Stereoselective Methylation of Co-ordinated Phenylphosphine: Crystal and Molecular Structure of [(*R**,*R**),(*R**)]-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}FePHMePh]PF_6·0.5CH_2Cl_2

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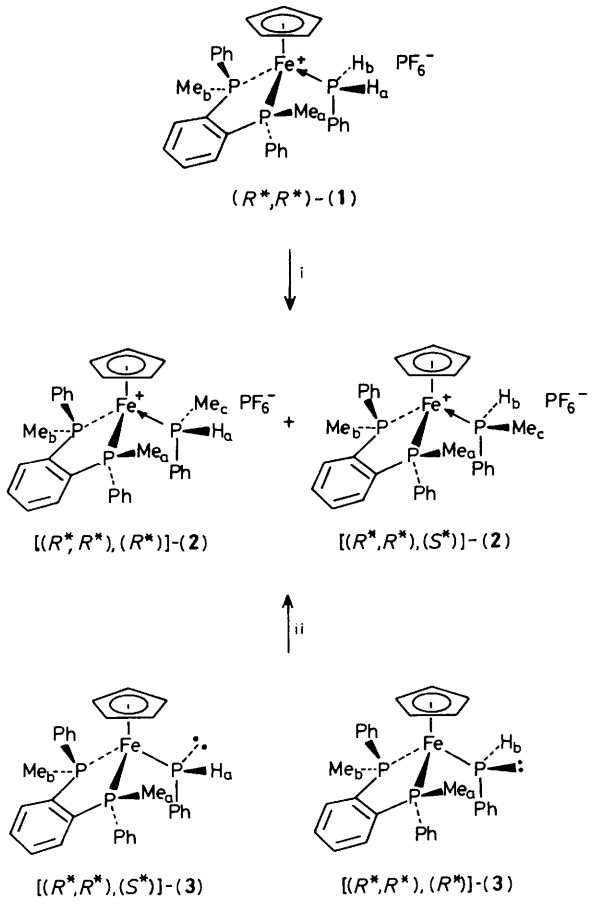
Reaction of (*R**,*R**)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}FePH$_2$Ph]PF_6 with iodomethane in the presence of triethylamine at 20 °C produces a separable 4 : 1 mixture of [(*R**,*R**),(*R**)]- and [(*R**,*R**),(*S**)]-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}-FePHMePh]PF_6; the crystal and molecular structure of the major [(*R**,*R**),(*R**)] diastereoisomer is reported.

Terminal phosphido–metal compounds (M–PX_2) are potentially important reagents for the synthesis of co-ordinated phosphines (M ← PX_3) and related compounds. Depending upon substituents, phosphido–metal groups are pyramidal and electronegative (M–PX_2) or planar and electropositive (M=PX_2).[1,2] Indeed, the phenylphosphido group in [$(Ph_3P)_2(CO)_2ClOsPHPh$] is amphoteric, reacting with both nucleophiles (OMe^-) and electrophiles (H^+ and Me^+) to give substituted phosphine complexes.[2] The versatility of phosphido–metal compounds as reagents will be greatly increased, however, if steric control, as well as electronic control, over reactivity is possible. To this end, we have examined the stereoselectivity of the base-catalysed methylation of the primary phosphine ligand in (*R**,*R**)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}FePH$_2$Ph]PF_6, (*R**,*R**)-(**1**), and of the stoicheiometric methylation of the phenylphosphido group in (*R**,*R**)-[(η-C_5H_5){1,2-C_6H_4(PMePh)$_2$}FePHPh]·thf, (*R**,*R**)-(**3**) (thf = tetrahydrofuran).

Phenylphosphine complex (*R**,*R**)-(**1**)†‡ is cleanly conver-

† This compound was obtained in 85% yield from phenylphosphine and (*R**,*R**)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}FeNCMe]PF_6 by heating the two in methanol; the acetonitrile complex was prepared with use of a method described by Treichel *et al.* for similar compounds.[3] All new compounds analysed satisfactorily.

‡ The stereochemical descriptors used here are consistent with recent Chemical Abstracts Service indexing practice; *R** and *S** refer to the relative configurations of the chiral centres.



Scheme 1. *Reagents and conditions;* i, MeI, Et_3N, thf, 20 °C; ii, MeI, thf, −65 or 20 °C. M.p. and selected ^1H n.m.r. data (CD_2Cl_2 at 20 °C): (R^*,R^*)-(**1**) (m.p. 223 °C, decomp.) δ 2.22 (d, $^2J_{PH}$ 8 Hz, PMe_a), 2.26 (d, $^2J_{PH}$ 8 Hz, PMe_b), 4.22 (q, $^3J_{PH}$ 2 Hz, C_5H_5), 4.65 (d of m, $^1J_{PH}$ 344 Hz, PH_a), and 5.40 (d of m, $^1J_{PH}$ 344 Hz, PH_b); $[(R^*,R^*),(R^*)]$-(**2**)·0.5CH_2Cl_2 (m.p. 230 °C, decomp.) δ 0.64 (d of d, $^2J_{PH}$ 10, $^3J_{HH}$ 6 Hz, PMe_c), 1.60 (d, $^2J_{PH}$ 9 Hz, PMe_a), 2.23 (d, $^2J_{PH}$ 8 Hz, PMe_b), 4.39 (q, $^3J_{PH}$ 2 Hz, C_5H_5), and 4.65 (d of m, $^1J_{PH}$ 333 Hz, PH_a); $[(R^*,R^*),(S^*)]$-(**2**)·Me_2CO (m.p. 138—140 °C) δ 1.55 (d of d, $^2J_{PH}$ 9, $^3J_{HH}$ 6 Hz, PMe_c), 2.12 (s, Me_2CO), 2.20 (d, $^2J_{PH}$ 9 Hz, PMe_a), 2.32 (d, $^2J_{PH}$ 8 Hz, PMe_b), 4.36 (q, $^3J_{PH}$ 2 Hz, C_5H_5), and 4.83 (d of m, $^1J_{PH}$ 333 Hz, PH_b); $[(R^*,R^*),(S^*)]$-(**3**), $[(R^*,R^*),(R^*)]$-(**3**)·thf (m.p. 169—171 °C) δ ([$^2H_8$]thf at −65 °C) 1.90 (d, $^2J_{PH}$ 8 Hz, PMe_a, major), 2.13 (d, $^2J_{PH}$ 7 Hz, PMe_b major), 2.15 (d, $^2J_{PH}$ 8 Hz, PMe_a, minor), 2.39 (d, $^2J_{PH}$ 8 Hz, PMe_b, minor), 3.65 (s, C_5H_5, major), and 3.71 (s, C_5H_5, minor); PH resonances obscured.

Only one of the enantiomers of each complex is shown.

ted into a 4 : 1 mixture of the secondary phosphine diastereoisomers $[(R^*,R^*),(R^*)]$- and $[(R^*,R^*),(S^*)]$-(**2**) by treatment with iodomethane in the presence of triethylamine at 20 °C (Scheme 1). The same mixture of diastereoisomers was obtained in reactions at lower temperatures, but the rates of methylation were lower. The diastereoisomers were separated by fractional crystallization. The major diastereoisomer crystallized from dichloromethane–n-hexane (as a hemidichloromethane solvate) and the more soluble minor diastereoisomer from acetone–diethyl ether (as a monoacetone solvate). Both compounds are stable to air in the solid state, and in solution. The cation of the major diastereoisomer has the structure shown in Figure 1, as determined by a single

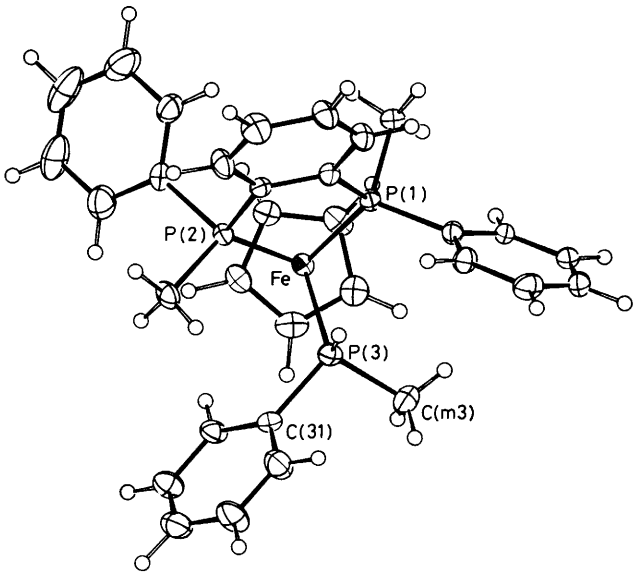


Figure 1. Molecular structure of the cation in $[(R^*,R^*),(R^*)]$-(**2**)·0.5CH_2Cl_2. Selected bond distances and angles are as follows: Fe–P(1) 2.176(2), Fe–P(2) 2.183(2), Fe–P(3) 2.175(2) Å, P(1)–Fe–P(2) 86.3(1), P(1)–Fe–P(3) 92.7(1), P(2)–Fe–P(3) 93.5(1), Fe–P(3)–C(m3) 116.6(2), Fe–P(3)–C(31) 121.2(2), and C(31)–P(3)–C(m3) 102.1(3)°.

crystal *X*-ray analysis of $[(R^*,R^*),(R^*)]$-(**2**)·0.5CH_2Cl_2.§ The secondary phosphine proton was not located, although the pyramidal geometry of the phosphorus stereocentre was clearly evident from the analysis.

In a parallel investigation, (R^*,R^*)-[(η^5-C_5H_5){1,2-C_6H_4($PMePh)_2$}FePHPh]·thf, (R^*,R^*)-(**3**), was prepared from (R^*,R^*)-(**1**) and KOBu^t, and then it was methylated under various conditions. The ^1H n.m.r. spectrum of (R^*,R^*)-(**3**) in [$^2H_8$]tetrahydrofuran at −65 °C contains sets of resonances in the ratio 4 : 1 due to the diastereoisomers $[(R^*,R^*),(S^*)]$- and $[(R^*,R^*),(R^*)]$-(**3**). As the temperature of the solution was raised both sets of signals broadened, coalesced, and sharpened with $\Delta G^{\ddagger}$ (253 K) = 60 ± 4 kJ mol^{-1} being calculated from $\Delta\delta(C_5H_5)$.[4] The relatively low inversion barrier of the phenylphosphido–iron group in (R^*,R^*)-(**3**) is consistent with the electronegative substituents present,[6] and with the value determined for the same group in [(η^5-C_5H_5)(Ph_3P)(NO)RePHPh] [$\Delta G^{\ddagger}$ (243 K) = 48.1 ± 0.4 kJ mol^{-1}].[7] Treatment of the equilibrium mixture of phenylphosphido–iron complexes with iodomethane at temperatures in the range −65 to 20 °C gave, after a work-up involving treatment with aqueous NH_4PF_6 at 20 °C, $[(R^*,R^*),(R^*)]$-(**2**) and $[(R^*,R^*),(S^*)]$-(**2**) with a diastereoselectivity corresponding to the equilibrium phenylphosphido–iron concentrations at −65 °C (4 : 1), which is coincident with the value obtained for the methylation of (R^*,R^*)-(**1**) in the presence of triethylamine at 20 °C. Thus, the diastereoselectivity of the

§ *Crystal data* $[(R^*,R^*),(R^*)]$-(**2**)·0.5CH_2Cl_2, $C_{32.5}H_{35}ClF_6FeP_4$, M = 755.8, monoclinic, space group $P2_1/n$ (non-standard No. 14), a = 11.013(9), b = 26.143(14), c = 11.551(4) Å, β = 90.65°, U = 3325.5 Å^3, D_c = 1.51 g cm^{-3} for Z = 4, $F(000)$ = 1548, μ(Mo-K_α) = 7.0 cm^{-1}. In space group $P2_1/n$ both enantiomers are present. Of 4288 measured intensities (Nicolet XRD P3, −150 °C), 2678 were considered observed [$I>3\sigma(I)$]. After Lorentz, polarisation, and absorption corrections, the structure was solved by the heavy atom method. Subsequent refinement (full-matrix, least-squares) afforded R and R' values of 0.051 and 0.046, respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

methylation is determined by the concentrations of the phenylphosphido–iron diastereoisomers at equilibrium (thermodynamic control), the rate of interconversion between the diastereoisomers being faster than the rates of methylation at temperatures above −65 °C. Complex (R^*,R^*)-(**3**) in tetrahydrofuran did not react appreciably with iodomethane below −65 °C.

The stereospecific alkylation of a primary phosphine ligand in a chiral complex is a potentially attractive route to the asymmetric synthesis of a co-ordinated secondary phosphine, and, indeed, to the optically pure secondary phosphine itself if a stereospecific displacement from the metal is effected. Accordingly, we have isolated [(*S*,*S*),(*S*)]-(**2**)·0.5H_2O, $[\alpha]_D$ −268° (CH_2Cl_2), and [(*S*,*S*),(*R*)]-(**2**), $[\alpha]_D$ −51° (CH_2Cl_2), the first complexes containing resolved unidentate secondary phosphine ligands.¶

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¶ The optically active complexes were isolated by the fractional crystallisation of the products of the reaction of (*S*, *S*)-(**1**) with MeI in the presence of triethylamine.

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