RMgBr (R = Et or Bn) in tetrahydrofuran (THF).



Scheme 3. Reagents and conditions (racemates depicted as enantiomers in each case): (i) H_2O/alumina or NaOH or TlOH in tetrahydrofuran (THF); (ii) KO^{t}Bu/MeI in THF; (iii) $SOCl_2$ in THF.

Both diastereomers of **6** and **7** react with thionyl chloride in tetrahydrofuran at 20°C to give the chlorarsine complex **8** with $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 2:1$. It was not found possible to separate or to crystallize selectively the diastereomers of **8**, which were considered to be in equilibrium in solution. NMR data for the various complexes are listed in Table 1.

2.3.3. With sodium borohydride

When reacted with sodium borohydride, a solution of $(R^*),(R^*,R^*)$-**2** $\cdot CH_2Cl_2$ in tetrahydrofuran at −15°C gave the respective secondary arsine complex with predominant retention of configuration at arsenic, *viz.* $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 2:1$.

3. Discussion

The substitution of fluoride in secondary fluoroarsine complexes in reactions involving Grignard reagents, water, hydroxide, and alkoxides, proceeds with predominant inversion of configuration at arsenic. The present system, a univalent complex cation, can be considered formally as an arsonium ion containing a large and electronegative organometallic substituent. Attack of a nucleophile at arsenic trans to fluorine will produce a relatively unstable (compared with phosphorus), short-lived, arsenic(V) species that will eliminate fluoride before pseudoration can occur, giving inversion at arsenic. A similar complex containing a secondary chlorophosphine shows predominant inversion at phosphorus with the phenoxide ion, but retention with carbon nucleophiles (from Grignard reagents) and hydride [3], consistent with longer-lived phosphorus(V) intermediates [11].

4. Experimental details

Experimental work was conducted by use of Schlenk techniques. Solvents were purified and dried by literature procedures and distilled under argon before use. ^{1}H NMR spectra were recorded in dichloromethane-d_2 unless otherwise stated on Varian VXR 300 or Bruker CXP 200 spectrometers operating at 20°C; chemical shifts are reported as δ values relative to internal Me_4Si. Elemental analyses were performed within the Research School of Chemistry.

4.1. (±)-Fluoromethylphenylarsine

A mixture of (±)-bromomethylphenylarsine (8.8 g, 36 mmol) and silver(I) fluoride (5 g, 39 mmol) in acetone (25 ml) was stirred for 12 h in the absence of light, after which the precipitate of AgBr was filtered off and the filtrate evaporated to dryness. Distillation of the residue gave the pure product as an almost colourless oil: b.p. 52°C (0.1 mmHg); 4.6 g (70%). ^{1}H NMR: δ 1.69 (d, 3 H, ^3J(FH) = 14.3 Hz, AsMe); 7.40–7.70 (m, 5H, aromatics).

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

A solution of (R^*,R^*)-**1** (1.0 g, 1.6 mmol) and (±)-fluoromethylphenylarsine (4.5 g, 24 mmol) in dichloromethane (30 ml) was boiled for 12 h in darkness. Dilution of the cooled mixture with diethyl ether caused the precipitation of the product as a yellow powder with $(R^*),(R^*,R^*)/(S^*),(R^*,R^*) = 2.5:1$. Fractional crystallization of this mixture from dichloromethane by the careful addition of petroleum ether (b.p. 40–60°C) gave the pure $(R^*),(R^*,R^*)$ diastereomer as yellow needles of the 1-dichloromethane sol-

vate; m.p. 155–158°C; 0.87 g (64%). Anal. Found: C, 45.9; H, 4.1; F, 15.5; P, 10.8. $C_{33}H_{35}AsCl_2F_7FeP_3$ calc.: C, 46.1; H, 4.1; F, 15.5; P, 10.8%. ^{1}H NMR: δ 1.11 (d, 3H, ^3J(FH) = 8 Hz, AsMe); 2.22 (m, 6H, PMe); 4.32 (t, 5H, ^3J(PH) = 1.9 Hz, C_5H_5); 6.83–7.71 (m, 19H, aromatics).

4.3. [(S),(R*,R*)]-(±)-(η^5-Cyclopentadienyl)(fluoromethylphenylarsine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate–1-acetone ((S*),(R*,R*)-2 · Me$_2$CO)*

After removal of (*R**),(*R**,*R**)-**2** · CH_2Cl_2 (see above), the mother liquor was evaporated to dryness and the residue was dissolved in acetone and the solution was treated with diethyl ether. Pure (*S**),(*R**,*R**)-**2** · Me_2CO crystallized from this mixture as yellow needles; m.p. 146°C; 0.21 g (15%). Anal. Found: C, 50.1; H, 4.6; F, 11.5; P, 16.2. $C_{35}H_{39}AsF_7FeOP_3$ calc.: C, 50.5; H, 4.7; F, 11.2; P, 16.0%. ^{1}H NMR: δ 2.09 (d, 3H, ^3J(FH) = 7.2 Hz, AsMe); 2.12 (s, 6H, Me_2CO); 2.20 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 9.3$ Hz, PMe); 2.51 (d, 3H, $|^2J(PH) + {}^4J(P'H| = 10.1$ Hz, PMe); 4.43 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5); 6.88–7.57 (m, 19H, aromatics).

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

(±)-Bromomethylphenylarsine and (*R**,*R**)-**1** when heated together in dichloromethane (30 ml) for 12 h gave the product, which was obtained from the reaction mixture by dilution with diethyl ether as a yellow powder with (*R**),(*R**,*R**)/(*S**),(*R**,*R**) = 2 : 1; m.p. 190–191°C; (91% yield). Anal. Found: C, 45.4; H, 3.8; Br, 9.8; P, 11.4. $C_{32}H_{33}AsBrF_6FeP_3$ calc.: C, 46.0; H, 4.0; Br, 9.6; P, 11.1%. ^{1}H NMR: δ 1.49 (s, 3H, AsMe-major); 2.16 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 9.0$ Hz, PMe-major); 2.17 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 8.4$ Hz, PMe-minor); 2.36 (s, 3H, AsMe-minor); 2.47 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 10.1$ Hz, PMe-major), 2.56 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 9.2$ Hz, PMe); 4.36 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5-major); 4.40 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5-minor); 7.10–7.76 (m, 38H, aromatics).

4.5. [(R),(R*,R*)] / (S*),(R*,R*)]-(±)-(Ethylmethylophenylarsine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R*),(R*,R*) / (S*),(R*,R*)-4)*

A solution of (*R**),(*R**,*R**)-**2** · CH_2Cl_2(0.05 g, 0.06 mmol) in tetrahydrofuran (30 ml) was treated with a solution of ethylmagnesium bromide in diethyl ether (3 ml, 0.22 M, 0.65 mmol) at 20°C. After 12 h the solvent was removed and the residue dissolved in dichloromethane; the solution was washed with aqueous NH_4PF_6 and the organic fraction was separated and dried over $MgSO_4$. Removal of the solvent from the dried solution afforded a residue that was purified by chromatography on basic alumina (Activity-1) with dichloromethane as eluent. The pure product was obtained from the eluate after drying and concentration as an orange powder with (*R**),(*R**,*R**)/(*S**),(*R**,*R**) = 1.5 : 1; m.p. 206°C; 0.03 g (60%). Anal. Found: C, 51.7; H, 4.9; P, 11.8. $C_{34}H_{38}AsF_6FeP_3$ calc.: C, 52.1; H, 4.9; P, 11.9%. ^{1}H NMR: δ 0.54 (t, 3H, AsMe-major); 0.55 (t, 3H, $AsCH_2$*Me*-minor); 0.68 (m, 1H, As-C*H*HMe-major); 0.72 (t, 3H, ^3J(HH) = 7.6 Hz, $AsCH_2$*Me*-minor); 1.06 (s, 3H, AsMe-major); 1. 21 (m, 1H, AsCH*H*Me-major); 1.30 (m, 1H, AsC*H*HMe-minor); 1.62 (m, 1H, AsCH*H*Me-minor); 2.13 (d, 3H, ^2J(PH) = 7.9 Hz, PMe-major); 2.14 (d, 3H, ^2J(PH) = 8.6 Hz, PMe-minor); 2.28 (d, 3H, ^2J(PH) = 8.5 Hz, PMe-major); 2.42 (t, 3H, ^2J(PH) = 9.2 Hz, PMe-minor); 4.17 (t, 5H, ^2J(PH) = 1.8 Hz, C_5H_5-minor); 4.19 (t, 5H, ^3J(PH) = 1.7 Hz, C_5H_5-major); 6.83–8.01 (m, 38H, aromatics-major, minor). The ^{1}H NMR spectra for the two diastereomers corresponded exactly with those of the authentic optically active specimens described in [8].

4.6. [(R),(R*,R*)] / [(S*),(R*,R*)]-(±)-(Benzylmethylphenylarsine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R*),(R*,R*) / (S*),(R*,R*)-5)*

The reaction of (*R**),(*R**,*R**)-**2** · CH_2Cl_2 with benzylmagnesium bromide following the procedure for the ethyl compound afforded **5** as orange crystals with (*R**),(*R**,*R**)/(*S**),(*R**,*R**) = 4 : 1, m.p. 139°C; 61% yield. Anal. Found: C, 54.8; H, 4.8; P, 10.9. $C_{39}H_{40}AsF_6FeP_3$ calc.: C, 55.3; H, 4.8; P, 11.0%. ^{1}H NMR: δ 0.30 (s, 3H, AsMe-minor); 0.70 (s, 3H, AsMe-major); 2.09 (d, 1H, ^2J(HH) = 13.2 Hz, AsC*H*HPh-major); 2.15 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 8.6$, P*Me*-major); 2.15 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 8.1$ Hz, PMe-minor); 2.16 (d, 3H, $|^2J(PH) + {}^4J(P'H)| = 9.5$ Hz, PMe-major); 2.55 (d, 1H, ^2J(HH) = 11.7 Hz, AsCH*H*Ph-minor); 2.66 (d, 1H, ^2J(HH) = 13.0 Hz, AsC*H*HPh-major), 2.77 (d, 1H, ^2J(HH) = 13.0 Hz, AsC*H*HPh-minor); 4.24 (t, 5H, ^3J(PH) = 1.9 Hz, C_5H_5-minor); 4.26 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5-major); 6.15–8.10 (m, 48H, aromatics-major, minor). An authentic specimen of the (*S**),(*R**,*R**) diastereomer was prepared from [(*R**),(*R**,*R**)]-(±)-[(η^5-C_5H_5){1,2-C_6H_4($PMePh)_2$}Fe(AsHMePh)]PF_6 · CH_2Cl_2 and BnBr/KO^{t}Bu in tetrahydrofuran at −65°C according to the method described in [8].

4.7. [(S),(R*,R*)]-(±)-(η⁵-Cyclopentadienyl)[hydroxy(methyl)phenylarsine][1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((S*),(R*,R*)-6)*

A solution of (*R**),(*R**,*R**)-**2** · CH_2Cl_2 (0.05 g, 0.06 mmol) in tetrahydrofuran (30 ml) at 20°C was treated with NaOH (0.005 g, 0.12 mmol). After 12 h the solvent was evaporated off and the residue was extracted with dichloromethane, the extract washed with aqueous NH_4PF_6, and the organic layer separated and dried over $MgSO_4$. Concentration of the dried solution (to *ca.* 1 ml) followed by the addition of diethyl ether gave the product as yellow plates; m.p. 213°C; 0.038 g (84%). Anal. Found: C, 50.1; H, 4.6; F, 14.8. $C_{32}H_{34}AsF_6FeOP_3$ calc.: C, 49.8; H, 4.4; F, 14.8%. ^{1}H NMR: δ 1.69 (s, 3H, AsMe); 2.21 (d, 3H, $|^2J$ PH) + ^4J(P'H)| = 9.0 Hz, PMe); 2.53 (d, 3H, $|^2J$(PH) + ^4J(P'H)| = 9.8 Hz, PMe); 4.32 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5); 7.05–7.78 (m, 19H, aromatics). IR (Nujol): ν(OH) 3575 cm^{-1}. An identical specimen of this complex was obtained by treating (*S**),(*R**,*R**)-**2** · CH_2Cl_2 with TlOH at 20°C in the absence of light.

4.8. [(R),(R*,R*)]-(±)-(η⁵-Cyclopentadienyl)[hydroxy(methyl)phenylarsine][1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R*),(R*,R*)-6)*

With the use of (*S**),(*R**,*R**)-**2** · Me_2CO and sodium or thallium(I) hydroxide under similar conditions to those described above, pure (*R**),(*R**,*R**)-**6** was obtained as a yellow powder; m.p. 215°C; *ca.* 85% yield. Anal. Found: C, 50.0; H, 4.5; F, 14.8. $C_{32}H_{34}AsF_6FeOP_3$ calc.: C, 49.8; H, 4.4; F, 14.8%. ^{1}H NMR: δ 0.92 (s, 3H, AsMe); 2.17 (d, 3H, $|^2J$(PH) + ^4J(P'H)| = 8.9 Hz, PMe); 2.41 (d, 3H, $|^2J$(PH) + ^4J(P'H)| = 10.1 Hz, PMe); 4.24 (t, 5H, ^3J(PH) = 1.6 Hz, C_5H_5); 6.80–8.06 (m, 19H, aromatics). IR (Nujol): ν(OH) 3575 cm^{-1}.

4.9. [(R),(R*,R*)] / [(S*),(R*,R*)]-(±)-(η⁵-Chloromethylphenylarsine)(η⁵-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R*),(R*,R*) / (S*),(R*,R*)-8)*

Thionylchloride (0.02 ml, 0.28 mmol) was added to a solution of (*R**),(*R**,*R**)-**6** (0.05 g, 0.07 mmol) in tetrahydrofuran at 20°C. After 12 h, the mixture was evaporated to dryness and the residue was taken up in dichloromethane. The extract was washed with aqueous NH_4PF_6, separated, and dried ($MgSO_4$). Concentration of the filtrate to *ca.* 2 ml, followed by the addition of diethyl ether, gave the product as an orange powder with (*R**),(*R**,*R**)/(*S**),(*R**,*R**) = 2:1; m.p. 138°C; 0.4 g (78%). Anal. Found: C, 48.1; H, 4.2; Cl, 4.7; P, 12.1. $C_{32}H_{33}AsClF_6FeP_3$ calc.: C, 48.6; H, 4.2; Cl, 4.5; P, 11.8%. ^{1}H NMR: δ 1.33 (s, 3H, AsMe-major); 2.18 (d, 3H, ^2J(PH) = 7.5 Hz, PMe-minor); 2.19 (d, 3H, ^2J(PH) = 7.5 Hz, PMe-major); 2.25 (s, 3H, AsMe-minor); 2.43 (d, 3H, ^2J(PH) = 9.9 Hz, PMe-major); 2.57 (d, 3H, ^2J(PH) = 9.9 Hz, PMe-minor); 4.35 (t, 5H, ^3J(PH) = 1.8 Hz, C_5H_5-major); 4.41 (t, 5H, ^3J(PH) = 1.9 Hz, C_5H_5-minor); 6.95–8.05 (m, 38H, aromatics).

4.10. [(R),(R*,R*)]-(±)-(η⁵-Cyclopentadienyl)[methoxy(methyl)phenylarsine][1,2-phenylenebis(methylphenylphosphine)]iron(II) hexafluorophosphate ((R*),(R*,R*)-7)*

A mixture of (*R**),(*R**,*R**)-**1** · CH_2Cl_2 and (±)-bromomethylphenylarsine in methanol, when heated under reflux for 12 h, gave, upon cooling, pure (*R**),(*R**,*R**)-**7** as a yellow powder; m.p. 178–180°C; (94% yield). Anal. Found: C, 50.9; H, 4.7; P, 11.4. $C_{33}H_{36}AsF_6FeOP_3$ calc.: C, 50.4; H, 4.6; P, 11.8%. ^{1}H NMR: δ 0.80 (s, 3H, AsMe); 2.19 (d, 3H, $|^2J$(PH) + ^4J(P'H)| = 9.0 Hz, PMe); 2.39 (d, 3H, $|^2J$(PH) + ^4J(P'H)| = 10.3 Hz, PMe); 3.09 (s, 3H, AsOMe); 4.19 (t, 5H, ^3J(PH) = 1.9 Hz, C_5H_5); 6.95–7.95 (m, 19H, aromatics). When heated in tetrahydrofuran for 3 h, equimolar quantities of (*R**),(*R**,*R**)-**2** · CH_2Cl_2 and NaOMe gave the same compound, but with (*R**),(*R**,*R**)/(*S**),(*R**,*R**) = 3.5:1. The mixture crystallized from dichloromethane/diethyl ether as yellow plates; m.p. 132–135°C; 48% yield. ^{1}H NMR ((*S**),(*R**,*R**)): δ 1.85 (s, 3H, AsMe); 2.11 (d, 3H, $|^2J$(PH) + ^4J(P'H)| = 8.8 Hz); 2.42 (d, 3H, $|^2J$(PH) + ^4J(PH)| = 9.7 Hz, PMe); 2.94 (s, 3H, AsOMe); 4.18 (t, 5H, ^3J(PH) = 1.9 Hz, C_5H_5); 6.60–7.95 (m, 19H, aromatics). A similar reaction with (*S**), (*R**, *R**)-**2** · Me_2CO gave an identical result.

Diastereomerically enriched **7** ((*R**),(*R**,*R**)/(*S**),(*R**,*R**) = 10:1) was obtained when the hydroxide (*R**),(*R**,*R**)-**6** in tetrahydrofuran at 20°C was treated with 1 equiv. each of KO^{t}Bu and methyl iodide.

References and notes

1 T. Kruck, *Angew. Chem., Int. Ed. Engl., 6* (1967) 53; R.J. Clark and M.A. Busch, *Acc. Chem. Res., 6* (1973) 246; J.F. Nixon, *Adv. Inorg. Chem. Radiochem., 13* (1970) 363; *29* (1985) 41.

2 J. Muller and K. Fender, *Angew. Chem., Int. Ed. Engl., 10* (1971) 418.

3 G. Salem, G.B. Shaw, A.C. Willis and S.B. Wild, *J. Organomet. Chem., 444* (1993) 147.

4 G.T. Crisp, G. Salem, F.S. Stephens and S.B. Wild, *Organometallics, 8* (1989) 2360.

5 The nomenclature adopted here is based upon current Chemical Abstracts Service indexing practice. Diastereomers are indicated by the relative configurations of the chirotopic stereocentres present ((*R**,*R**) for the bis(tertiary phosphine) and (*R**) or (*S**) for the arsenic stereocentre). For clarity, the ordering in the

descriptors for the diastereomers of **3** is $(R^*),(R^*,R^*)$ and $(S^*),(R^*,R^*)$. The correct ordering for the $(S^*),(R^*,R^*)$ diastereomer is $(R^*),(S^*,S^*)$ [6].

6 *Index Guide to Chemical Abstracts, 76* (1972) para. 203.

7 Further crystallographic details (complete bond lengths and angles, H atom coordinates, temperature factors, structure factors) have been deposited at the Cambridge Crystallographic Data Centre.

8 G. Salem and S.B. Wild, *J. Organomet. Chem., 370* (1989) 33.

9 Note that the following transformations occur with inversion at arsenic: (*R*)-PhMeF$\overset{+}{\text{A}}$s–Fe → (*R*)-PhMeEt(or Bn)$\overset{+}{\text{A}}$s–Fe.

10 E.E. Turner and M.M. Harris, *Q. Rev., 1* (1947) 299.

11 R. Luckenbach, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements,* George Thieme, Verlag Stuttgart, 1973.