The Synthesis and Crystal Structure of (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PCl_3)]Cl\cdot 2MeCN$

Evamarie Hey* and S. Bruce Wild

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

Simon G. Bott and Jerry L. Atwood

Department of Chemistry, University of Alabama,
Alabama, 35486, U.S.A.

Z. Naturforsch. **44b**, 615–617 (1989);
received January 9, 1989

(η^5-Cyclopentadienyl)[1,2-phenylenebis(methylphenylphosphine)](phosphorus trichloride)iron(II) Chloride Di-acetonitrile Solvate, Synthesis, Crystal Structure

The unit cell of (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PCl_3)]Cl\cdot 2MeCN$ is orthorhombic, space group Pccn, with a = 1531.2(3), b = 2202.7(20), c = 1874.6(16) pm, and Z = 8. The salt crystallizes as a racemic compound with four pairs of asymmetric cations of opposite helicity and associated anions and solvent molecules in each unit cell.

Primary and secondary phosphine complexes are convenient precursors of terminal phosphido-metal compounds by deprotonation. Recent work has shown that the chiral tertiary phosphido-metal group Fe–PMePh can be generated stereospecifically by deprotonation of a resolved secondary phosphine complex at −90 °C, and, furthermore, that it can be alkylated with retention of configuration and complete stereoselectivity at that temperature [1, 2]. Here we report the synthesis of (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PCl_3)]Cl\cdot 2MeCN$ [3] and its crystal structure. The enantiomers of this compound are potential precursors of optically active phosphine complexes containing the $Fe^+\leftarrow PH_3$ group, which we intend to investigate as sources of optically active tertiary phosphine complexes ($Fe^+\leftarrow PR^1R^2R^3$) by asymmetric synthesis. To our knowledge, this is the first structurally authenticated iron-phosphorus trichloride complex.

The title complex was isolated by recrystallization from acetonitrile of the product obtained from the reaction between (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(NCMe)]PF_6$ [4] and excess PCl_3 in boiling tetrahydrofuran (20 h under reflux). The solvent free compound is obtained as a yellow powder of m.p. 211–212 °C. Recrystallization from THF/hexane/acetonitrile yields the di-acetonitrile solvate, which crystallizes as air stable red prisms. The ^1H NMR spectrum of the complex in [$^2H_2$]-dichloromethane contains a pair of doublets at δ 2.47 and δ 2.56 ($^3J_{PH}$ = 8.8 Hz) for the diastereotopic PMe groups of the bis(tertiary phosphine), as well as a quartet resonance for the η^5-C_5H_5 group at δ 4.87 ($^3J_{PH}$ = 1.8 Hz), a singlet resonance for the solvent molecules of crystallization at δ 2.10, and four broad multiplets for the aromatic protons at δ 7.10–8.10. In the ^{31}P NMR spectrum the phosphorus nuclei show the splitting pattern of an ABX spin system (δ 77.4 ($|J_{AB}|$ = 42 Hz, $|J_{AX}|$ = 73 Hz), P_A; δ 76.3 ($|J_{AB}|$ = 42 Hz, $|J_{BX}|$ = 67 Hz), P_B; δ 160.9 ($|J_{AX}|$ = 73 Hz, $|J_{BX}|$ = 67 Hz), P_X (PCl_3) [6]. In the infrared spectrum, the PCl_3 vibrations occur at 480, 485, 505, 517, and 549 cm^{-1}; these values are similar to those found in $[Mo(CO)_5(PCl_3)]$, *viz.* 476, 502, 526, and 549 cm^{-1} [7].

For the structure determination, the data were collected at 25 °C with use of an automatic four-circle diffractometer and graphite-monochromated MoK_α radiation (λ = 710.69 pm). The cell constants were determined from the setting angles of 25 reflections (Table I) and from the systematic absences the space group Pccn was determined. With the ω/θ scan mode 3462 reflections were collected in the range 2θ = 2–40° in a manner similar to that described previously [8]. Of the 3462 independent reflections, 1027 with $I > 3\sigma(I)$ were considered as observed and used for the refinement. The structure was solved with use of Patterson methods. In the final refinement all non-hydrogen atoms were assigned anisotropic temperature parameters. Refinement converged at R = 0.078, R_w = 0.075 for 139 variables. Table II lists the

Table I. Crystal data for (R^*,R^*)-(±)-$[(\eta^5\text{-}C_5H_5)\{1,2\text{-}C_6H_4(PMePh)_2\}Fe(PCl_3)]Cl\cdot 2MeCN$*.

Molecular formula	$C_{25}H_{25}Cl_4FeP_3\cdot 2C_2H_3N$	
Molecular weight	616.06 (698.17 incl. solvent)	
Crystal class	orthorhombic	
Space group	Pccn	
Lattice constants	a	= 1531.2(3) pm
	b	= 2202.7(20) pm
	c	= 1874.6(16) pm
Cell volume	V	= $6323\cdot 10^6$ pm^3
Formula units	Z	= 8
Density (calc.)	Q_x	= 1.467 $g\cdot cm^{-3}$

* Reprint requests to Dr. Evamarie Hey at her present address: Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, D-7000 Stuttgart 80, FRG.

* Further details of the structure determination have been deposited as Supplementary Publication No. CSD 53614. Copies may be obtained through the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2.

Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen
0932–0776/89/0500–0615/$ 01.00/0

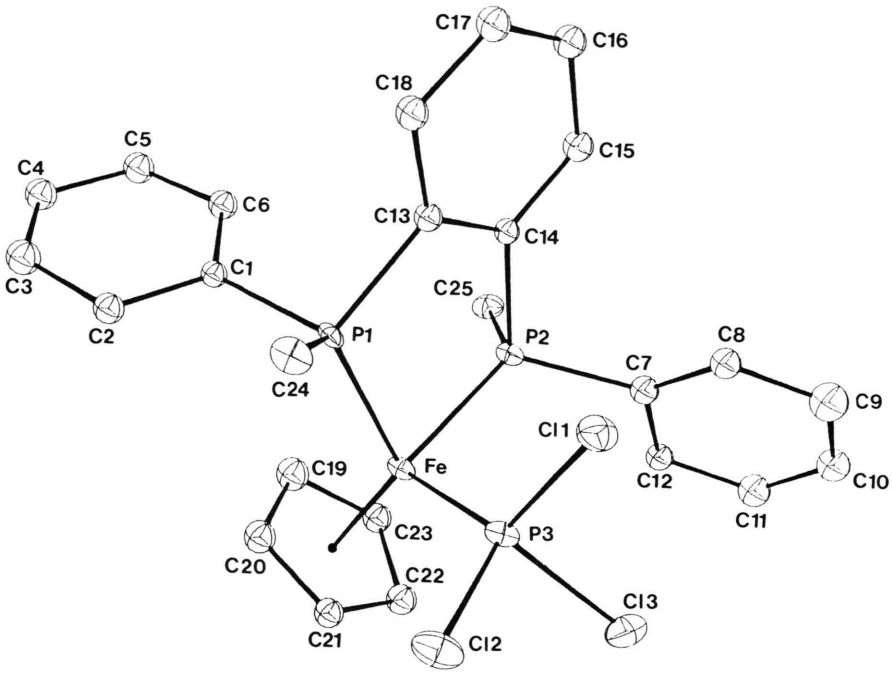

Fig. 1. Molecular structure of the cation in (R^*,R^*)-$(\pm)$-$[(\eta^5$-$C_5H_5)$-$\{1,2$-$C_6H_4(PMePh)_2\}$-$Fe(PCl_3)]Cl \cdot 2\,MeCN$ showing the atom numbering scheme employed. The atoms are drawn as 50% thermal motion ellipsoids.

Table II. Selected bond distances (pm) and angles (deg.) for (R^*,R^*)-$(\pm)$-$[(\eta^5$-$C_5H_5)\{1,2$-$C_6H_4(PMePh)_2\}$-$Fe(PCl_3)]Cl \cdot 2\,MeCN$.

Bond distances		Bond angles	
Fe–P(1)	219.4(8)	P(1)–Fe–P(2)	86.5(3)
Fe–P(2)	221.5(8)	P(1)–Fe–P(3)	96.0(3)
Fe–P(3)	206(1)	P(2)–Fe–P(3)	95.7(3)
P(3)–Cl(1)	203(1)	Fe–P(3)–Cl(1)	122.5(5)
P(3)–Cl(2)	202(1)	Fe–P(3)–Cl(2)	118.3(5)
P(3)–Cl(3)	204(1)	Fe–P(3)–Cl(3)	116.9(5)
		Cl(1)–P(3)–Cl(2)	97.3(5)
		Cl(1)–P(3)–Cl(3)	99.1(5)
		Cl(2)–P(3)–Cl(3)	98.1(5)

Table III. Atomic positional parameters for Non-Hydrogen Atoms in (R^*,R^*)-$(\pm)$-$[(\eta^5$-$C_5H_5)\{1,2$-$C_6H_4(PMePh)_2\}$-$Fe(PCl_3)]Cl \cdot 2\,MeCN$.

Atom	x	y	z	U(eqv)
Fe	0.5206(3)	0.1616(2)	0.2919(2)	0.046
P(1)	0.4561(5)	0.1009(3)	0.2155(4)	0.046
P(2)	0.5034(6)	0.0880(3)	0.3711(4)	0.050
P(3)	0.6462(6)	0.1385(3)	0.2641(5)	0.058
Cl(1)	0.6817(5)	0.0518(3)	0.2409(5)	0.083
Cl(2)	0.6995(6)	0.1783(4)	0.1772(5)	0.099
Cl(3)	0.7424(6)	0.1592(4)	0.3357(5)	0.091
Cl(4)	0.0169(6)	0.2380(4)	0.0557(4)	0.090
C(1)	0.341(2)	0.115(1)	0.198(1)	0.045
C(2)	0.318(2)	0.151(1)	0.139(1)	0.061
C(3)	0.226(2)	0.161(1)	0.128(2)	0.078
C(4)	0.166(2)	0.142(1)	0.171(2)	0.070
C(5)	0.189(2)	0.109(1)	0.229(2)	0.071
C(6)	0.275(2)	0.095(1)	0.243(2)	0.059
C(7)	0.596(2)	0.068(1)	0.428(2)	0.060
C(8)	0.652(2)	0.021(1)	0.414(2)	0.064
C(9)	0.725(2)	0.012(2)	0.459(2)	0.103
C(10)	0.740(3)	0.052(1)	0.509(2)	0.082
C(11)	0.690(2)	0.099(2)	0.519(2)	0.082
C(12)	0.615(2)	0.110(1)	0.481(1)	0.059
C(13)	0.453(2)	0.023(1)	0.254(2)	0.051
C(14)	0.474(2)	0.018(1)	0.323(1)	0.043
C(15)	0.467(2)	−0.039(1)	0.358(2)	0.061
C(16)	0.444(2)	−0.089(1)	0.315(1)	0.066
C(17)	0.429(2)	−0.084(2)	0.245(2)	0.070
C(18)	0.430(2)	−0.027(1)	0.210(2)	0.062
C(19)	0.416(2)	0.222(1)	0.309(2)	0.085
C(20)	0.464(2)	0.240(1)	0.247(2)	0.073
C(21)	0.546(2)	0.252(1)	0.266(1)	0.063
C(22)	0.554(2)	0.245(1)	0.399(2)	0.072
C(23)	0.475(2)	0.227(1)	0.365(2)	0.067
C(24)	0.505(2)	0.092(1)	0.126(1)	0.073
C(25)	0.416(2)	0.093(1)	0.437(1)	0.066
C(26)	0.5530	0.1054	−0.0555	0.089
C(27)	0.4237	0.0637	−0.0599	0.055
N(1)	0.3673	0.0773	−0.0655	0.052
C(28)	0.4230	0.1413	−0.0657	0.100
C(29)	0.3220	0.1509	−0.0693	0.139
N(2)	0.2920	0.1917	−0.0618	0.100

most important bond distances and angles in the cation and Table III gives the positional parameters. In space group Pccn both enantiomers of the chiral cation are present. The salt therefore crystallizes as a racemic compound. The coordination geometry around the iron atom is distorted tetrahedral. The bond distances and angles in the bis(tertiary phoshine)-iron chelate ring are consistent with those found in a closely related structure [1]. The P–Cl bond lengths of the PCl_3 ligand are similar to those found for PCl_3 itself at −100 °C, *viz.* 203.4(1) and 201.8(2) pm, although the Cl–P–Cl bond angles are slightly compressed when compared with those of the un-coordinated molecule at −110°, *viz.* 100.04(7) and 100.19(7)° [9]. The Fe–P bond length of the Fe–PCl_3 group is 206(1) pm.

One of us, E. H., would like to thank the Deutsche Forschungsgemeinschaft for financial support.

[1] G. T. Crisp, G. Salem, F. S. Stephens, and S. B. Wild, J. Chem. Soc. Chem. Commun. **1987,** 600.
[2] G. Salem and S. B. Wild, J. Chem. Soc. Chem. Commun. **1987,** 1378.
[3] The stereochemical descriptors used here are consistent with Chemical Abstracts indexing practice: R^* and S^* refer to the relative configurations of the chiral centres.
[4] This compound was prepared with use of a method described by Treichel *et al.* for similar compounds [5].
[5] P. M. Treichel and D. C. Molzahn, Synth. React. Inorg. Met.-Org. Chem. **9,** 21 (1979).
[6] The NMR spectra were recorded with a Varian XL 200 spectrometer at 20°. Proton NMR chemical shifts are quoted as δ values (ppm) relative to internal Me_4Si; ^{31}P NMR chemical shifts are quoted as δ values relative to external 85% aq. H_3PO_4.
[7] R. Poilblanc and M. Bigorgne, Bull. Soc. Chim. Fr. **1962,** 1301.
[8] J. Holton, M. F. Lappert, D. G. H. Ballard, R. Pearce, J. L. Atwood, and W. E. Hunter, J. Chem. Soc. Daltan Trans. **1979,** 45.
[9] H. Hartl, M. Rama, A. Simon, and H.-J. Deiseroth, Z. Naturforsch. **34b,** 1035 (1979).

Satz und Druck: Allgäuer Zeitungsverlag GmbH, Kempten