bond suggests **8c,d** as a source of new, hitherto unknown products.

Acknowledgment. Support of this work by Deutsche Forschungsgemeinschaft, Bonn/Bad Godesberg, by Fonds der Chemischen Industrie, Frankfurt/Main, and by Degussa AG is gratefully acknowledged. Thanks are also due to Prof. Dr. J. Strähle for providing the facilities for X-ray investigations and A. Carvill for reading the manuscript.

Registry No. 1, 52621-15-5; **2a**, 17656-09-6; **2b**, 670-54-2; **3a**, 122145-45-3; **3b**, 122145-46-4; **4c**, 762-42-5; **4d**, 762-21-0; **4e**, 692-50-2; **8c**, 122145-47-5; **8d**, 122145-48-6; **9e**, 122171-17-9; **10c**, 122145-49-7; **10d**, 122145-50-0; **13c**, 6237-59-8; **13d**, 91620-99-4.

Supplementary Material Available: Tables of least-squares planes, final positional and anisotropic parameters, and interatomic distances and angles for **8d** (7 pages); a listing of observed and calculated structure factors for **8d** (21 pages). Ordering information is given on any current masthead page.

Stereoselective Syntheses of Coordinated Secondary and Tertiary Phosphines. Crystal and Molecular Structure of $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$

Geoffrey T. Crisp, Geoffrey Salem, and S. Bruce Wild*

Research School of Chemistry, Australian National University, Canberra, Australian Capital Territory 2601, Australia

Frederick S. Stephens

School of Chemistry, Macquarie University, Sydney, New South Wales 2109, Australia

Received March 2, 1989

Reaction of (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PH_2Ph)]PF_6$ with methyl or ethyl iodide in the presence of triethylamine at 20 °C produces separable mixtures of the corresponding alkyl derivatives $[(R^*,R^*),(R^*)]$-(±)- and $[(R^*,R^*),(S^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHRPh)]PF_6$ (R = Me or Et) with ca. 3.5:1 diastereoselectivity in favor of the $[(R^*,R^*),(R^*)]$ diastereomer in each case. Major diastereomer $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$ crystallizes in the monoclinic space group $P2_1/n$ (nonstandard No. 14) with a = 11.013 (9) Å, b = 26.143 (14) Å, c = 11.551 (4) Å, β = 90.65 (5)°, V = 3325.5 Å^3, d_{calcd} = 1.51 g cm^{-3}, Z = 4, and R = 0.051 (R_w = 0.046) for 2768 data having $[I > 3\sigma(I)]$. The secondary phosphido–iron complex (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FePHPh]$·thf was isolated by deprotonation of the primary phosphine compound with KOBu-t in tetrahydrofuran; variable-temperature ^{1}H NMR spectra of this complex in [$^2H_8$]tetrahydrofuran gave $\Delta G^{\ddagger}$ (253 K) = 60 ± 4 kJ mol^{-1} for the inversion barrier of the pyramidal phenylphosphido–iron phosphorus stereocenter in the molecule with the diastereomer ratio $[(R^*,R^*),(R^*)]$:$[(R^*,R^*),(S^*)]$ = 4.5:1 at the slow-exchange limit (−65 °C). Alkylations of the secondary phenylphosphido–iron intermediate at −65 °C give secondary phosphine complexes with diastereoselectivities corresponding to the concentrations of secondary phosphido–iron diastereomers at equilibrium (4.5:1). At −95 °C, however, deprotonation of the secondary phosphine complex $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$ is stereospecific giving the tertiary phosphido–iron complex $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FePMePh]$ with complete stereoselectivity, as demonstrated by the quantitative recovery of the diastereomerically pure starting material following acidification of the reaction mixture at this temperature. Alkylations of the tertiary phosphido–iron complex, generated and maintained at −95 °C, also proceed with retention of configuration and complete stereoselectivity; reactions above this temperature give mixtures of thermodynamic products because of the relatively low barrier to inversion of the pyramidal phosphorus stereocenter in the intermediate tertiary phosphido–iron complex ($\Delta G^{\ddagger}$ (278 K) = 59 ± 2 kJ mol^{-1}). The corresponding optically active complexes of (±)-methylphenylphosphine have also been prepared, the first examples of complexes containing resolved secondary phosphines.

Introduction

Primary and secondary phosphine–metal complexes[1,2] are readily deprotonated giving terminal phosphido–metal complexes.[2-6] Depending upon substituents, the terminal phosphido–metal groups in the complexes are pyramidal and nucleophilic (M—PX_2) or planar and electrophilic (M^-=P^+X_2).[4-6] For example, pyramidal phosphido–metal complexes react with metal ions to give bridging phosphido–metal complexes[3,7] and with alkyl halides to give substituted phosphine–metal complexes.[6] Secondary

(1) Kosolopoff, C. M.; Maier, L. *Organophosphorus Compounds*; Wiley: New York, 1972; Vol. 1. Stelzer, O. *Top. Phosphorus Chem.* **1977**, *9*, 1.

(2) Bohle, D. S.; Roper, W. R. *Organometallics* **1986**, *5*, 1607 and references cited therein.

(3) Kraihanzel, C. S. *J. Organomet. Chem.* **1974**, *73*, 137.

(4) Bohle, D. S.; Jones, T. C.; Richard, C. E. F.; Roper, W. R. *Organometallics* **1986**, *5*, 1612 and references cited therein.

(5) Malisch, W.; Angerer, W.; Cowley, A. H.; Norman, W. C. *J. Chem. Soc., Chem. Commun.* **1985**, *5*, 1811. Buhro, W. E.; Georgiou, S.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 3346. Karsch, H. H.; Reischar, H. U.; Huber, B.; Muller, G.; Malisch, W.; Jorg, K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 455.

(6) Weber, L.; Reizig, K.; Boese, R. *Chem. Ber.* **1985**, *118*, 1193. Weber, L.; Reizig, K.; Boese, R. *Organometallics* **1985**, *4*, 1890. Malisch, W.; Jorg, K.; Gross, E.; Schmeusser, M.; Meyer, A. *Phosphorus Sulfur* **1986**, *26*, 25. Angerer, W.; Sheldrick, W. S.; Malisch, W. *Chem. Ber.* **1985**, *118*, 1261. Weber, L.; Reizig, K.; Frebel, M. *Chem. Ber.* **1986**, *119*, 1857. Weinand, R.; Werner, H. *Chem. Ber.* **1986**, *119*, 2055. Grobe, J.; Haubold, R. *Z. Anorg. Allg. Chem.* **1986**, *534*, 100. Neif, F.; Mercier, F.; Mathey, F. *J. Organomet. Chem.* **1987**, *328*, 349.

(7) Scherer, O. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924. Hey, E.; Willis, A. C.; Wild, S. B. *Z Naturfursch.*, in press.

0276-7333/89/2308-2360$01.50/0

Table I. Selected ^{1}H NMR Chemical Shift Data for (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FeL]PF_6$ (Type 1 Complexes) and for (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FePRPh]$ (Type 2 Complexes)[a]

			1,2-$C_6H_4(PMePh)_2$		L or R		
compound	L or R	$\delta(\eta^5\text{-}C_5H_5)$	δ(PMe)	δ(PMe)	δ(PH)	δ(PMe)	δ(PCH_2Me)
			For Type 1 Complexes				
(R^*,R^*)-1	MeCN	4.17 t	2.10 d	2.34 d			
(R^*,R^*)-2	PH_2Ph	4.22 q	2.22 d	2.26 d	4.65 dm 5.40 dm		
$[(R^*,R^*),(R^*)]$-3	PHMePh	4.39 q	1.60 d	2.23 d	4.65 dm	0.64 dd	
$[(R^*,R^*),(S^*)]$-3	PHMePh	4.36 q	2.20 d	2.32 d	4.83 dm	1.55 dd	
$[(R^*,R^*),(R^*)]$-4	PHEtPh	4.38 q	1.56 d	2.20 d	4.29 dt		0.47 m
$[(R^*,R^*),(S^*)]$-4	PHEtPh	4.22 q	2.18 d	2.40 d	4.37 dm		0.69 dt
$[(R^*,R^*),(R^*)]$-5	PHBnPh	4.50 q	1.45 d	2.23 d	4.42 dt		
$[(R^*,R^*),(S^*)]$-5	PHBnPh	4.42 q	2.16 d	2.51 d	4.67 dm		
$[(R^*,R^*),(R^*)]$-6	PEtMePh	4.10 q	2.07 d	2.32 d		1.40 d	0.46 m
$[(R^*,R^*),(S^*)]$-6	PEtMePh	4.10 q	2.09 d	2.45 d		0.64 d	0.62 dt
$[(R^*,R^*),(R^*)]$-7	PBnMePh	4.24 q	2.14 d	2.22 d		1.06 d	
$[(R^*,R^*),(S^*)]$-7	PBnMePh	4.24 q	2.13 d	2.61 d		0.46 d	
			For Type 2 Complexes[b]				
$[(R^*,R^*),(R^*)]$-8	H (1:4.5)	3.71 s	2.15 d	2.39 d	*c*		
$[(R^*,R^*),(S^*)]$-8	H	3.65 s	1.90 d	2.13 d	*c*		
$[(R^*,R^*),(R^*)]$-9	Me (4.5:1)	4.04 s	1.97 d	2.33 d		0.43 d	
$[(R^*,R^*),(S^*)]$-9	Me	3.91 s	2.28 d	2.35 d		1.60 d	
$[(R^*,R^*),(R^*)]$-10[d]	Et (6:1)	3.89 s	1.74 d	2.10 d			0.35 m
$[(R^*,R^*),(S^*)]$-10[d]	Et	3.70 s	2.05 d	2.13 d			*c*
$[(R^*,R^*),(R^*)]$-11[d]	Bn (3:1)	4.08 s	1.52 d	2.11 d			
$[(R^*,R^*),(S^*)]$-11[d]	Bn	3.91 s	2.11 d	2.18 d			

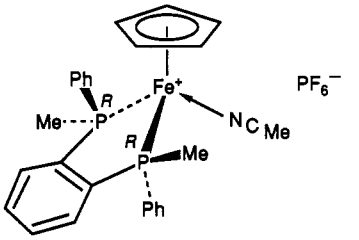
[a] Chemical shift values quoted relative to Me_4Si (^{1}H) or 85% H_3PO_4 (^{31}P) in [$^2H_2$]dichloromethane at 20 °C (type 1 complexes) or in [$^2H_8$]tetrahydrofuran at −65 °C (type 2 complexes). [b] Diastereomeric ratio $[(R^*,R^*),(R^*)]$:$[(R^*,R^*),(S^*)]$ at −65 °C quoted in parentheses. [c] Resonances obscured. [d] Generated in situ.

phosphine complexes also undergo base-catalyzed cyclizations with vinylphosphines[8] and with certain dicarbonyl compounds[9] to give linear and macrocyclic multidentate phosphine complexes.

The aim of the present work was 2-fold: (a) to determine if metal complexation is a feasible method of resolution for secondary phosphines chiral at phosphorus and (b) to establish conditions for the stereocontrolled synthesis of multidentate tertiary phosphines from coordinated primary and secondary phosphines. Thus, we have studied the stereoselectivity of the base-promoted monoalkylation of the diastereotopic P–H protons in the primary phosphine complex (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PH_2Ph)]PF_6$ ((R^*,R^*)-2) to give coordinated secondary phosphine complexes chiral at phosphorus.[10] We have also studied the stereoselectivity of deprotonation and subsequent alkylation of the coordinated secondary phosphine P–H proton in the diastereomerically pure racemate $[(R^*,R^*),(R^*)]$-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PHMePh)]PF_6\cdot 0.5CH_2Cl_2$ ($[(R^*,R^*),(R^*)]$-3) under kinetically and thermodynamically controlled conditions. Preliminary accounts of the work have been published.[12,13] Previous investigations in our group have established that metal complexation is an extremely effective method for the resolution of a variety of tertiary phosphines and arsines.[14] Highly stereoselective syntheses of enantiomers of 14-membered *trans*-As_2S_2[15] and *trans*-As_2N_2[16] chelating macrocycles have been effected following resolutions of appropriate tertiary arsine precursors.

Results and Discussion

The complex (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(NCMe)]PF_6$ ((R^*,R^*)-1) was obtained in



(R^*,R^*) - 1[a]

[a] *R* enantiomer depicted

93% yield as an air-stable solid by UV irradiation of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Br]$ with (R^*,R^*)-(±)-$C_6H_4(PMePh)_2$[17] in acetonitrile and treatment of the reaction mixture with NH_4PF_6.[18] Complex (R^*,R^*)-1 is a convenient precursor of compounds of the type (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FeL]PF_6$ by substitution of the acetonitrile ligand. Thus, (R^*,R^*)-1 reacts with primary or secondary phosphines in boiling methanol to give the corresponding phosphine derivatives in high yield. Chiral secondary phosphines give equimolar mixtures of diastereomers that can be separated by fractional crystallization from suitable

(8) Waid, R. D.; Meek, D. W. *Inorg. Chem.* **1984**, *23*, 779.
(9) Bartsch, R.; Hietkamp, S.; Morton, S.; Stelzer, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 375. Bartsch, R.; Hietkamp, S.; Morton, S.; Peters, H.; Stelzer, O. *Inorg. Chem.* **1983**, *22*, 3624. Brauer, D. J.; Gol, F.; Hietkamp, S.; Peters, H.; Sommer, H.; Stelzer, O.; Sheldrick, W. S. *Chem. Ber.* **1986**, *119*, 349.
(10) The stereochemical nomenclature adopted here for racemates is consistent with recent Chemical Abstracts Service Index practice; R^* and S^* refer to the relative absolute configurations of the chiral centers.[11]
(11) Cahn, R. S.; Ingold, C. K.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385.
(12) Crisp, G. T.; Salem, G.; Stephens, F. S.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1987**, 600.
(13) Salem, G.; Wild, S. B. *J. Chem. Soc., Chem. Commun.* **1987**, 1378.
(14) Leung, P.-H.; McLaughlin, G. M.; Martin, J. W. L.; Wild, S. B. *Inorg. Chem.* **1986**, *25*, 3392 and references cited therein.
(15) Kerr, P. G.; Leung, P.-H.; Wild, S. B. *J. Am. Chem. Soc.* **1987**, *109*, 4321.
(16) Martin, J. W. L.; Stephens, F. S.; Weerasuria, K. D. V.; Wild, S. B. *J. Am. Chem. Soc.* **1988**, *110*, 4346.
(17) Roberts, N. K.; Wild, S. B. *J. Am. Chem. Soc.* **1979**, *101*, 6254.
(18) The procedure is based upon published details for a similar compound. Treichel, P. M.; Molzahn, D. C. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 21.

Table II. Crystallographic Data, Data Collection Parameters, and Refinement Parameters for [(*R,*R**),(*R**)]-3•0.5CH_2Cl_2[a]**

formula	$C_{32.5}H_{35}ClF_6FeP_4$
fw	755.8
lattice type	monoclinic
space group	$P2_1/n$ (nonstd. No. 14)
a, Å	11.013 (9)
b, Å	26.143 (14)
c, Å	11.551 (4)
β, deg	90.65 (5)
V, Å^3	3325.5
Z	4
F(000)	1548
d(calcd), g cm^{-3}	1.51
μ(Mo Kα),[b] cm^{-1}	7.0
radiatn (λ, Å)	0.710 69
monochromator	graphite
temp, °C	−100
2θ range, deg	3–46
no. of unique reflcns obsd	4288
N_o[c]	2678
N_p (no. of params refined)	405
R[d]	0.051
R_w[e]	0.046

[a] The estimated standard deviation in the best significant digit is shown in parentheses for each entry in this and subsequent tables. [b] Lorentz, polarization effects, and absorption corrections applied. [c] $I > 3\sigma(I)$. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

solvents (Table I). Complexes **2–7** are stable to the atmosphere as solids and in solution. Thus, the enantiomers of the (*R**,*R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}Fe]$^+$ auxiliary appear to be excellent resolving agents for chiral secondary phosphines. Accordingly, we have isolated [*S*-[(*R**,*R**),(*S**)]]-**3**, [α]$_D$ −51° (CH_2Cl_2), and [*S*-[(*R**,*R**),(*R**)]]-**3**, [α]$_D$ −268° (CH_2Cl_2), the first complexes containing resolved unidentate secondary phosphine ligands.[12]

X-ray Crystal Structure of [(*R,*R**),(*R**)]-3.** The diastereomers of **3** were separated by fractional crystallization from dichloromethane–petroleum ether mixture; [(*R**,*R**),(*R**)]-**3** crystallizes as a hemidichloromethane solvate in the monoclinic space group $P2_1/n$ (nonstandard No. 14). In this space group both enantiomers of the cation are present. Crystal data for the complex are given in Table II. Table III gives the positional parameters, and Table IV lists most important distances and angles in the complex.

The geometry of the cation is illustrated in Figure 1, which also shows the atomic numbering scheme employed. The secondary phosphine-*P* stereocenter in the structure is pyramidal (although the P–H proton was not located), and the three chiral phosphorus stereocenters in the racemate have the same relative absolute configurations: accordingly, the cation has the stereochemical descriptor [(*R**,*R**),(*R**)].[10]

NMR Spectra of Complexes. Compounds **1–9** were characterized by ^{1}H and ^{31}P NMR spectroscopy; selected data for the complexes are given in Table I. The relative absolute configurations of the chiral phosphorus stereocenters were assigned on the basis of ^{1}H NMR data for solutions of the complexes in [$^2H_2$]dichloromethane with knowledge of the solid-state structure of [(*R**,*R**),(*R**)]-**3**. The bis(tertiary phosphine) P*Me* resonances in [(*R**,*R**),(*R**)] diastereomers containing secondary phosphines are separated by ca. 0.6 ppm; the chemical shift differences for the P*Me* resonances of the [(*R**,*R**),(*S**)] diastereomers are separated by ca. 0.2 ppm. In the complexes containing methyl-substituted unidentate phosphines, the P*Me* resonances occur in the range 1.1–1.6 ppm for [(*R**,*R**),(*R**)] diastereomers and in the range 0.4–0.6 ppm for [(*R**,*R**),(*S**)] diastereomers. There are also similarities in the chemical shift values for the PCH_2Me groups in complexes **4** and **6**: for [(*R**,*R**),(*R**)] diastereomers the PCH_2Me resonances occur between 0.62 and 0.69 ppm; for [(*R**,*R**),(*S**)] diastereomers the resonances occur between 0.46 and 0.47 ppm.

Stereoselective Monoalkylation of Coordinated Phenylphosphine in (*R,*R**)-2.**[19] Treatment of a so-

Table III. Atomic Coordinates for [(*R,*R**),(*R**)]-3•0.5CH_2Cl_2**

atom	x	y	z
Fe	1503.6 (9)	1892.2 (4)	16.6 (9)
P(1)	2785 (2)	2065 (1)	1409 (2)
P(2)	1165 (2)	1175 (1)	926 (2)
P(3)	2906 (2)	1562 (1)	−1063 (2)
P(4)	2364 (2)	4105 (1)	2089 (2)
F(1)	3486 (4)	3735 (2)	2258 (4)
F(2)	1262 (5)	4474 (2)	1941 (7)
F(3)	3074 (4)	4425 (2)	1151 (4)
F(4)	1659 (5)	3791 (2)	3023 (6)
F(5)	1844 (4)	3741 (2)	1130 (5)
F(6)	2932 (6)	4464 (2)	3059 (4)
Cl	404 (2)	5386 (1)	4197 (2)
C	731 (17)	4849 (7)	4826 (19)
C(p1)	1216 (7)	2563 (3)	−931 (7)
C(p2)	717 (7)	2619 (3)	181 (7)
C(p3)	−181 (6)	2238 (3)	335 (6)
C(p4)	−225 (7)	1944 (3)	−703 (7)
C(p5)	605 (7)	2157 (3)	−1467 (6)
C(m1)	2316 (6)	2517 (3)	2517 (6)
C(m2)	1216 (7)	552 (3)	212 (6)
C(m3)	3768 (7)	2006 (3)	−1955 (6)
C(1)	3059 (6)	1504 (3)	2302 (6)
C(2)	2268 (6)	1099 (3)	2106 (6)
C(3)	2339 (7)	670 (3)	2818 (7)
C(4)	3202 (8)	654 (3)	3697 (7)
C(5)	3988 (7)	1057 (3)	3898 (6)
C(6)	3914 (6)	1486 (3)	3210 (6)
C(11)	4276 (6)	2307 (3)	1036 (6)
C(12)	5298 (6)	1991 (3)	977 (6)
C(13)	6404 (7)	2195 (4)	644 (7)
C(14)	6503 (8)	2708 (4)	388 (7)
C(15)	5509 (8)	3019 (3)	441 (6)
C(16)	4396 (7)	2818 (3)	742 (6)
C(21)	−286 (7)	1130 (3)	1655 (7)
C(22)	−413 (7)	1295 (3)	2778 (8)
C(23)	−1514 (10)	1268 (4)	3309 (9)
C(24)	−2515 (10)	1085 (4)	2726 (13)
C(25)	−2403 (8)	922 (4)	1606 (11)
C(26)	−1320 (8)	951 (3)	1040 (8)
C(31)	2564 (7)	1052 (3)	−2075 (6)
C(32)	1403 (7)	953 (3)	−2485 (6)
C(33)	1183 (7)	550 (3)	−3247 (7)
C(34)	2115 (9)	237 (3)	−3567 (7)
C(35)	3294 (8)	332 (3)	−3163 (8)
C(36)	3508 (7)	735 (3)	−2418 (7)

Table IV. Selected Bond Distances and Angles for [(*R,*R**),(*R**)]-3•0.5CH_2Cl_2**

	(a) Bond Distances (Å)		
Fe–P(1)	2.176 (2)	P(1)–C(m1)	1.821 (7)
Fe–P(2)	2.183 (2)	P(2)–C(2)	1.826 (7)
Fe–P(3)	2.175 (2)	P(2)–C(21)	1.818 (7)
Fe–C(Cp)$_{av}$	2.090	P(2)–C(m2)	1.828 (7)
P(1)–C(1)	1.818 (7)	P(3)–C(31)	1.811 (7)
P(1)–C(11)	1.815 (7)	P(3)–C(m3)	1.826 (7)
	(b) Bond Angles (deg)		
P(1)–Fe–P(2)	86.3 (1)	Fe–P(1)–C(11)	118.5 (2)
P(1)–Fe–P(3)	92.7 (1)	Fe–P(1)–C(m1)	117.9 (2)
P(1)–Fe–Cp	125.2	Fe–P(2)–C(2)	109.6 (2)
P(2)–Fe–P(3)	93.5 (1)	Fe–P(2)–C(21)	115.8 (2)
P(2)–Fe–Cp	126.3	Fe–P(2)–C(m2)	122.8 (2)
P(3)–Fe–Cp	122.5	Fe–P(3)–C(31)	121.2 (2)
Fe–P(1)–C(1)	110.7 (2)	Fe–P(3)–C(m3)	116.6 (2)

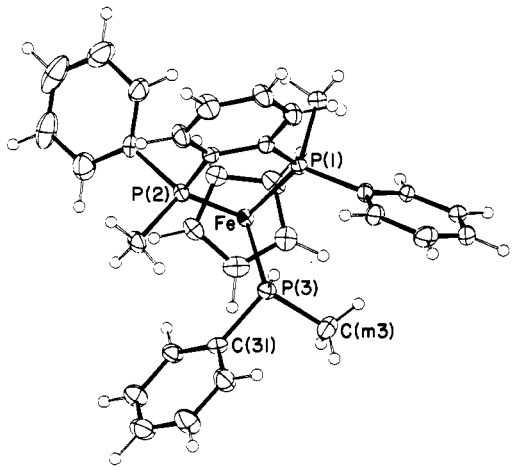
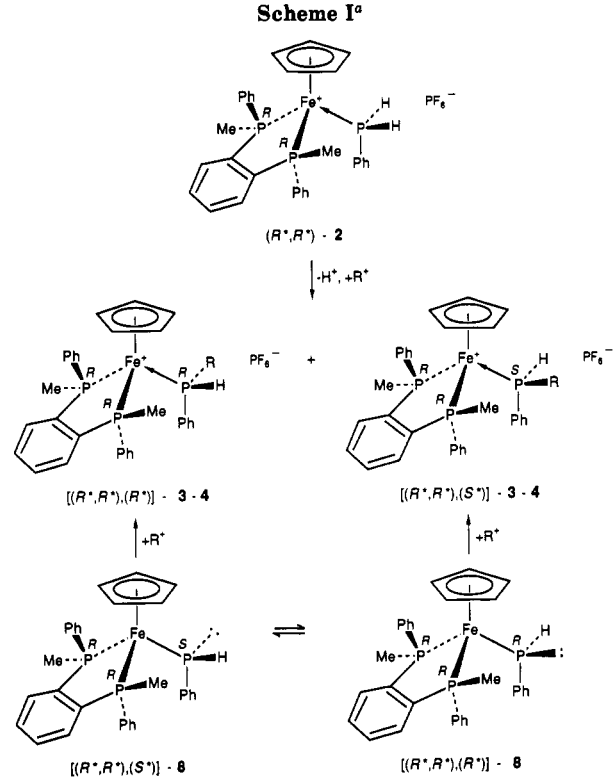


Figure 1. View of the $[(R^*,R^*),(R^*)]$-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}PHMePh]^+$ cation in $[(R^*,R^*)\text{-}(R^*)]\text{-}3\cdot 0.5CH_2Cl_2$ showing the atom-labeling scheme of the non-hydrogen atoms. Thermal ellipsoids enclose 35% probability levels (for clarity in the figure hydrogen atoms have $B = 1.0$ Å^2).

lution of (R^*,R^*)-**2** in tetrahydrofuran with methyl iodide in the presence of triethylamine at 20 °C gives an $[(R^*,R^*),(R^*)]$:$[(R^*,R^*),(S^*)]$ = 3.5:1 mixture of diastereomers of the secondary phosphine complex **3**. Reaction of (R^*,R^*)-**2** with ethyl iodide under similar conditions gives **4** with the same diastereoselectivity. The alkylations do not proceed at measurable rates at −65 °C; the reactions proceed at −40 °C, although diastereoselectivities are not significantly better than those found at 20 °C. The mixtures of secondary phosphine diastereomers (compounds **3** and **4**) were separated by fractional crystallization of the diastereomerically enriched mixtures resulting from the stereoselective syntheses.

Deprotonation of (R^*,R^*)-**2** with KOBu-*t* in tetrahydrofuran gives the secondary phosphido–iron complex (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}FePHPh]$ ($[R^*,R^*),(R^*)]$-**8**/$[(R^*,R^*),(S^*)]$-**8**) which was isolated as a *monotetrahydrofuran solvate*, mp 169–171 °C. The ^{1}H NMR spectrum of the solvate at −65 °C contains sets of resonances in the ratio 1:4.5 for the pair of diastereomers epimeric at the secondary phenylphosphido-*P* stereocenter. As the temperature of the solution containing the two diastereomers is raised, the η^5-cyclopentadienyl-^1H resonances for the diastereomers broaden, coalesce (T_c = 253 K), and sharpen into a singlet, $\Delta G^\ddagger$ (253 K) = 60 ± 4 kJ mol^{-1} being calculated from the NMR data.[21] The relatively low barrier to inversion of the pyramidal $PhHPFe^{II}$ group in the complex (compared to the value for free tertiary phosphines[23]) is consistent with the presence of the strongly electronegative iron(II) substituent on the phosphorus and with the value $\Delta G^\ddagger$ (243 K) = 48.1 ± 0.4 kJ mol^{-1} calculated for $PhHPRe^I$ inversion in $[(\eta^5\text{-}C_5H_5)(Ph_3P)(NO)RePHPh]$.[24] Treatment of the tetrahydrofuran solution of $[(R^*,R^*),(R^*)]$-**8**/$[(R^*,R^*),(S^*)]$-**8** at −65 °C with iodomethane gives a 4.5:1 mixture of $[(R^*,R^*),(R^*)]$- and $[(R^*,R^*),(S^*)]$-**3**, which corresponds to methylation of the phenylphosphido–iron intermediates in their equilibrium concentrations at this temperature. At 20 °C, methylation gives $[(R^*,R^*),(R^*)]$-**3**:$[(R^*,R^*),(S^*)]$-**3** = 3.5:1, the ratio observed for the based-catalyzed methylation. Thus, the diastereoselectivity of methylation at −65 °C and above is determined by the concentrations of the phenylphosphido–iron diastereomers at equilibrium (thermodynamic control), the rate of interconversion between the diastereomers being faster than the rates of methylation.

Scheme I[a]



[a] One enantiomer of each racemate is depicted.

Stereospecific and Stereoselective Alkylation of Coordinated Secondary Phosphines.[19] Diastereomer $[(R^*,R^*),(R^*)]$-**3**, when treated consecutively with KOBu-*t* and ethyl iodide in tetrahydrofuran at −95 °C, produces the tertiary phosphine complex $[(R^*,R^*),(S^*)]$-**6**[25] in high yield, diastereomerically pure, according to high-resolution ^{1}H and ^{31}P NMR spectroscopy.[26] Under the same conditions $[(R^*,R^*),(S^*)]$-**3** is converted stereospecifically into $[(R^*,R^*),(R^*)]$-**6**. At temperatures above −95 °C the diastereoselectivity of the alkylation of the intermediate phosphido species is reduced, the same results being observed for reactions of pure $[(R^*,R^*),(R^*)]$-**3** or of pure $[(R^*,R^*),(S^*)]$-**3**, viz. $[(R^*,R^*),(S^*)]$-**6**:$[(R^*,R^*),(R^*)]$-**6** = 4.5:1 (−65 °C) and 3.2:1 (20 °C). Reprotonations at dif-

(19) Under the conditions of the experiment, the stereochemistries of the chiral tertiary phosphine-*P* stereocenters of the chelating bis(tertiary phosphine) are immutable; thus, the monomethylation of (R^*,R^*)-**2** cannot be stereospecific, although it may be stereoselective with exclusive or predominant formation of one or other of the secondary phosphine diastereomers $[(R^*,R^*),(R^*)]$-**3** or $[(R^*,R^*),(S^*)]$-**3**. Ethylation of the latter complexes, however, can be stereospecific as well as stereoselective, since there are two diastereomers of the starting material, each of which leads to the same pair of product diastereomers, viz. $[(R^*,R^*),(R^*)]$-**6** and $[(R^*,R^*),(S^*)]$-**6**.[20]

(20) For further discussion on these terms, see: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 119.

(21) Binsch, G.; Kesler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411. Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961. In the analysis of variable-temperature NMR spectra containing unequal populations of two diastereomers in equilibrium, T_c is the temperature at which the valley between two appropriate peaks disappears. For the present system, $[(R^*,R^*),(R^*)] \rightleftarrows [(R^*,R^*),(S^*)]$, $\Delta G^\ddagger$ is quoted for the forward reaction at T_c with use of the program DNMR3[22] to analyze the shapes of the cyclopentadienyl resonances.

(22) Binsch, G. *QCPE* **1969**, *10*, 140.

(23) Mislow, K. *Trans. N. Y. Acad. Sci.* **1973**, *35*, 227.

(24) Buhro, W. E.; Gladysz, J. A. *Inorg. Chem.* **1985**, *24*, 3505.

(25) The replacement of a proton by an ethyl group changes the priority of that ligand from 4 to 3; since this is an odd change (4 − 3 = 1), the CIP descriptor for the chiral stereocenter is changed by the replacement.[11]

(26) The minor diastereomer not detected in the crude reaction products by ^{1}H (200 MHz) or ^{31}P (80.98 MHz) NMR spectroscopy.

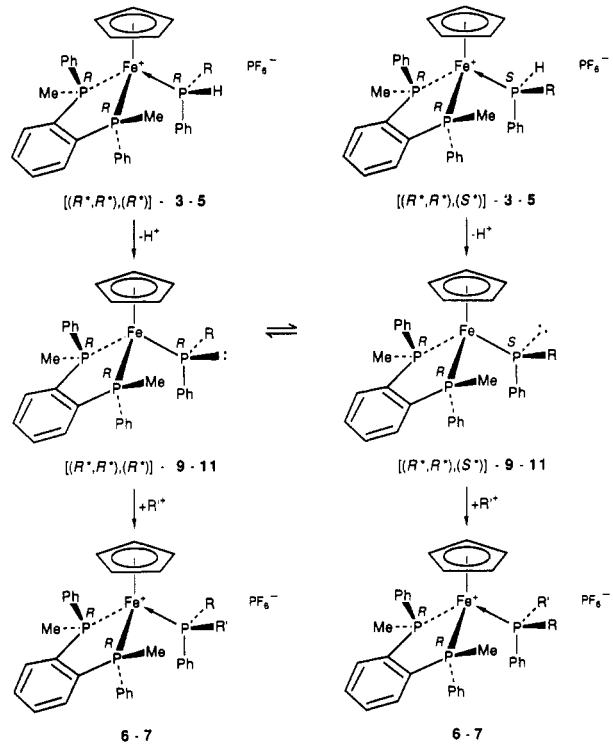
ferent temperatures regenerate [(*R**,*R**),(*R**)]-**3** with diastereoselectivities consistent with the alkylation experiments. The intermediate tertiary methylphenylphosphido–iron complex (*R**,*R**)-(±)-[(η^5-C_5H_5){1,2-C_6H_4(PMePh)$_2$}FePMePh]·thf ([(*R**,*R**),(*R**)]-**9**/[(*R**,*R**),(*S**)]-**9**) was isolated from the reaction of [(*R**,*R**),(*R**)]-**3** with KOBu-*t* in tetrahydrofuran. In the ^{1}H NMR spectrum of the *tetrahydrofuran solvate* in [$^2H_8$]tetrahydrofuran at 20 °C, the C_5H_5 proton resonances for the two diastereomers, epimeric at the tertiary phosphido-*P* stereocenter, are coalesced; at −65 °C, however, separate resonances for the two diastereomers are observed with the intensity ratio 4.5:1 [$\Delta G^{\ddagger}$ (278 K) = 58.8 ± 1.2 kJ mol^{-1}]. (Secondary phosphine complex [(*R**,*R**),(*R**)]-**3** can be deprotonated by KOBu-*t* in tetrahydrofuran at −95 °C, but at this temperature the deprotonated complex crystallizes out of the solution.) Deprotonations and alkylations of [(*R**,*R**),(*R**)]-**4** or [(*R**,*R**),(*R**)]-**5** (or their diastereomers) in tetrahydrofuran at −95 °C are also stereospecific giving the corresponding tertiary phosphine diastereomers with complete stereoselectivity. The ethylation of [(*R**,*R**),(*R**)]-**3** and the methylation of [(*R**,*R**),(*S**)]-**4**, both performed at −95 °C, give [(*R**,*R**),(*S**)]-**6**, thus confirming the stereochemistries assigned. ^{1}H NMR data for the tertiary phosphine and tertiary phosphido–iron complexes are given in Table I. Retention of absolute configurations at the asymmetric phosphido–iron-*P* stereocenters after deprotonation was demonstrated by reprotonation and methylation of the intermediates at −95 °C: diastereomerically pure starting materials [(*R**,*R**),(*R**)]-**4** or -**5** and methylation products [(*R**,*R**),(*R**)]-**6** or -**7** were generated from the respective reactions. At −65 °C deprotonations of the secondary phosphine complexes give equilibrium mixtures of tertiary phosphido–iron complexes with the following diastereomeric ratios being observed for reactions of [(*R**,*R**)(*R**)]-**4** and -**5**: [(*R**,*R**),(*R**)]-**10**:[(*R**,*R**),(*S**)]-**10** = 6:1; [(*R**,*R**),(*R**)]-**11**:[(*R**,*R**),(*S**)]-**11** = 3:1. Identical results were obtained for reactions of [(*R**,*R**),(*S**)]-**4** and -**5** at −65 °C. Subsequent methylations of the tertiary phosphido–iron complexes **10** and **11** at −65 °C give [(*R**,*R**),(*R**)]-**6**:[(*R**,*R**),(*S**)]-**6** = 6:1 and [(*R**,*R**),(*R**)]-**7**:[(*R**,*R**),(*S**)]-**7** = 3:1, respectively. Thus, the diastereoselectivity of product formation in reactions of the primary or secondary phosphine–iron(II) complexes at −65 °C (or above) reflect quantitative conversions of the secondary or tertiary phosphido–iron intermediates in their equilibrium concentrations with retention of absolute configurations at the phosphido–iron-*P* stereocenters. When both deprotonation and subsequent alkylation of the diastereomerically pure secondary phosphine complexes are performed at −95 °C, however, tertiary phosphine complexes are produced stereospecifically as kinetic products with complete stereoselectivity (de > 99%).[27]

The high stereoselectivities observed for low-temperature alkylations of tertiary phosphido–iron(II) phosphorus stereocenters in this work augur well for our ultimate objective of stereoselectively synthesizing multidentate phosphorus macrocycles and cages from coordinated primary and secondary phosphine complexes.

Conclusion

Phenylphosphine coordinated to the chiral auxiliary (*R**,*R**)-(±)-(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) reacts with alkyl halides in the presence of bases in the temperature range −40 to 20 °C to produce unequal mixtures of diastereomers of chiral secondary phosphine–iron(II) complexes with diastereoselectivities reflecting the equilibrium concentrations of the intermediate phenylphosphido–iron(II) diastereomers at the reaction temperature. Deprotonations of diastereomerically pure secondary phosphine–iron(II) complexes chiral at phosphorus with KOBu-*t* at −95 °C produce highly reactive tertiary phosphido–metal complexes, diastereomerically pure, that can be reprotonated or alkylated with complete stereoselectivity at the phosphorus stereocenter at this temperature. Because of the relatively low barriers to inversion of the pyramidal tertiary phosphido–iron(II) phosphorus stereocenters in the intermediates (ca. 60 kJ mol^{-1}), however, reactions above −95 °C give thermodynamic mixtures of chiral tertiary phosphine–iron(II) complexes with diastereoselectivities reflecting stereosepcific alkylations of equilibrium concentrations of intermediates. Moreover, use of the optically active iron(II) auxiliary gives optically active secondary phosphine complexes that are potential sources of resolved secondary phosphines.

Scheme II[a]



[a] One enantiomer of each racemate is depicted.

Experimental Section

Reactions were performed under a positive pressure of argon. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker CXP-200 spectrometer at 20 °C in [$^2H_2$]dichloromethane unless stated otherwise with chemical shift values quoted relative to Me_4Si (^{1}H) or 85% H_3PO_4(^{31}P{^{1}H}). 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.

(*R,*R**)-(±)-(Acetonitrile)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ((*R**,*R**)-1).** Following a method used previously for the preparation of [(η^5-C_5H_5)($Ph_2PCH_2CH_2PPh_2$)-FeNCMe]PF_6,[18] a suspension of [(η^5-C_5H_5)Fe(CO)$_2$Br] (2.0 g, 7.8 mmol) and (*R**,*R**)-1,2-C_6H_4(PMePh)$_2$[17] (2.52 g, 7.8 mmol) in acetonitrile (50 mL) was irradiated for 50 min with a Hanovia 125-W UV lamp. The resulting brown solution was reduced in volume (to ca. 10 mL) and treated with aqueous NH_4PF_6 (12.5%, 40 mL). Diethyl ether (30 mL) was added to the reaction mixture,

(27) Sheldrick, G. M. *SHELTX User Manual, Revision 3*; Nicolet XRD Corp.: Cupertino, CA, 1981.

which was then stirred for ca. 18 h. The brick red product was collected, washed with diethyl ether, and dried: mp 238–240 °C dec; yield 4.6 g (93%). Anal. Calcd for $C_{27}H_{28}F_6FeNP_3$: C, 51.5; H, 4.5; N, 2.2; P, 14.8. Found: C, 51.9; H, 4.6; N, 2.0; P, 14.6. ^1H NMR: δ 1.70 (t, 3 H, $^5J_{PH}$ = 1.2 Hz, MeCN), 2.10 (d of d, 3 H, $^2J_{PH}$ = 8.0 Hz, $^5J_{PH}$ = 2.2 Hz, PMe), 2.34 (d of d, 3 H, $^2J_{PH}$ = 7.4 Hz, $^5J_{PH}$ = 1.8 Hz, PMe), 4.17 (t, 5 H, $^3J_{PH}$ = 1.7 Hz, η^5-C_5H_5), 7.20–7.85 (m, 14 H, aromatics). $^{31}P\{^1H\}$ NMR: δ 86.8, 87.5 (AB m, 2 P, $^2J_{AB}$ = 47.0 Hz).

[*S*-(*R,*R**)]-(−)-(Acetonitrile)[(η⁵-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron (II) Hexafluorophosphate ((*S*,*S*)-1).** This compound was obtained from $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Br]$ and [*R*-(*R**,*R**)]-(+)-1,2-$C_6H_4(PMePh)_2$[17] in acetonitrile by the method described for the corresponding racemate, but with a reaction time of 30 min; the pure enantiomer crystallized as orange needles: mp 230–231 °C dec; 76% yield; $[\alpha]_D$ −399° (*c* 0.22, CH_2Cl_2). Anal. Calcd for $C_{27}H_{28}F_6FeNP_4$: C, 51.5; H, 4.5; N, 2.2; P, 14.8. Found: C, 51.6; H, 4.5; N, 2.3; P, 14.9. ^1H and $^{31}P\{^1H\}$ NMR: identical with those of the corresponding racemate.

(*R,*R**)-(±)-(η⁵-Cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)](phenylphosphine)iron(II) Hexafluorophosphate ((*R**,*R**)-2).** A mixture of (*R**,*R**)-1 (2.0 g, 3.2 mmol) and phenylphosphine (0.35 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. The product crystallized as yellow needles, which were washed with diethyl ether and dried: mp 225–227 °C dec; yield 1.9 g (84%). Anal. Calcd for $C_{31}H_{32}F_6FeP_4$: C, 53.3; H, 4.6; P, 17.7. Found: C, 53.5; H, 4.7; P, 18.1. ^1H NMR: δ 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, η^5-C_5H_5), 4.65 (d of m, 1 H, $^1J_{PH}$ = 344 Hz, P*H*H′Ph), 5.40 (d of m, 1 H, $^1J_{PH}$ = 344 Hz, PH*H*′Ph), 6.70–7.75 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR: δ −4.5, 80.9, 83.1 (ABX m, 3 P, $|^2J_{AB}|$ = 43.6 Hz, $|^2J_{AX}|$ = 58.8 Hz, $|^2J_{BX}|$ = 55.4 Hz).

[(*R,*R**),(*R**)]-(±)-(η⁵-Cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Hemidichloromethane Solvate ([(*R**,*R**),(*R**)]-3). Method 1.** A solution of (*R**,*R**)-2 (0.5 g, 0.72 mmol) in tetrahydrofuran (50 mL) was treated with methyl iodide (0.09 mL, 1.4 mmol) and triethylamine (0.60 mL, 4.3 mmol). After 12 h, the solvent was evaporated from the reaction mixture and the residue was chromatographed on basic alumina (Activity I) with dichloromethane as eluent. The eluate, after drying over $MgSO_4$ and evaporation, yielded the product as the major component of a 3.5:1 mixture of itself with the corresponding [(*R**,*R**),(*S**)] diastereomer. Fractional crystallization of the mixture from dichloromethane (10 mL) 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 dec; yield 0.42 g (78%). Anal. Calcd for $C_{32.5}H_{35}ClF_6FeP_4$: C, 51.7; H, 4.7; Cl, 4.7; P, 16.4. Found: C, 52.0; H, 4.7; Cl, 4.8; P, 15.8. ^1H NMR: δ 0.64 (d of d, 3 H, $^2J_{PH}$ = 9.5 Hz, $^3J_{HH}$ = 6.1 Hz, PH*Me*Ph), 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, η^5-C_5H_5), 4.65 (d of m, 1 H, $^1J_{PH}$ = 333 Hz, P*H*MePh), 6.75–8.00 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 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). **Method 2.** Reaction of (*R**,*R**)-1 with (±)-PHMePh over 2 h, as described for the preparation of (*R**,*R**)-2, gave an equimolar mixture of [(*R**,*R**),(*R**)]- and [(*R**,*R**),(*S**)]-3; fractional crystallization of the mixture from dichloromethane–petroleum ether gave pure [(*R**,*R**),(*R**)]-3 in 45% of the calculated yield.

[(*R,*R**),(*S**)]-(±)-(η⁵-Cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Monoacetone Solvate ([(*R**,*R**),(*S**)]-3). Method 1.** The mother liquor from the isolation of [(*R**,*R**),(*R**)]-3 was evaporated to dryness, and the residue was recrystallized from acetone–diethyl ether mixture giving yellow needles of [(*R**,*R**),(*S**)]-3: mp 138–140 °C; yield 0.05 g (9%). Anal. Calcd for $C_{35}H_{40}F_6FeOP_4$: C, 54.6; H, 5.6; P, 16.1. Found: C, 54.4; H, 5.2; P, 16.2. ^1H NMR: δ 1.55 (d of d, 3 H, $^2J_{PH}$ = 8.8 Hz, $^3J_{HH}$ = 6.1 Hz, PH*Me*Ph), 2.12 (s, 6 H, Me_2CO), 2.20 (d, 3 H, $^2J_{PH}$ = 9.0 Hz, P*Me*), 2.32 (d, 3 H, $^2J_{PH}$ = 8.3 Hz, PMe), 4.36 (q, 5 H, $^3J_{PH}$ = 2.0 Hz, η^5-C_5H_5), 4.83 (d of m, 1 H, $^1J_{PH}$ = 333 Hz, P*H*MePh), 6.80–7.75 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.1, 81.7, 81.0 (ABX m, 3 P, $|^2J_{AB}|$ = 42.8 Hz, $|^2J_{AX}|$ = 55.6 Hz, $|^2J_{BX}|$ = 56.1 Hz). **Method 2.** Recrystallization of the residue remaining after evaporation of the solvent from the mother liquor from the preceding method 2 preparation and isolation of [(*R**,*R**),(*R**)]-3 gave [(*R**,*R**),(*S**)]-3 in 41% yield.

[*S*-[(*R,*R**),(*S**)]]-(−)-(η⁵-Cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ([(*S*,*S*),(*R*)]-3).** Reaction of (*S*,*S*)-1 with (±)-PHMePh according to method 2 for the corresponding racemate gave the pure enantiomer as the first fraction from the acetone–diethyl ether recrystallization of the initial 1:1 mixture of enantiomers: yellow needles; mp 225–226 °C; 33% yield; $[\alpha]_D$ − 51° (*c* 0.23, CH_2Cl_2). Anal. Calcd for $C_{32}H_{34}F_6FeP_4$: C, 54.0; H, 4.8; P, 17.4. Found: C, 53.8; H, 5.0; P, 17.6. ^1H and $^{31}P\{^1H\}$ NMR: identical with those of the corresponding racemate.

[*S*-[(*R,*R**),(*R**)]]-(−)-(η⁵-Cyclopentadienyl)(methylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Hemihydrate ([(*S*,*S*),(*S*)]-3).** This enantiomer was isolated from the preparation described above as the second fraction from dichloromethane–diethyl ether: yellow prisms; mp 231–232 °C dec; 31% yield; $[\alpha]_D$ −268° (*c* 0.22, CH_2Cl_2). Anal. Calcd for $C_{32}H_{35}F_6FeO_{0.5}P_4$: C, 53.3; H, 4.9; P, 17.2. Found: C, 53.2; H, 5.0; P, 16.7. ^1H and $^{31}P\{^1H\}$ NMR: identical with those of the corresponding racemate.

The following compounds were prepared similarly. **[(*R**,*R**),(*R**)]-(±)-(η⁵-Cyclopentadienyl)(ethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Hemidichloromethane Solvate ([(*R**,*R**),(*R**)]-4):** yellow needles from dichloromethane–petroleum ether; mp 191–193 °C; 52% yield of major component of 3.4:1 diastereomeric mixture (method 1), 36% yield of 1:1 mixture (method 2). Anal. Calcd for $C_{33.5}H_{37}ClF_6FeP_4$: C, 52.3; H, 4.9; P, 16.1. Found: C, 52.3; H, 5.0; P, 16.6. ^1H NMR: δ 0.47 (m, 4 H, PC*HH*′*Me*), 1.26 (m, 1 H, PCH*H*′Me), 1.56 (d, 3 H, $^2J_{PH}$ = 9.2 Hz, PMe), 2.20 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, PMe), 4.29 (d of t, $^1J_{PH}$ = 335 Hz, $^3J_{HH}$ = 10.0 Hz, P*H*EtPh), 4.38 (q, 5 H, $^3J_{PH}$ = 1.6 Hz, η^5-C_5H_5), 6.85–8.00 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 60.4, 80.1, 83.0 (ABX m, 3 P, $|^2J_{AB}|$ = 43.2 Hz, $|^2J_{AX}|$ = 56.5 Hz, $|^2J_{BX}|$ = 53.3 Hz). **[(*R**,*R**),(*S**)]-(±)-(η⁵-Cyclopentadienyl)(ethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ([(*R**,*R**),(*S**)]-4):** yellow needles from acetone–diethyl ether; mp 234–236 °C dec; 10% yield of minor component of 3.4:1 mixture of diastereomers (method 1), 39% yield of 1:1 mixture of diastereomers (method 2). Anal. Calcd for $C_{33}H_{36}F_6FeP_4$: 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, $^3J_{PH}$ = 15.2 Hz, $^3J_{HH}$ = 7.4 Hz, PCH_2Me), 1.26 (m, 1 H, PC*H*H′Me), 1.58 (, 1 H, PCH*H*′Me), 2.18 (d, 3 H, $^2J_{PH}$ = 8.2 Hz, PMe), 2.40 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, PMe), 4.22 (d, 5 H, $^3J_{PH}$ = 1.8 Hz, η^5-C_5H_5), 4.37 (d of m, 1 H, $^1J_{PH}$ = 341 Hz, P*H*EtPh), 7.01–7.87 (m, 19 H, aromatics). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 59.4, 81.4, 83.4 (ABX m, 3 P, $|^2J_{AB}|$ = 43.1 Hz, $|^2J_{AX}|$ = 54.1 Hz, $|^2J_{BX}|$ = 53.2 Hz). **[(*R**,*R**),(*R**)]-(±)-(Benzylphenylphosphine)(η⁵-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Monodichloromethane Solvate ([(*R**,*R**),(*R**)]-5).** An equimolar mixture of diastereomers of **5** was obtained by reaction of (*R**,*R**)-1 with (±)-benzylphenylphosphine in boiling tetrahydrofuran (method 2). Recrystallization of the mixture from acetone–diethyl ether gave the [(*R**,*R**),(*R**)] diastereomer as a *monoacetone solvate*; a further recrystallization of this material from dichloromethane–diethyl ether mixture gave the *monodichloromethane solvate* as yellow needles: mp 248–250 °C dec; 35% yield of initial 1:1 mixture of diastereomers. Anal. Calcd for $C_{39}H_{40}Cl_2F_6FeP_4$: C, 53.6; H, 4.6; Cl, 8.1; F, 13.0; P, 14.2. Found: C, 53.1; H, 4.5; Cl, 8.4; F, 13.0; P, 14.0. ^1H NMR: δ 1.45 (d, 3 H, $^2J_{PH}$ = 9.2 Hz, PMe), 1.99 (m, 1 H, PC*H*H′Ph), 2.23 (d, 3 H, $^2J_{PH}$ = 8.4 Hz, PMe), 2.58 (m, 1 H, PCH*H*′Ph), 4.42 (d of t, 1 H, $^1J_{PH}$ = 341 Hz, $^2J_{PH}$ = 10.2 Hz, P*H*BnPh), 4.50 (q, 5 H, $^3J_{PH}$ = 1.5 Hz, η^5-C_5H_5), 6.07–8.04 (m, 24 H, aromatics). $^{31}P\{^1H\}$ NMR: 64.7, 78.8, 82.2 (ABX m, 3 P, $|^2J_{AB}|$ = 43.0 Hz, $|^2J_{AX}|$ = 53.3 Hz, $|^2J_{BX}|$ = 51.0 Hz). **[(*R**,*R**),(*S**)]-(±)-(Benzyl-**

phenylphosphine)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ([(*R,*R**),(*S**)]-5)**: yellow needles from acetonitrile–diethyl ether; mp 255–256 °C dec; 33% yield of 1:1 mixture of diastereomers (method 2). Anal. Calcd for $C_{38}H_{38}F_6FeP_4$: C, 57.9; H, 4.9; P, 15.7. Found: C, 58.0; H, 4.9; P, 15.4. ^{1}H NMR: δ 2.16 (d, 3 H, $^2J_{PH}$ = 8.2 Hz, PMe), 2.51 (d, 3 H, $^2J_{PH}$ = 8.5 Hz, PMe), 2.81 (m, 1 H, PC*H*H'Ph), 3.04 (m, 1 H, PCH*H'*Ph), 4.42 (q, 5 H, $^3J_{PH}$ = 1.8 Hz, η^5-C_5H_5), 4.67 (d of m, 1 H, $^1J_{PH}$ = 341 Hz, P*H*BnPh), 6.40–7.71 (m, 24 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 63.1, 80.4, 81.9 (ABX m, 3 P, $|^2J_{AB}|$ = 42.7 Hz, $|^2J_{AX}|$ = 53.4 Hz, $|^2J_{BX}|$ = 50.5 Hz). **[(*R**,*R**),(*R**)]-(±)-(η^5-Cyclopentadienyl)(ethylmethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Hemidichloromethane Solvate ([(*R**,*R*),(*R**)]-6).** A solution of [(*R**,*R**),(*S**)]-3 (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 orange; after ca. 5 min iodoethane (0.05 mL, 0.65 mmol) was added and the source of cooling was removed. When the reaction mixture had reached room temperature, the solvent was evaporated off, the residue was dissolved in dichloromethane (20 mL), and aqueous 5% NH_4PF_6 (20 mL) was added. The mixture was shaken for several minutes, and then the two layers were separated. After drying over $MgSO_4$, the organic layer was concentrated to ca. 5 mL and diluted with diethyl ether. The product crystallized as orange needles: mp 139–141 °C; yield 0.043 g (84%). Anal. Calcd for $C_{34.5}H_{39}ClF_6FeP_4$: C, 52.9; H, 5.0. Found: C, 53.1; H, 4.9. ^{1}H NMR: δ 0.46 (m, 4 H, PC*H*H'*Me*), 1.32 (m, 1 H, PCH*H'*Me), 1.40 (d, 3 H, $^2J_{PH}$ = 7.7 Hz, P*Me*EtPh), 2.07 (d, 3 H, $^2J_{PH}$ = 9.5 Hz, PMe), 2.32 (d, 3 H, $^2J_{PH}$ = 8.8 Hz, PMe), 4.10 (q, 5 H, $^3J_{PH}$ = 1.8 Hz, η^5-C_5H_5), 6.65–8.13 (m, 19 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 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). ([(*R**,*R**),(*R**)]-6 can also be prepared in pure form from [(*R**,*R**),(*R**)]-4 and iodomethane under similar conditions.)

The following compounds were prepared similarly. **[(*R**,*R**),(*S**)]-(±)-(η^5-Cyclopentadienyl)(ethylmethylphenylphosphine)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate ([(*R**,*R**),(*S**)]-6)**: orange needles after recrystallization from dichloromethane–diethyl ether ([(*R**,*R**),(*R**)]-3 with KOBu-*t*/EtI or [(*R**,*R**),(*S**)]-4 with KOBu-*t*/MeI); mp $^2J_{HH}$ °C; 82% yield. 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, $^3J_{PH}$ = 14.1 Hz, $^3J_{HH}$ = 7.4 Hz, PCHH'*Me*), 0.64 (d, 3H, $^2J_{PH}$ = 8.0 Hz, P*Me*EtPh), 1.40 (m, 1 H, PC*H*H'Me), 1.76 (m, 1 H, PCH*H'*Me), 2.09 (d, 3 H, $^2J_{PH}$ = 8.0 Hz, PMe), 2.45 (d, 3 H, $^2J_{PH}$ = 8.4 Hz, PMe), 4.10 (q, 5 H, $^3J_{PH}$ = 1.8 Hz, η^5-C_5H_5), 6.86–8.12 (m, 19 H, aromatics). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 42.4, 78.7, 80.2 (ABX m, 3 P, $|^2J_{AB}|$ = 43.0 Hz, $|^2J_{AX}|$ = 54.7 Hz, $|^2J_{BX}|$ = 52.0 Hz). **[(*R**,*R**),(*R**)]-(±)-(Benzylmethylphenylphosphine)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Hemidichloromethane Solvate ([(*R**,*R**),(*R**]]-7)**: orange prisms from dichloromethane-diethyl ether following reaction between [(*R**,*R**),(*R**)]-5 and KOBu-*t*/MeI; mp 259–260 °C dec; 84% yield. Anal. Calcd for $C_{39.5}H_{41}ClF_6FeP_4$: C, 56.1; H, 4.9; P, 14.7. Found: C, 56.6; H, 4.9; P, 14.3. ^{1}H NMR: δ 1.06 (d, 3 H, $^2J_{PH}$ = 7.2 Hz, PBn*Me*Ph), 2.02 (d of d, 1 H, $^2J_{HH}$ = 14.4 Hz, $^2J_{PH}$ = 3.2 Hz, PC*H*H'Ph), 2.14 (d, 3 H, $^2J_{PH}$ = 7.7 Hz, PMe), 2.22 (d, 3 H, $^2J_{PH}$ = 8.2 Hz), 2.86 (d of d, 1 H, $^2J_{HH}$ = 14.5 Hz, $^2J_{PH}$ = 6.8 Hz), 4.24 (q, 5 H, $^3J_{PH}$ = 1.8 Hz, η^5-C_5H_5), 6.06–8.16 (m, 24 H, aromatics). ^{31}P{^{1}H} NMR: δ 41.1, 77.8, 78.9 (ABX m, 3 P, $|^2J_{AB}|$ = 42.6 Hz, $|^2J_{AX}|$ = 56.3, $|^2J_{BX}|$ = 50.4 Hz). **[(*R**,*R**),(*S**)]-(±)-(Benzylmethylphenylphosphine)(η^5-cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)]iron(II) Hexafluorophosphate Hemidichloromethane Solvate ([*R**,*R**),(*S**)]-7)**: yellow plates from dichloromethane-diethyl ether following reaction between [(*R**,*R**),(*S**)]-5 and KOBu-*t*/MeI: mp 219-220 °C; 85% yield. Anal. Calcd for $C_{39.5}H_{41}ClF_6FeP_4$: C, 56.2; H, 4.9; P, 14.7. Found: C, 56.6; H, 4.8; P, 15.0. ^{1}H NMR: δ 0.46 (d, 3 H, $^2J_{PH}$ = 7.4 Hz, PBn*Me*Ph), 2.13 (d, 3 H, $^2J_{PH}$ = 8.2 Hz, PMe), 2.58 (d of d, 1 H, $^2J_{HH}$ = 14.6 Hz, $^2J_{PH}$ = 3.1 Hz, PC*H*H'Ph), 2.61 (d, 3 H, $^2J_{PH}$ = 8.0 Hz, PMe), 2.88 (d of d, 1 H, $^2J_{HH}$ = 14.6 Hz, $^2J_{PH}$ = 5.9 Hz, PCH*H'*Ph), 4.24 (q, 5 H, $^3J_{PH}$ = 1.8 Hz, η^5-C_5H_5), 6.27–8.13 (m, 24 H, aromatics). ^{31}P{^{1}H} NMR: δ 42.4, 77.2, 79.6 (ABX m, 3 P, $|^2J_{AB}|$ = 42.6 Hz, $|^2J_{AX}|$ = 54.8 Hz, $|^2J_{BX}|$ = 50.7 Hz).

[(*R,*R**),(*R**)]/[(*R**,*R**),(*S**)]-(±)-(η^5-Cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)](phenylphosphido)iron(II) Monotetrahydrofuran Solvate ([*R**,*R**),(*R**)]/[(*R**,*R**),(*S**)]-8).** A suspension of (*R**,*R**)-2 (1 g, 1.4 mmol) and KOBu-*t* (0.32 g, 2.8 mmol) in tetrahydrofuran (50 mL) was stirred for 10 min. The deep red solution was then taken to dryness, and the residue was extracted with toluene (50 mL) to separate the product from KPF_6. After filtration, the filtrate was taken to dryness *in vacuo* and the residue was crystallized by dissolving it in tetrahydrofuran and diluting the solution with *n*-hexane. The product crystallized as deep red needles: mp 169–171 °C; yield 0.77 g (86%). Anal. Calcd for $C_{35}H_{39}FeOP_3$: C, 67.3; H, 6.3; P, 14.9. Found: C, 67.1; H, 6.3; P, 14.3. ^{1}H NMR ([$^2H_8$]tetrahydrofuran, −65 °C): δ 1.90 (d, 2.5 H, $^2J_{PH}$ = 8.2 Hz, PMe), 2.13 (d, 2.5 H, $^2J_{PH}$ = 7.2 Hz, PMe), 2.15 (d, 0.5 H, $^2J_{PH}$ = ca. 8 Hz, PMe), 2.39 (d, 0.5 H, $^2J_{PH}$ = 7.9 Hz, PMe), 3.65 (s, 4.1 Hz, η^5-C_5H_5), 3.71 (s, 0.9 H, η^5-C_5H_5), 6.17–7.65 (m, 19 H, aromatics) (P*H* resonances obscured). ^{31}P{^{1}H} NMR ([$^2H_8$]tetrahydrofuran, −65 °C): δ −57.5, 86.1, 87.8 (ABX m, 2.4 P, $|^2J_{AB}|$ = 49 Hz, $|^2J_{AX}|$ = 10.6 Hz, $|^2J_{BX}|$ = 0.3 Hz, major), −46.3, 88.1, 89.8 (ABX m, 0.6 P, $|^2J_{AB}|$ = 47.1 Hz, $|^2J_{AX}|$ = 14.8 Hz, $|^2J_{BX}|$ = 5.2 Hz, minor). ^{31}P NMR ([$^2H_8$]tetrahydrofuran, −65 °C): $^1J_{PH}$ = 176 Hz (major diastereomer), 195 Hz (minor diastereomer). Treatment of [(*R**,*R**),(*R**)]/[(*R**,*R**),(*S**)]-8 in tetrahydrofuran at −65 °C with iodomethane gave a 4.5:1 mixture of [(*R**,*R**),(*R**)]- and [(*R**,*R**),(*S**)]-3 which corresponds to methylation of the phosphido–iron intermediates in their equilibrium concentrations at that temperature. At 20 °C [(*R**,*R**),(*R**)]-3:[(*R**,*R**),(*S**)]-3 = 3.2:1. The following compound was prepared similarly. **[(*R**,*R**),(*R**)]/[(*R**,*R**),(*S**)]-(±)-(η^5-Cyclopentadienyl)(methylphenylphosphido)[1,2-phenylenebis(methylphenylphosphine]iron(II) Monotetrahydrofuran Solvate ([(*R**,*R**),(*R**)]/[(*R**,*R**),(*S**)]-9)**: red needles from tetrahydrofuran/*n*-hexane following reaction of [(*R**,*R**),(*R**)]-3 (or [(*R**,*R**),(*S**)]-3) with KOBu-*t*: mp 93–95 °C; 78% yield. Anal. Calcd for $C_{36}H_{41}FeOP_3$: C, 67.7, H, 6.5; P, 14.6. Found: C, 67.5; H, 6.4; P, 14.3. ^{1}H NMR ([$^2H_8$]tetrahydrofuran, −65 °C): δ 0.43 (d, 2.5 H, $^2J_{PH}$ = 3.5 Hz, PMe), 1.60 (d, 0.5 H, $^2J_{PH}$ = 5.3 Hz, PMe), 1.97 (d, 2.5 H, $^2J_{PH}$ = 8.2 Hz, PMe), 2.28 (d, 0.5 H, $^2J_{PH}$ = ca. 8 Hz, PMe), 2.33 (d, 2.5 H, $^2J_{PH}$ = 7.2 Hz, PMe), 2.35 (d, 0.5 H, $^2J_{PH}$ = ca. 8 Hz, PMe), 3.91 (s, 0.9 H, η^5-C_5H_5), 4.04 (s, 4.1 H, η^5-C_5H_5), 6.83–7.88 (m, 19 H, aromatics). ^{31}P{^{1}H} NMR ([$^2H_8$]-tetrahydrofuran, −65 °C): δ −16.5, 84.1, 84.6 (ABX m, 2.4 P, $|^2J_{AB}|$ = 46.8 Hz, $|^2J_{AX}|$ = 13.8 Hz, $|^2J_{BX}|$ = 6.3 Hz, major), −30.4, 80.8, 89.5 (ABX m, 0.6 P, $|^2J_{AB}|$ = 46.9 Hz, $|^2J_{AX}|$ = 4.6 Hz, $|^2J_{BX}|$ = 34.7 Hz, minor).

Crystal Structure Analysis of [(*R,*R**),(*R**)]-3.** Deep orange crystals of [(*R**,*R**),(*R**)]-3·0.5CH_2Cl_2 suitable for crystal structure analysis were obtained by dilution of a solution of the complex in dichloromethane with petroleum ether. Crystal unit cell data, established from precession photographs, were determined accurately by least-squares fit to measurements obtained on a Nicolet XRD P3 diffractometer as indicated in Table II. The intensities were corrected for Lorentz and polarization effects, and absorption corrections were applied by using an empirical method (transmission factor 0.908–0.791).[27] The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques. The function minimized was $\sum w\Delta^2$, and the weight, w, for each reflection was derived from the counting statistics. Approximate positions for the H atoms were obtained from a difference map; the positions were optimized (C–H = 1.0 Å), but at no stage were they allowed to vary. Anisotropic thermal parameters were employed for all non-hydrogen atoms. Refinement was terminated when the maximum shift in any parameter was $<0.1\sigma$. A final difference map showed $\rho < |0.6|$ e Å^{-3}. All calculations for the analysis were performed on a FACOM 340S computer with programs written by F.S.S. Neutral-atom scattering factors were used.[28]

Acknowledgment. We thank Dr. Ward T. Robinson, of the Chemistry Department, University of Canterbury,

(28) *International Tables of Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

Christchurch, New Zealand, for recording for us the crystallographic data on compound [(*R**,*R**),(*R**)]-**3**·0.5CH_2Cl_2.

Registry No. (*R**,*R**)-**1**, 113587-85-2; (*S*,*S*)-**1**, 122331-51-5; (*R**,*R**)-**2**, 113587-95-4; (*R**,*R**)-**3**, 113572-53-5; [(*S*,*S*),(*R*)]-**3**, 113666-19-6; [(*S*,*S*),(*S*)]-**3**, 113666-17-4; (*R**,*R**)-**3**·0.5CH_2Cl_2, 113572-54-6; (*R**,*R**)-**4**, 116994-76-4; (*R**,*R**)-**5**, 122270-80-8; (*R**,*R**)-**6**, 116994-74-2; (*R**,*R**)-**7**, 122270-82-0; (*R**,*R**)-**8**, 113572-55-7; (*R**,*R**)-**9**, 122270-83-1; (*R**,*R**)-**10**, 122270-84-2; (*R**,*R**)-**11**, 122270-85-3; [(η^5-C_5H_5)Fe($CO)_2$Br], 12078-20-5; (*R**,*R**)-1,2-C_6H_4($PMePh)_2$, 122331-49-1; [*R*-(*R**,*R**)]-(+)-1,2-C_6H_4($PMePh)_2$, 72150-36-8; (±)-PHMePh, 113581-29-6; PH_2Ph, 638-21-1; (±)-PHBnPh, 122270-78-4.

Supplementary Material Available: Crystal data, a view of [(*R**,*R**),(*R**)]-**3**·0.5CH_2Cl_2, full tables of bond lengths and angles, and tables of anisotropic thermal factors, final atomic coordinates, and calculated hydrogen atom parameters for [(*R**,*R**),(*R**)]-**3**·0.5CH_2Cl_2 (12 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

Scope and Mechanism of Oxidative Addition of C=S Bonds to Trinuclear Platinum and Palladium Complexes

Arleen M. Bradford, Michael C. Jennings, and Richard J. Puddephatt*

Department of Chemistry, University of Western Ontario, London, Canada N6A 5B7

Received March 8, 1989

The coordinatively unsaturated complex [$Pt_3(\mu_3$-CO)(μ-dppm)$_3$]$^{2+}$ (dppm = $Ph_2PCH_2PPh_2$) reacts with the heterocumulenes S=C=E, where E = N^-, O, S, or NR, to give the corresponding adducts [Pt_3(S=C=E)(μ_3-CO)(μ-dppm)$_3$]$^{2+}$, followed by oxidative addition of the C=S bond and loss of CO to give the products [$Pt_3(\mu_3$-S)(C≡E)(μ-dppm)$_3$]$^{2+}$. These products were characterized by elemental analysis and multinuclear NMR spectroscopy. A further intermediate, identified by ^{31}P and ^{13}C NMR as [$Pt_3(\mu_3$-S)(CO)(μ-dppm)$_3$]$^{2+}$, was formed in the cases where E = O or NR but not when E = S or N^-. The complex [$Pd_3(\mu_3$-CO)(μ-dppm)$_3$]$^{2+}$ reacts with CS_2 to give a complex that was tentatively identified as [$Pd_3(\mu$-CS_2)(μ-dppm)$_3$]$^{2+}$. In these reactions, the nuclearity of the complexes is maintained by the bridging dppm ligands, and this leads to important differences from related chemistry of other Pt_3 and Pd_3 clusters. The reaction of [M_3(SCN)(μ-CO)(μ-dppm)$_3$]$^{2+}$ to give [$M_3(\mu_3$-S)(CN)(μ-dppm)$_3$]$^+$ and CO is retarded by free CO, under conditions of either thermal (M = Pd) or photochemical (M = Pt) activation, and the thermal reaction of [$Pt_3(\mu_3$-CO)(μ-dppm)$_3$]$^{2+}$ with CS_2 is also retarded by free CO. Two different mechanisms of reaction are throught to operate, and these are discussed.

Introduction

The reactions of the heterocumulenes CS_2 and COS with low oxidation state platinum complexes have been studied thoroughly. Complexes with η^2-C,S binding are formed first, but cleavage of a C=S bond can then occur to give coordinated S and CS or CO.[1-5] The C=S bond cleavage requires a second platinum(0) center, and the favored reaction sequence is shown in Scheme I (E = S or O, L = tertiary phosphine).[5] Carbon disulfide causes fragmentation of the trinuclear cluster [$Pt_3(\mu$-$CO)_3L_3$] (L = P-*t*-Bu_2Ph) to give [$Pt_2(\mu_2$-η^3-$CS_2)_2L_2$] or [$Pt_2(\mu$-S)$(CO)_2L_2$] and adds to the Pt–Pt bond of [$Pt_2Cl_2(\mu$-dppm)$_2$] (dppm = $Ph_2PCH_2PPh_2$) to give [$Pt_2Cl_2(\mu_2$-η^2-$CS_2)(\mu$-dppm)$_2$].[6-8] It was of interest to extend this chemistry to studies with the locked trinuclear clusters [$M_3(\mu_3$-CO)(μ-dppm)$_3$]$^{2+}$ (M = Pd, or Pt), which are much more stable to fragmentation than the clusters [$Pt_3(\mu$-$CO)_3L_3$] studied by Farrar and co-workers,[6,7] in the hope that the mechanism of C=S bond cleavage at a cluster center might be clearer if the nuclearity could be maintained by the bridging dppm ligands.

Scheme I

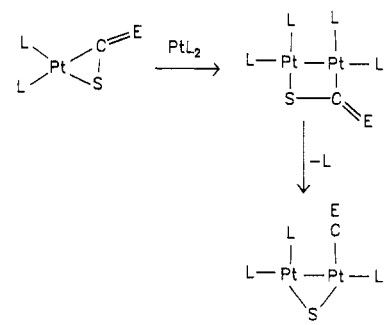


Table I. ^{31}P NMR Parameters of the Complexes [$Pt_3(\mu_3$-CO)(SCE)(μ-dppm)$_3$]$^{2+}$

complex SCE	$\delta(^{31}P)$, ppm	^1J(PtP), Hz
	−9.1	3710
SCN^-	−17.7	3670
COS	−16.4	3380
MeNCS	−16.7	3714
t-BuNCS	−16.7	3660
PhNCS	−17.1	3570

It has been shown that thiocyanate adds to the complexes [$M_3(\mu_3$-CO)(μ-dppm)$_3$]$^{2+}$ to give an adduct [M_3(SCN)(μ_3-CO)(μ-dppm)$_3$]$^+$, which then undergoes CS bond cleavage to give [$M_3(\mu_3$-S)CN(μ-dppm)$_3$]$^+$.[9] The C=S bond cleavage of SCN^- and RNCS has been much less studied than that of CS_2 or COS,[1-11] and this work de-

(1) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 865.
(2) Hawling, W. M.; Walker, A.; Woitzik, M. A. *J. Chem. Soc., Chem. Commun.* **1983**, 11.
(3) Ma, E.; Semelhago, G.; Walker, A.; Farrar, D. H.; Gukathasan, R. R. *J. Chem. Soc., Dalton Trans.* **1985**, 2595.
(4) Ebner, M.; Werner, H. *Chem. Ber.* **1988**, *121*, 1449.
(5) Werner, H.; Ebner, M.; Otto, H. *J. Organomet. Chem.* **1988**, *350*, 257.
(6) Farrar, D. H.; Gukathasan, R. R.; Morris, S. A. *Inorg. Chem.* **1984**, *23*, 3258.
(7) Browning, C. S.; Farrar, D. H.; Gukathasan, R. R.; Morris, S. A. *Organometallics* **1985**, *4*, 1750.
(8) Camerson, T. S.; Gardner, P. A.; Grundy, K. A. *J. Organomet. Chem.* **1981**, *212*, C19.
(9) Ferguson, G.; Lloyd, B. R.; Manojlović-Muir, Lj.; Muir, K. W.; Puddephatt, R. J. *Inorg. Chem.* **1986**, *25*, 4190.

0276-7333/89/2308-2367$01.50/0