# Stereoselective Syntheses of Co-ordinated Phosphines: Stereospecific Generation and Alkylation of the Tertiary Phosphido–Metal Group in (*R**,*R**)-[($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($PMePh_2$)$_2$}FePMePh] at −90 °C

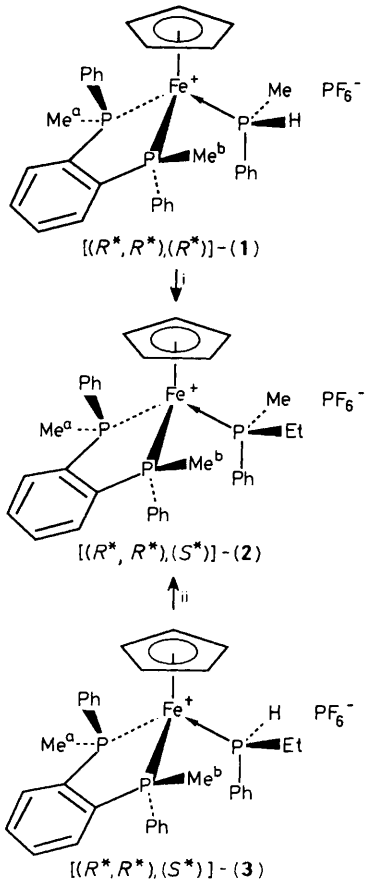
**Geoffrey Salem and S. Bruce Wild***

*Research School of Chemistry, Australian National University, Canberra, A.C.T. 2601, Australia*

Deprotonation of [(*R**,*R**),(*R**)]-[($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($PMePh_2$)$_2$}FePHMePh]$PF_6$ (**1**) with $KOBu^t$ below −90 °C, followed by treatment of the intermediate tertiary phosphido–metal complex with iodoethane at the same temperature, produces [(*R**,*R**),(*S**)]-[($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($PMePh_2$)$_2$}FePEtMePh]$PF_6$ in >99% diastereoisomeric excess.

Highly selective alkylations of terminal phosphido–metal groups (M–$PX_2$) are required for syntheses of macrocyclic poly(secondary or tertiary phosphines) on metal ions in order to avoid separations of complex mixtures of diastereoisomeric products.[1] In recent work, we showed that the methylation of the secondary phosphido–metal group Fe–PHPh in the complex (*R**,*R**)-[($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($PMePh_2$)$_2$}-FePHPh]·thf (thf = tetrahydrofuran) is stereoselective in the temperature range −65 to +20 °C, giving separable mixtures of the thermodynamic secondary phosphine diastereoisomers [(*R**,*R**),(*R**)]- and [(*R**,*R**),(*S**)]-(**1**)† {[(*R**,*R**),(*R**)] : [(*R**,*R**),(*S**)] = 4 : 1}.[2] We now report that the asymmetric tertiary phosphido–metal group Fe–PMePh is generated stereospecifically by deprotonation of [(*R**,*R**),(*R**)]-(**1**)·0.5$CH_2Cl_2$[2] with $KOBu^t$ below −90 °C, and moreover, that it is reprotonated or ethylated with retention of configuration at this temperature, giving kinetic products [(*R**,*R**),(*R**)]-(**1**) or [(*R**,*R**),(*S**)]-(**2**) in >99% diastereoisomeric excess (d.e.).‡ Treatment of [(*R**,*R**),(*S**)]-(**3**)§ with $KOBu^t$–MeI below −90 °C gives [(*R**,*R**),(*S**)]-(**2**) in >99% d.e. However, the barrier to inversion of the Fe–PMePh group in the terminal phosphido–metal intermediate (*R**,*R**)-[($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($PMePh_2$)$_2$}-FePMePh]¶ is relatively low [$\Delta G^{\ddagger}$(278 K) = 58.8 ± 1.2 kJ $mol^{-1}$],[3] and reactions at temperatures above −65 °C give mixtures of the thermodynamic products for both protonation and ethylation in the ratio [(*R**,*R**),(*R**)] : [(*R**,*R**),(*S**)] = 4.5 : 1.

These results auger well for stereoselective syntheses of poly(secondary or tertiary phosphines) on metal ions; recent results have shown that metal complexes can be highly effective resolving agents, protecting reagents, and chiral auxiliaries for stereoselective syntheses of macrocyclic quadridentate tertiary arsines.[4]




**Scheme 1.** *Reagents and conditions:* i, $KOBu^t$, EtI, tetrahydrofuran (thf), −90 °C; ii, $KOBu^t$, MeI, thf, −90 °C.

M.p. and selected $^1$H n.m.r. data ($CD_2Cl_2$ at 20 °C): [(*R**,*R**),(*R**)]-(**1**)·0.5$CH_2Cl_2$, see ref. 2; [(*R**,*R**),(*S**)]-(**2**): m.p. 158—160 °C; δ 0.62 (d of t, $^3J_{PH}$ 14, $^3J_{HH}$ 7 Hz, PCHH′*Me*), 0.64 (d, $^2J_{PH}$ 8 Hz, PMe), 1.40 (m, PC*H*H′Me), 1.76 (m, PCH*H*′Me), 2.09 (d, $^2J_{PH}$ 8 Hz, PMe$^a$), 2.45 (d, $^2J_{PH}$ 8 Hz, PMe$^b$), 4.10 (q, $^3J_{PH}$ 2 Hz, $C_5H_5$); [(*R**,*R**),(*S**)]-(**3**): m.p. 234—236 °C; δ 0.69 (d of t, $^3J_{PH}$ 15 Hz, $^3J_{HH}$ 7 Hz, PCHH′*Me*), 1.26 (m, PC*H*H′Me), 1.58 (m, PCH*H*′Me), 2.18 (d, $^2J_{PH}$ 8 Hz, PMe$^a$), 2.40 (d, $^2J_{PH}$ 8 Hz, PMe$^b$), 4.22 (q, $^3J_{PH}$ 2 Hz, $C_5H_5$), 4.37 (d of m, $^1J_{PH}$ 341 Hz, PH).

The *R* enantiomer of each diastereoisomer is shown.

*Received, 10th April 1987; Com. 473*

## References

1 E. P. Kyba, C. N. Clubb, S. B. Larson, V. J. Schueler, and R. E. Davis, *J. Am. Chem. Soc.*, 1985, **107**, 2141; D. J. Brauer, F. Gol, S. Hietkamp, H. Peters, H. Sommer, O. Stelzer, and W. S. Sheldrick, *Chem. Ber.*, 1986, **119**, 349; M. Ciampolini, N. Nardi, P. L. Orioli, S. Mangani, and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1985, 1425.

2 G. T. Crisp, G. Salem, F. S. Stephens, and S. B. Wild, *J. Chem. Soc., Chem. Commun.*, 1987, 600.

3 G. Binsch and H. Kessler, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 411.

4 P. G. Kerr, P.-H. Leung, and S. B. Wild, *J. Am. Chem. Soc.*, 1987, **109**, 4321.

† 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.

‡ The fully characterized [(*R**,*R**),(*S**)] diastereoisomer of (**1**) or the [(*R**,*R**),(*R**)] diastereoisomer of (**2**) could not be detected by high resolution $^1$H n.m.r. spectroscopy (200 MHz).

§ This compound, obtained by reaction of (*R**,*R**)-[($\eta^5$-$C_5H_5$){1,2-$C_6H_4$($PMePh_2$)$_2$}FeNCMe]$PF_6$ and (±)-PHEtPh in boiling methanol, was separated from its diastereoisomer by fractional crystallization from an acetone–diethyl ether mixture.

¶ This compound was isolated by deprotonation of [(*R**,*R**),(*R**)]-(**1**)·0.5$CH_2Cl_2$ with $KOBu^t$ in tetrahydrofuran (thf) at 20 °C.