

# Stereoselective Synthesis of a Phenylphosphido-Bridged Dimetallic Complex: Crystal and Molecular Structure of

**$[(\underline{R}^*, \underline{R}^*), (\underline{R}^*)]-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{FePHPh}\{\text{Cr}(\text{CO})_5\}]\cdot 2\text{H}_2\text{O}\cdot 0.5\text{CH}_2\text{Cl}_2\cdot 0.5\text{C}_4\text{H}_8\text{O}$**

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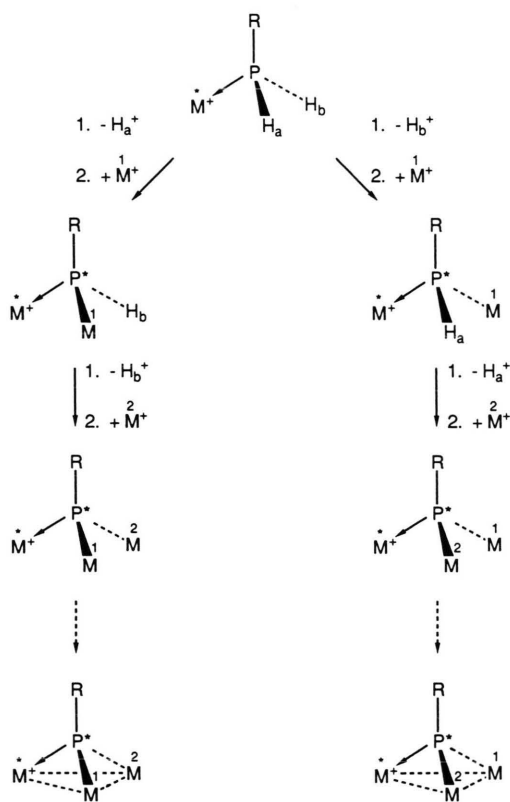
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Stereoselective Synthesis, Dimetallic, Bridging Phenylphosphido, Crystal Structure

Deprotonation of  $(\underline{R}^*, \underline{R}^*)-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PH}_2\text{Ph})]\text{PF}_6$  with *n*-BuLi in tetrahydrofuran at 20 °C, followed by treatment of the intermediate phenylphosphido-iron complex with  $[\text{Cr}(\text{CO})_5(\text{NMe}_3)]$  produces a separable 3:2 mixture of the diastereomers  $[(\underline{R}^*, \underline{R}^*), (\underline{R}^*)]$ - and  $[(\underline{R}^*, \underline{R}^*), (\underline{S}^*)]-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}-\text{PH}(\text{Ph})\rightarrow\text{Cr}(\text{CO})_5]$ . The major component of the mixture crystallizes from dichloromethane-tetrahydrofuran in the atmosphere as the mixed solvate  $[(\underline{R}^*, \underline{R}^*), (\underline{R}^*)]-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}-\text{PH}(\text{Ph})\rightarrow\text{Cr}(\text{CO})_5]\cdot 2\text{H}_2\text{O}\cdot 0.5\text{CH}_2\text{Cl}_2\cdot 0.5\text{C}_4\text{H}_8\text{O}$  in the triclinic space group  $P\bar{1}$  with two formula units in the unit cell; the lattice constants are  $a = 10.933(2)$  Å,  $b = 13.161(4)$  Å,  $c = 15.249(3)$  Å,  $\alpha = 76.83(1)^\circ$ ,  $\beta = 75.62(3)^\circ$ , and  $\gamma = 79.31(1)^\circ$ . In the structure, the pyramidal phenylphosphido group bridges the dissimilar metals *via* relatively long metal-phosphorus bonds, *viz.*,  $\text{Fe}-\text{P} = 2.285(5)$  Å,  $\text{Cr}-\text{P} = 2.511(4)$  Å.

Sequential deprotonations and metallations of diastereotopic P–H atoms in chiral complexes of primary phosphines may lead to single and potentially optically pure diastereomers of phosphido-bridged cluster compounds if complete stereoselectivity can be achieved in each step of the sequence shown in Scheme 1. Recent work on the stereoselective alkylation of phenylphosphine in a chiral iron(II) complex has shown that the first two steps of the sequence are feasible. Thus, we have shown that phenylphosphine is methylated stereoselectively in  $(\underline{R}^*, \underline{R}^*)-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PH}_2\text{Ph})]\text{PF}_6$ ,  $(\underline{R}^*, \underline{R}^*)\text{-I}^1$ , under ambient conditions in the presence of base to give  $[(\underline{R}^*, \underline{R}^*), (\underline{R}^*)]-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PHMePh})]\text{PF}_6$ ,  $[(\underline{R}^*, \underline{R}^*), (\underline{R}^*)]\text{-2}$ , in 60% diastereomeric excess as the thermodynamic product [1]. Furthermore, it was subsequently shown that the secondary phosphine in

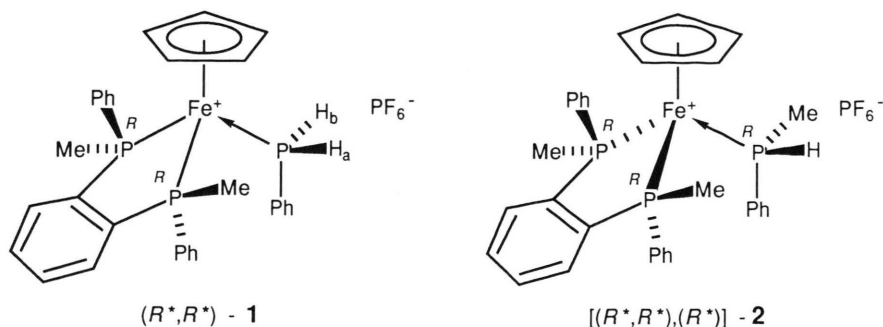


Scheme 1

<sup>1</sup> The stereochemical descriptors used here are consistent with recent Chemical Abstracts Service practice;  $\underline{R}^*$  and  $\underline{S}^*$  refer to the relative configurations of the chiral centres. In the structural diagrams, one of the two enantiomers of each racemate is depicted.

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$[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{R}}^*)]\text{-2}$  could be deprotonated stereospecifically at  $-90^\circ\text{C}$  with complete stereoselectivity and retention of configuration at the chiral phosphorus stereocentre to give  $[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{S}}^*)]\text{-(}\pm\text{)}\text{-}[(\eta^5\text{-C}_5\text{H}_5)\text{-}\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{FePMePh}]$  as demonstrated by the quantitative and highly stereoselective synthesis ( $>99\%$  diastereomeric excess) of  $[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{S}}^*)]\text{-(}\pm\text{)}\text{-}[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{Fe}(\text{PEtMePh})]\text{PF}_6$  when iodoethane was added to the intermediate phosphido-complex at  $-90^\circ\text{C}$ . Reactions of  $[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{R}}^*)]\text{-2}$ , however, when carried out in the temperature range  $-65$  to  $+20^\circ\text{C}$  give mixtures of thermodynamic products due to the relatively low barrier to inversion of the pyramidal  $\text{Fe-PMePh}$  group [ $\Delta G^\ddagger$  (278 K) =  $58.8 \pm 1.2 \text{ kJ mol}^{-1}$  [2]].

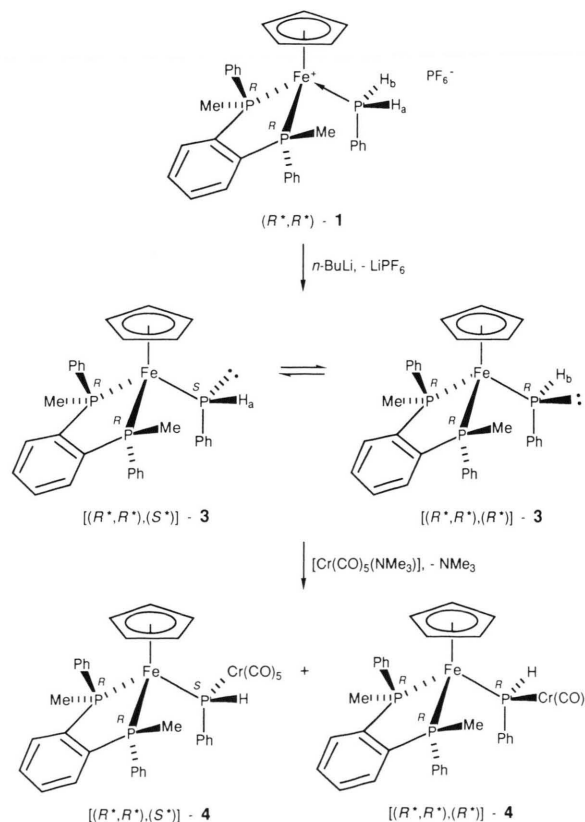
Work in the field of phosphido-bridged transition metal clusters has emanated from the groups of Stelzer [3] and Vahrenkamp [4]. Thus,  $[(\text{CO})_4\text{Fe} \leftarrow \text{PH}_2\text{Ph}]$  reacts with  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Br}]$  in the presence of diethylamine to give  $[(\text{CO})_4\text{Fe} \leftarrow \text{PH}(\text{Ph})\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]$  [3]; and, in a similar fashion,  $[(\text{CO})_4\text{Fe} \leftarrow \text{PH}_2\text{R}]$  (where R = Me, *t*-Bu, or Ph) and  $[\text{Fe}_2(\text{CO})_6(\text{PHR})_2]$  (where R = Me, *t*-Bu, Ph, or *p*-Tol) react with  $[\text{Co}_2(\text{CO})_8]$  or  $[\text{Fe}_2(\text{CO})_{12}]$  to give various phosphido-bridged Fe, Co and Fe, Fe clusters, respectively [4]. In this paper, we describe our work concerning the stereoselective metallation of phenylphosphine in a chiral iron(II) complex.

## Results and Discussion

### Preparations and properties of complexes

Reaction of ( $\underline{\text{R}}^*$ ,  $\underline{\text{R}}^*$ )-**1** with *n*-BuLi in an *n*-hexane-tetrahydrofuran mixture at 20 °C, followed by treatment of the resulting solution of the intermediate phenylphosphido-iron complex with  $[\text{Cr}(\text{CO})_5(\text{NMe}_3)]$  [5], produces a 3:2 mixture of  $[(\text{R}^*, \text{R}^*), (\text{R}^*)]$ - and

$[(\underline{R}^*, \underline{R}^*), (\underline{S}^*)]-(\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{-Fe-PR}(\text{Ph}) \rightarrow \text{Cr}(\text{CO})_5]$ ,  $[(\underline{R}^*, \underline{R}^*), (\underline{R}^*)]$  and  $[(\underline{R}^*, \underline{R}^*), (\underline{S}^*)]$ -**4**, respectively (Scheme 2). The intermediate phenyl phosphido-iron complex can be isolated from tetrahydrofuran as a crystalline *monotetrahydrofuran solvate* [1]. In solution, the intermediate exists as an equilibrium mixture of two diastereomers, epimeric at the chiral phosphido-P stereocentre, with



Scheme 2

$[(R^*, R^*), (S^*)]-3 : [(R^*, R^*), (R^*)]-3 = 4:1$  at  $-65^\circ\text{C}$ . The relative proportions of the Fe, Cr diastereomers were determined from the  $^1\text{H}$  NMR spectra of the crude products before recrystallization. Chemical yields for the mixtures of dimetallic complexes over several runs ranged between 67 and 80%. The diastereomeric ratio  $[(R^*, R^*), (R^*)]-4 : [(R^*, R^*), (S^*)]-4 = 3:2$  differs considerably from the value found for the methylation of  $[(R^*, R^*), (S^*)]/[(R^*, R^*), (R^*)]-3$  between  $-65$  and  $20^\circ\text{C}$ , where  $[(R^*, R^*), (R^*)]-2 : [(R^*, R^*), (S^*)]-2 = 4:1$ ; the major diastereomer of **2** corresponds to stereoselective derivatization of  $H_b$  in  $(R^*, R^*)-1$ , the major diastereomer of **4** to stereoselective derivatization of  $H_a$  (Fig. 2). The mixture can be separated by fractional crystallization from various solvent mixtures. From dichloromethane/*n*-hexane the minor  $(R^*, R^*), (S^*)$  diastereomer crystallizes as red prisms of the fractional dichloromethane solvate  $[(R^*, R^*), (S^*)]-4 \cdot 0.6 \text{CH}_2\text{Cl}_2$ , m. p.  $183\text{--}185^\circ\text{C}$ . The major  $(R^*, R^*), (R^*)$  diastereomer crystallizes from tetrahydrofuran-dichloromethane in an open vessel as the mixed solvate  $[(R^*, R^*), (R^*)]-4 \cdot 2 \text{H}_2\text{O} \cdot 0.5 \text{CH}_2\text{Cl}_2 \cdot 0.5 \text{C}_4\text{H}_8\text{O}$ : red needles, m. p.  $178\text{--}179^\circ\text{C}$ . Crystals of the *mixed solvate* were suitable for X-ray diffraction studies. Because of the tendency of the complex to lose solvent of crystallization in the atmosphere, the crystallographic specimen was transferred to a capillary tube for the X-ray analysis. The separated diastereomers

of **4** can be redissolved in  $\text{CD}_2\text{Cl}_2$  without loss of identity, as determined by  $^1\text{H}$  NMR spectroscopic measurements on solutions of the separated diastereomers.

#### Crystal structure determination

The compound  $[(R^*, R^*), (R^*)](\pm)-[(\eta^5\text{-C}_5\text{H}_5)\{1,2\text{-C}_6\text{H}_4(\text{PMePh})_2\}\text{FePH}(\text{Ph}) \rightarrow \text{Cr}(\text{CO})_5] \cdot 2 \text{H}_2\text{O} \cdot 0.5 \text{CH}_2\text{Cl}_2 \cdot 0.5 \text{C}_4\text{H}_8\text{O}$ ,  $[(R^*, R^*), (R^*)]-4 \cdot 2 \text{H}_2\text{O} \cdot 0.5 \text{CH}_2\text{Cl}_2 \cdot 0.5 \text{C}_4\text{H}_8\text{O}$ , crystallizes triclinic in the space group  $P\bar{1}$  with two molecules of the neutral complex in each unit cell, as well as the solvent molecules. The crystallographic details are given in Table I. Table II gives selected bond distances and angles for the structure, and Table III lists atomic coordinates for the complex at  $20^\circ\text{C}^2$ .

In space group  $P\bar{1}$  both enantiomers of the chiral molecule are present; thus, the complex crystallizes as a racemic compound. The structure of the *S* enantiomer of the complex is depicted in Fig. 1. Disordered solvent molecules occupy voids in the lattice. The identification of the solvent molecules in the lattice is reasonably well established with the final model giving a fit of the observed electron density data that is consistent with the solvents used in the preparation, recrystallization, and isolation of the compound.

Formula	$\text{C}_{38.5}\text{H}_{40}\text{CrClFeO}_{7.5}\text{P}_3$
Mol. wt	858.96
Crystal size	$0.22 \text{ mm} \times 0.21 \text{ mm} \times 0.32 \text{ mm}$
Crystal system, space group	triclinic, $P\bar{1}$
Cell constants	$a = 10.933(2)$ , $b = 13.161(4)$ , $c = 15.249(3) \text{ \AA}$ , $\alpha = 76.83(1)^\circ$ , $\beta = 75.62(3)^\circ$ , $\gamma = 79.31(1)^\circ$ $V = 2050.1 \text{ \AA}^3$
Cell volume	$1.388 \text{ g/cm}^3$
Density (calcd)	$Z = 2$
Formula units per unit cell	Philips PW 1100/20
Diffractometer	MoK $\alpha$ (graphite monochromator)
Radiation	$21(1)^\circ\text{C}$
Temperature	$\theta - 2\theta$ , $\theta = (0.90 + 0.346 \tan \theta)^\circ$
Scan mode, scan width	$1.5 \text{ deg./min}$
Scan speed ( $\theta$ )	2445 with $I > 3\sigma(I)$
Number of unique data	441
Number of parameters	Patterson method
Structure solution	All atoms except H anisotropic
Refinement	[8]
Computer programme	International Tables 1974
Scattering factors, $\Delta f'$ , $\Delta f''$	7.6%
$R = \sum   F_o  -  F_c   / \sum  F_o $	9.4%
$R_w = [\sum w( F_o  -  F_c )^2 / \sum w F_o ^2]^{1/2}$	

Table I. Summary of crystal parameters and experimental data for X-ray diffraction measurements on  $[(R^*, R^*), (R^*)]-4 \cdot 2 \text{H}_2\text{O} \cdot 0.5 \text{CH}_2\text{Cl}_2 \cdot 0.5 \text{C}_4\text{H}_8\text{O}$ .

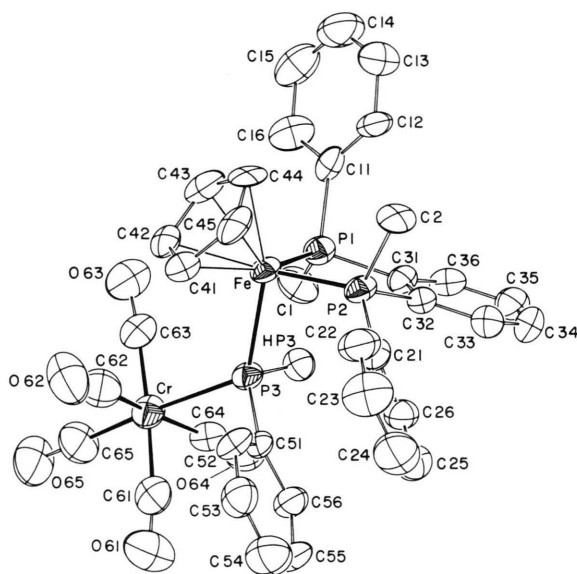


Fig. 1. ORTEP [9] drawing of  $[(R^*,R^*), (R^*)]-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}FePH(Ph) \rightarrow Cr(CO)_5]$  (*S* enantiomer is depicted) showing atomic numbering scheme. Thermal ellipsoids enclose 50% probability levels. Hydrogen atoms with the exception of H(P3) are omitted.

The Fe–P(1) and Fe–P(2) bond distances in  $[(R^*,R^*), (R^*)]-4$ , 2.185(4) and 2.187(3) Å, respectively, are similar in length to those in the related secondary phosphine complex  $[(R^*,R^*), (R^*)]-2 \cdot 0.5 CH_2Cl_2$ , *viz.*, 2.176 Å (av.) [1]. The bridging secondary phosphido-iron bond Fe–P(3) [2.285(5) Å] is longer than the coordinate secondary phosphine-

Table III. Final fractional coordinates.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Fe	0.37310(16)	0.39400(13)	0.23813(13)
Cr	0.37831(20)	0.69613(16)	0.28991(16)
P(1)	0.2941(3)	0.3371(3)	0.3839(3)
P(2)	0.5237(3)	0.2600(3)	0.2508(3)
P(3)	0.4729(3)	0.5095(3)	0.2776(2)
C(1)	0.2413(13)	0.4210(9)	0.4693(10)
C(11)	0.1573(10)	0.2658(10)	0.4083(8)
C(12)	0.1759(11)	0.1603(10)	0.3921(9)
C(13)	0.0684(13)	0.1114(11)	0.4080(12)
C(14)	−0.0490(14)	0.1563(14)	0.4335(13)
C(15)	−0.0699(12)	0.2596(14)	0.4471(11)
C(16)	0.0369(12)	0.3132(12)	0.4328(10)
C(2)	0.5012(12)	0.1427(9)	0.2122(9)
C(21)	0.6892(11)	0.2662(9)	0.1979(9)
C(22)	0.7320(12)	0.2576(11)	0.1050(11)
C(23)	0.8565(15)	0.2649(13)	0.0597(11)
C(24)	0.9425(13)	0.2773(12)	0.1086(13)
C(25)	0.9032(12)	0.2833(11)	0.1987(11)
C(26)	0.7776(11)	0.2818(9)	0.2413(10)
C(31)	0.4105(11)	0.2404(9)	0.4334(9)
C(32)	0.5211(11)	0.2066(9)	0.3719(9)
C(33)	0.6161(12)	0.1286(10)	0.4043(10)
C(34)	0.6001(12)	0.0900(10)	0.4965(11)
C(35)	0.4885(12)	0.1215(10)	0.5605(10)
C(36)	0.3960(11)	0.1979(9)	0.5277(9)
C(41)	0.3669(12)	0.4848(10)	0.1068(10)
C(42)	0.2516(11)	0.5108(9)	0.1682(9)
C(43)	0.1920(12)	0.4218(11)	0.2064(10)
C(44)	0.2700(12)	0.3349(10)	0.1658(10)
C(45)	0.3774(12)	0.3727(11)	0.1055(9)
C(51)	0.6406(11)	0.5231(9)	0.2223(9)
C(52)	0.6841(11)	0.5347(10)	0.1282(9)
C(53)	0.8084(14)	0.5524(11)	0.0854(10)
C(54)	0.8931(14)	0.5635(13)	0.1384(13)
C(55)	0.8478(12)	0.5513(11)	0.2327(11)
C(56)	0.7259(11)	0.5299(10)	0.2748(10)
C(61)	0.5393(13)	0.7412(10)	0.2584(9)
O(61)	0.6326(10)	0.7793(8)	0.2387(8)
C(62)	0.3836(14)	0.7222(11)	0.1624(12)
O(62)	0.3916(12)	0.7413(8)	0.0826(8)
C(63)	0.2154(12)	0.6635(10)	0.3218(9)
O(63)	0.1066(8)	0.6488(8)	0.3409(7)
C(64)	0.3937(11)	0.6536(10)	0.4128(9)
O(64)	0.4045(9)	0.6301(7)	0.4882(7)
C(65)	0.3137(14)	0.8364(10)	0.3030(11)
O(65)	0.2751(11)	0.9195(7)	0.3096(8)
Cl(1) <sup>a</sup>	0.902(2)	0.914(1)	0.332(1)
Cl(2A) <sup>b</sup>	1.099(4)	0.914(4)	0.129(3)
Cl(2B) <sup>b</sup>	1.010(4)	0.845(3)	0.161(3)
C(50A) <sup>b,c</sup>	0.950	0.835	0.216
C(50B) <sup>b,c</sup>	0.920	0.922	0.200
C(51) <sup>a,c</sup>	0.840	0.980	0.190
C(52) <sup>a,c</sup>	0.880	0.970	0.130
C(53) <sup>a,c</sup>	0.980	0.970	0.125
C(54) <sup>a,c</sup>	1.000	0.960	0.210
C(55) <sup>a,c</sup>	0.910	0.950	0.260
OW(4) <sup>a</sup>	0.296(4)	0.131(4)	0.004(3)
OW(5) <sup>a</sup>	0.249(4)	0.058(4)	0.085(3)
OW(6) <sup>a</sup>	0.420(4)	0.025(4)	0.013(4)
OW(7) <sup>a</sup>	0.230(5)	0.033(4)	−0.017(4)

<sup>a</sup> Occupancy 0.5; <sup>b</sup> occupancy 0.25; <sup>c</sup> atom coordinates not refined in least-squares.

Table II. Selected bond lengths (Å) and angles (deg.).

Fe–P(1)	2.185(4)	Cr–P(3)	2.511(4)
Fe–P(2)	2.187(3)	Cr–C(61)	1.876(14)
Fe–P(3)	2.285(5)	Cr–C(62)	1.885(19)
Fe–C(41)	2.095(14)	Cr–C(63)	1.830(13)
Fe–C(42)	2.113(12)	Cr–C(64)	1.870(14)
Fe–C(43)	2.102(14)	Cr–C(65)	1.887(14)
Fe–C(44)	2.103(17)	P(2)–C(2)	1.849(15)
Fe–C(45)	2.092(15)	P(2)–C(21)	1.797(12)
P(1)–C(1)	1.816(16)	P(2)–C(32)	1.815(14)
P(1)–C(11)	1.828(13)	P(3)–C(51)	1.842(11)
P(1)–C(31)	1.802(12)		
P(1)–Fe–P(2)	86.11(14)	Fe–P(1)–C(1)	123.8(4)
P(1)–Fe–P(3)	89.99(16)	Fe–P(1)–C(11)	115.8(5)
P(2)–Fe–P(3)	96.18(15)	Fe–P(1)–C(31)	109.7(4)
Fe–P(3)–Cr	124.2(16)	Fe–P(2)–C(2)	115.3(4)
Fe–P(3)–C(51)	119.9(5)	Fe–P(2)–C(21)	124.0(4)
Cr–P(3)–C(51)	102.2(4)	Fe–P(2)–C(32)	109.5(4)

to-iron bond in the reference compound, which is 2.175(2) Å. The Cr–P bond in  $[(R^*, R^*), (R^*)]-4$  [2.511(4) Å], however, is also longer than the coordinate bonds in related chromium carbonyl compounds, *viz.*, 2.309 Å in  $[Cr(CO)_5(PPh_3)]$  and 2.422 Å in  $[Cr(CO)_5\{P(OPh)_3\}]$  [6]. Thus, the secondary phenyl phosphido-iron group in  $[(R^*, R^*), (R^*)]-4$  appears to be weakened by the transfer of electron density from the phosphorus to the electrophilic  $Cr(CO)_5$  group, with which it forms a relatively weak coordinate bond. Although the P–H proton was not located in the structure analysis, the phosphorus geometry is clearly pyramidal (see Table II) and similar to that found in  $[(R^*, R^*), (R^*)]-2 \cdot 0.5 CH_2Cl_2$  [1].

### $^1H$ and $^{31}P$ NMR spectra

The  $^1H$  NMR data for the diastereomers of **4** are given in the Experimental Section. With knowledge of the structure of  $[(R^*, R^*), (R^*)]-4$  from the X-ray analysis, complete assignments of the  $^1H$  NMR spectra for the two diastereomers of **4** are possible. In each case, the assignments are consistent with those for the corresponding diastereomers of  $(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe(PHMePh)PF_6]$  [1]: the resonances to highest field in the spectra of both complexes correspond to the replacement of  $H_b$  in  $(R^*, R^*)-1$ . Thus, the pair of high-field bis(tertiary phosphine)-PMe resonances, the high-field P–H resonance, and the high-field  $\eta-C_5H_5$  resonance, are due to the minor diastereomer  $[(R^*, R^*), (S^*)]-4$ . The values of  $J(PH)$  for the diastereomers of **4** (260 and 266 Hz) are larger than those found for the corresponding coupling constant in the terminal phenylphosphido complex  $[(\eta^5-C_5H_5)Re(NO)(PPh)(PPh_3)]$  at  $-74^\circ C$  (199 and 209 Hz), but they are smaller than those for the diastereomers of the secondary phosphine complex **2** (333 Hz), consistent with the bonding arrangement  $Fe-PH(Ph) \rightarrow Cr$  in the dimetallic complex **4**.

The observed and calculated  $^{31}P\{^1H\}$  NMR parameters are given in the Experimental Section. The calculated values were obtained according to the method given in ref. [7]. For each diastereomer of **4**, ABX spin systems are observed with the X portions

of the spectra ( $\mu-P$ ) consisting of 1:2:1 triplets because  $J_{AX} \sim J_{BX}$ . When coupled to PH the triplets split into doublets of triplets with  $^1J_{PH} = 266$  Hz (for  $[(R^*, R^*), (S^*)]-4$ ) or  $^1J_{PH} = 260$  Hz (for  $[(R^*, R^*), (R^*)]-4$ ).

### Chemical reactivity of diastereomers of **4**

Attempts to deprotonate either diastereomer of **4** with *n*-BuLi, MeLi, (*iso*-Pr)<sub>2</sub>NLi, or *t*-BuOK in tetrahydrofuran were unsuccessful. In contrast, the compound  $[(CO)_4Fe \leftarrow PH(Ph) \rightarrow Fe(CO)_2(\eta^5-C_5H_5)]$  is lithiated by MeLi, although the lithium derivative does not react with MeI or Me<sub>3</sub>SiCl [3]. It is not obvious from the structure of  $[(R^*, R^*), (R^*)]-4$  why the P–H proton should be so unreactive.

## Experimental Section

### 1. General methods

Reactions were performed under a positive pressure of argon.  $^1H$  and  $^{31}P\{^1H\}$  NMR spectra were recorded on a Bruker CXP 200 spectrometer at  $20^\circ C$  with chemical shift values being quoted relative to Me<sub>4</sub>Si ( $^1H$ ) or external 85% H<sub>3</sub>PO<sub>4</sub> ( $^{31}P\{^1H\}$ ). Elemental analyses were performed by staff within the Research School of Chemistry. Literature methods were used to prepare the compounds  $(R^*, R^*)-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}-Fe(PH_2Ph)]PF_6$  [1] and  $[Cr(CO)_5(NMe_3)]$  [5].

### 2. Synthesis and separation of diastereomers of $(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe-PH(Ph) \rightarrow Cr(CO)_5]$

A suspension of 3.52 g (5.04 mmol) of  $(R^*, R^*)-(\pm)-[(\eta^5-C_5H_5)\{1,2-C_6H_4(PMePh)_2\}Fe(PH_2Ph)]PF_6$ ,  $(R^*, R^*)-1$ , in 50 ml tetrahydrofuran was treated with 3.2 ml of a 1.6 M solution of *n*-BuLi in *n*-hexane (5.12 mmol) at  $20^\circ C$ . The solid dissolved to give a red solution of the corresponding phenylphosphido-iron complex  $[(R^*, R^*), (S^*)]/[(R^*, R^*), (R^*)]-3$  upon the addition of the base. After 30 min, 1.26 g (5.04 mmol) of  $[Cr(CO)_5(NMe_3)]$  was added to the reaction mixture. No obvious change in colour occurred. After *ca.* 6 h the solvent was removed; the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and the solution was washed several times with water to remove LiPF<sub>6</sub>. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated and dried (MgSO<sub>4</sub>) and then it was evaporated to dryness. The crude product was thus isolated as a viscous red oil. The  $^1H$  NMR spectrum of the oil in CD<sub>2</sub>Cl<sub>2</sub> indicated a 3:2 mixture of  $[(R^*, R^*), (R^*)]-$  and  $[(R^*, R^*), (S^*)]-4$ . Chromatography (CH<sub>2</sub>Cl<sub>2</sub> as solvent, Kieselgur 60 H, 15 cm column) and evaporation of the solvent

<sup>2</sup> Further information on the structure determination have been deposited as Supplementary Publication No. CSD 53846. Copies may be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, FRG.

yielded a mixture of both diastereomers of **4** as a red solid (67–80% yield over several runs). Recrystallization of this mixture from  $\text{CH}_2\text{Cl}_2/n$ -hexane afforded crystals of the less soluble minor  $[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{S}}^*)]$  diastereomer, which crystallized with  $0.6 \text{ CH}_2\text{Cl}_2$ .

Red prisms. Yield (not optimized): *ca.* 0.8 g (*ca.* 20%), m.p.: 183–185 °C.

$\text{C}_{36.6}\text{H}_{32.2}\text{Cl}_{1.2}\text{CrFeO}_5\text{P}_3$  (795.4)

Calcd C 55.3 H 4.1 Cl 5.4 P 11.7,

Found C 55.5 H 4.2 Cl 5.3 P 12.5.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta(\text{PMe}) = 1.14$ , dd, 3H,  $^2J(\text{PH}) = 8.8$ ;  $\delta(\text{PMe}) = 1.94$ , dd, 3H,  $^2J(\text{PH}) = 7.5$ ;  $\delta(\text{PH}) = 2.81$ , dm, 1H,  $^1J(\text{PH}) = 266$ ;  $\delta(\text{C}_5\text{H}_5) = 4.41$ , q, 5H,  $^3J(\text{PH}) = 2$ ;  $\delta(\text{C}_6\text{H}_5, \text{C}_6\text{H}_4) = 6.7$ – $7.8$ , m, 14H.

$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta(\text{P}_\text{A}) = 78.4$ ,  $|J_{\text{AB}}| = 45.8$ ,  $|J_{\text{AX}}| = 34.9$ ;  $\delta(\text{P}_\text{B}) = 77.3$ ,  $|J_{\text{AB}}| = 45.8$ ,  $|J_{\text{BX}}| = 34.9$ ;  $\delta(\text{P}_\text{X}) = -27.3$ ,  $|J_{\text{AX}}| = 34.9$ ,  $|J_{\text{BX}}| = 34.9$ .

The mother liquor from the isolation of  $[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{S}}^*)]\text{-4} \cdot 0.6 \text{ CH}_2\text{Cl}_2$  was evaporated to dryness, and the residue was recrystallized from dichloromethane-tetrahydrofuran mixture in an open

vessel. In this manner, the major diastereomer crystallized as the *mixed solvate*  $[(\underline{\text{R}}^*, \underline{\text{R}}^*), (\underline{\text{R}}^*)]\text{-4} \cdot 2 \text{ H}_2\text{O} \cdot 0.5 \text{ CH}_2\text{Cl}_2 \cdot 0.5 \text{ C}_4\text{H}_8\text{O}$ .

Red needles. Yield (not optimized): *ca.* 0.6 g (*ca.* 14%), m.p. 178–179 °C.

$\text{C}_{38.5}\text{H}_{40}\text{CrClFeO}_{7.5}\text{P}_3$  (858.96)

Calcd C 57.8 H 4.8 P 12.3,

Found C 57.2 H 4.7 P 11.6.

$^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta(\text{PMe}) = 1.88$ , dd, 3H,  $^2J(\text{PH}) = 7$ ;  $\delta(\text{PMe}) = 2.22$ , dd, 3H,  $^2J(\text{PH}) = 8$ ;  $\delta(\text{PH}) = 2.84$ , dm, 1H,  $^1J(\text{PH}) = 260$ ;  $\delta(\text{C}_5\text{H}_5) = 4.43$ , q, 5H,  $^3J(\text{PH}) = 2$ ;  $\delta(\text{C}_6\text{H}_5, \text{C}_6\text{H}_4) = 6.7$ – $7.8$ , m, 14H.

$^{31}\text{P}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta(\text{P}_\text{A}) = 80.8$ ,  $|J_{\text{AB}}| = 43.7$ ,  $|J_{\text{AX}}| = 33.8$ ;  $\delta(\text{P}_\text{B}) = 79.3$ ,  $|J_{\text{AB}}| = 43.7$ ,  $|J_{\text{BX}}| = 34.5$ ;  $\delta(\text{P}_\text{X}) = -26.4$ ,  $|J_{\text{AX}}| = 33.8$ ,  $|J_{\text{BX}}| = 34.5$ .

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