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Optically Active Transition-metal Compounds.
93*. X-ray Determination of the Structure and Absolute Configuration of $(+)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$

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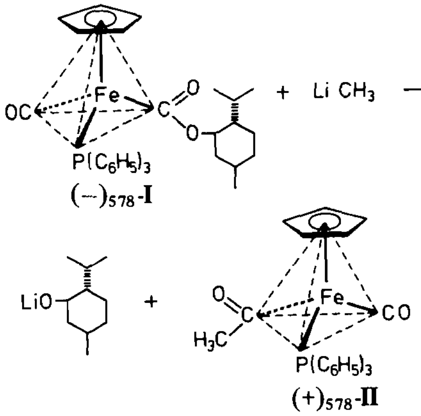
Abstract

The structure and absolute configuration of $(+)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$ have been determined by single crystal X-ray diffraction methods. The substance crystallizes in the monoclinic space group $P2_1$ with cell constants of $a = 8.084(14)$, $b = 8.527(2)$, $c = 32.706(21)$ Å and $\beta = 104.32(10)°$; $V = 2184.18$ Å^3 and D(calc: $Z = 4$ mol/unit cell) = 1.381 g cm^{-3}. There are two independent molecules in the asymmetric unit, which allowed us to gauge the effect of packing on the conformation of those groups able, in principle, to be twisted by crystalline forces. Only minor changes in conformations were observed, the largest being at the terminal CH_3 of the acetyl ligand (0.065 Å). All other differences in conformation are less than 0.036 Å. The plane of the acetyl ligand is close to being aligned with the Fe–C(CO) bond, making the acetyl oxygen point in the direction of the phosphorus atom. It is suggested that in phosphine exchange reactions this conformation persists in solution while the acetyl oxygen, intramolecularly, attacks the adjacent phosphorus atom to form a dihapto acetyl species as the first intermediate, in which there is retention of configuration at Fe.

With the priority of the ligand sequence as $C_5H_5 > P(C_6H_5)_3 > CO > COCH_3$, the absolute configuration at Fe is (S). So, the formation of $(-)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$ by reaction of $(+)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$ and $LiCH_3$ requires an inversion to occur at the Fe center.

Introduction

In the reaction of the ester $(-)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$ ($(-)_{578}$-**I**) [2] with $LiCH_3$, the acetyl $(+)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$ ($(+)_{578}$-**II**) was formed, [3–6] according to Scheme 1. As the product $(+)_{578}$-**II** was still optically active, the reaction must have been stereoselective or even stereospecific with respect to the Fe atom. On the basis of the opposite chiroptical properties, ORD and CD spectra of $(-)_{578}$-**I** and $(+)_{578}$-**II**, it was concluded that the reaction occurs with inversion of the relative configuration at the Fe atom. It was argued that lithium methyl does not attack $(-)_{578}$-**I** at the ester group but rather at the carbonyl group. In this reaction, the addition of the methyl group causes the carbonyl ligand to be transformed into the new functional group, whereas by loss of menthoxide the former functional group is converted into the new carbonyl ligand. Thus, by a role change between the carbonyl group and the functional group the relative iron configuration is inverted although none of the bonds from the iron atom to the ligands is cleaved in this reaction. The racemization at the iron center in the transesterification of ester $(-)_{578}$-$C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$ ($(-)_{578}$-**I**) supports this mechanism [4–6]. However, the reactions of the isoelectronic manganese ester $(-)_{578}$-$C_5H_5Mn(NO)$-



Scheme 1.

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*For part 92 see ref. 1.

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$[P(C_6H_5)_3]COOC_{10}H_{19}$ with $LiCH_3$ and $NaOCH_3$, respectively, occur with retention of configuration at the Mn center [5–7]. Therefore, a reactivity sequence CO > COOR > NO towards nucleophilic attack has been deduced for these compounds [5, 6]. (+)- and (−)-$C_5H_5Fe(CO)[P(C_6H_5)_3]COCH_3$ have become the basis for a variety of stereospecific syntheses derivatizing the acetyl ligand [8, 9].

The problems associated with a configurational assignment by a CD comparison of compounds as different as $(-)_{578}$-**I** and $(+)_{578}$-**II** has been discussed [6, 10]. Therefore, an X-ray structure analysis of a single crystal of $(+)_{578}$-**II** was carried out which, together with the known absolute configuration of $(-)_{578}$-**I** (obtained by chemical correlation) [11–13], proves the inversion of the relative configuration at the iron atom. Simultaneously, it reveals interesting details on the conformation of the acetyl ligand and the arrangement of the substituents about the Fe–P bond.

Experimental

Treatment of a sample of $(-)_{578}$-**I** [$(-)_{546}$-, $(+)_{436}$-rotation in benzene solution] with $LiCH_3$ gave $(+)_{578}$-**II** [$(+)_{546}$-, $(-)_{436}$-rotation in benzene solution], as described [2, 3]. A crystal of $(+)_{578}$-**II** suitable for X-ray determination was grown from a solvent mixture ether/pentane/methylene-chloride 8:5:2 at 0 °C. After carrying out the X-ray structure analysis the crystal used was dissolved in benzene; the solution exhibited $(+)_{578}$-, $(+)_{546}$-, and $(-)_{436}$-rotation.

X-ray Data Collection, Solution and Refinement of the Structure

A yellow crystal of $(+)_{578}$-**II** (size *ca.* 0.3 × 0.4 × 0.4 mm) was mounted on a translation head and onto a CAD-4 diffractometer using OS/4 software. Details of data collection are described in refs. 14 and 15; specific parameters are listed in Table I.

The solution of the Patterson function for the positions of the two Fe atoms in the unit cell was trivial and all heavier atoms quickly appeared in difference maps. However, since there are 60 heavy atoms and 46 hydrogen atoms in the asymmetric unit, the rigid Cp and Ph rings were idealized and refined with individual, isotropic, thermal parameters for the carbon atoms and a single overall thermal parameter for the hydrogen atoms (Table II). As discussed below, the results justify this procedure. All calculations were done with SHELX-76 [16] and local programs [14, 15]. Bond lengths and angles are listed in Tables III and IV, selected planes in Table V and torsional angles important to the 'Discussion' in Table VI. The absolute configuration was not determined using the Bijvoet test since we have already shown that the results of deciding the absolute configuration on the basis of *R* factor arguments are identical with those derived from the Bijvoet test [17]. Drawings of the molecule and the crystal packing (Figs. 1 and 2) were generated with ORTEP-2 [18] and the superposed molecules (Fig. 3) with BMFIT [19] which also provided the data listed in Table VII.

TABLE I. Summary of Data Collection and Processing Parameters

Space group	$P2_1$, monoclinic
Cell constants	$a = 8.084(14)$ Å
	$b = 8.527(2)$ Å
	$c = 32.706(21)$ Å
	$\beta = 104.32(10)°$
Cell volume	$V = 2184.18$ Å^3
Molecular formula	$C_{26}H_{23}O_2PFe$
Molecular weight	454.287 g mol^{-1}
Density (calc: $Z = 4$)	1.381 g cm^{-3}
Radiation	Mo Kα ($\lambda = 0.71073$ Å)
Absorption coefficient	$\mu = 6.00$ cm^{-1}
Data collection range	$4.0 \leqslant 2\theta \leqslant 48.0$
Scan width	$\Delta\theta = (0.90 + 0.35 \tan\theta)$
Maximum scan time	240 s
Scan speed range	0.35 to 4.03° min^{-1}
Total data collected	3329
Data with $I = 3\sigma(I)$ [a]	2069
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.0623
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.0487
Weights	$w = [\sigma(F_o)]^{-2}$

[a] The difference between total data collected and this number is due to subtraction of standards, redundant data and those which do not meet the criterion of having $I = 3\sigma(I)$.

Description of the Molecule

The Fe atom in $(+)_{578}$-**II** has the classical octahedral coordination found in many $CpFeL_1L_2L_3$ compounds [12, 14, 20–22]. This is demonstrated by the angles at the $FeL_1L_2L_3$ fragment which are all nearly 90° (Table IV) and, thus, constitute one of the *fac* segments of the octahedron. The same is true for $C_5H_5Fe(CO)[P(C_6H_5)_3]COOC_{10}H_{19}$ ($(-)_{578}$-**I**) [12], the starting material for the synthesis of $(+)_{578}$-**II**, and $C_5H_5Fe(CO)[(C_6H_5)_2PN(H)CH(CH_3)(C_6H_5)]COCH_3$ (**III**) [14] a closely related acetyl compound, in which triphenylphosphine is replaced by an aminophosphine.

The Fe–C(Cp) distances of **IIa** and **IIb**, the two independent molecules of $(+)_{578}$-**II** in the unit cell, average 2.135 Å and the Fe–(Cp ring centroid) distance is 1.76 Å. These results are in excellent agreement with **I** (2.131 and 1.76 Å), with **III** (2.131 and 1.76 Å) as well as with other literature data [20–22]. Therefore, since the agreement between our rigid body refinement of Cp in **IIa**, **IIb**, and **III**

TABLE II. Atomic Coordinates and Thermal Parameters (× 100, Fe and P × 1000)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	−0.6449(3)	0.0876(0)	−0.4258(1)	23(0)	23(0)	23(0)	0(0)	6(0)	0(0)
P	−0.7182(5)	−0.0110(6)	−0.3711(1)	25(3)	38(3)	37(3)	0(2)	5(2)	−4(2)
O6	−0.993(1)	0.193(2)	−0.464(1)	5(1)	14(1)	8(1)	2(1)	1(1)	3(1)
O7	−0.471(1)	0.298(2)	−0.364(1)	7(1)	7(1)	9(1)	−1(1)	0(1)	0(1)
C6	−0.861(2)	0.155(2)	−0.448(1)	6(2)	7(1)	7(2)	0(1)	2(1)	2(1)
C7	−0.579(2)	0.285(2)	−0.397(1)	3(1)	9(2)	6(1)	2(1)	1(1)	3(1)
C1	−0.558(1)	0.090(1)	−0.483(1)	47(4)					
C2	−0.419(1)	0.119(1)	−0.447(1)	54(5)					
C3	−0.402(1)	−0.014(1)	−0.420(1)	47(5)					
C4	−0.530(1)	−0.124(1)	−0.439(1)	46(5)					
C5	−0.626(1)	−0.060(1)	−0.478(1)	48(5)					
C8	−0.656(2)	0.432(2)	−0.416(1)	88(7)					
C9	−0.807(1)	0.126(1)	−0.339(1)	35(4)					
C10	−0.976(1)	0.174(1)	−0.354(1)	44(5)					
C11	−1.044(1)	0.289(1)	−0.332(1)	49(5)					
C12	−0.944(1)	0.355(1)	−0.296(1)	58(5)					
C13	−0.775(1)	0.306(1)	−0.280(1)	68(6)					
C14	−0.707(1)	0.191(1)	−0.302(1)	51(5)					
C15	−0.891(1)	−0.157(1)	−0.384(1)	38(4)					
C16	−0.974(1)	−0.205(1)	−0.353(1)	43(5)					
C17	−1.100(1)	−0.321(1)	−0.363(1)	49(5)					
C18	−1.143(1)	−0.388(1)	−0.403(1)	55(5)					
C19	−1.060(1)	−0.339(1)	−0.434(1)	52(5)					
C20	−0.935(1)	−0.224(1)	−0.424(1)	42(5)					
C21	−0.546(1)	−0.116(1)	−0.333(1)	34(4)					
C22	−0.562(1)	−0.271(1)	−0.322(1)	42(5)					
C23	−0.431(1)	−0.343(1)	−0.292(1)	51(5)					
C24	−0.284(1)	−0.259(1)	−0.273(1)	57(5)					
C25	−0.267(1)	−0.103(1)	−0.285(1)	54(5)					
C26	−0.398(1)	−0.032(1)	−0.315(1)	46(5)					
H1	−0.603(1)	0.169(1)	−0.509(1)	99(7)					
H2	−0.341(1)	0.223(1)	−0.442(1)	99(7)					
H3	−0.308(1)	−0.028(1)	−0.391(1)	99(7)					
H4	−0.550(1)	−0.237(1)	−0.426(1)	99(7)					
H5	−0.732(1)	−0.116(1)	−0.499(1)	99(7)					
H8A	−0.751(2)	0.406(2)	−0.445(1)	99(7)					
H8B	−0.558(2)	0.505(2)	−0.423(1)	99(7)					
H8C	−0.715(2)	0.493(2)	−0.394(1)	99(7)					
H10	−1.053(1)	0.124(1)	−0.383(1)	99(7)					
H11	−1.175(1)	0.327(1)	−0.344(1)	99(7)					
H12	−0.997(1)	0.443(1)	−0.279(1)	99(7)					
H13	−0.697(1)	0.357(1)	−0.252(1)	99(7)					
H14	−0.576(1)	0.154(1)	−0.290(1)	99(7)					
H16	−0.940(1)	−0.154(1)	−0.322(1)	99(7)					
H17	−1.164(1)	−0.359(1)	−0.339(1)	99(7)					
H18	−1.240(1)	−0.478(1)	−0.411(1)	99(7)					
H19	−1.094(1)	−0.391(1)	−0.465(1)	99(7)					
H20	−0.871(1)	−0.186(1)	−0.448(1)	99(7)					
H22	−0.676(1)	−0.336(1)	−0.336(1)	99(7)					
H23	−0.444(1)	−0.463(1)	−0.283(1)	99(7)					
H24	−0.182(1)	−0.314(1)	−0.250(1)	99(7)					
H25	−0.153(1)	−0.038(1)	−0.270(1)	99(7)					
H26	−0.386(1)	0.089(1)	−0.324(1)	99(7)					
Fe′	−0.7927(3)	−0.4932(3)	−0.0743(1)	17(1)	48(1)	62(2)	−1(1)	17(1)	7(1)
P′	−0.9761(5)	−0.3929(6)	−0.1286(1)	28(3)	36(3)	47(3)	2(3)	17(2)	−2(3)
O6′	−1.065(2)	−0.598(2)	−0.035(1)	7(1)	13(1)	9(1)	−1(1)	4(1)	4(1)
O7′	−0.742(2)	−0.705(1)	−0.135(0)	9(1)	6(1)	10(1)	2(1)	5(1)	−1(1)
C6′	−0.962(2)	−0.561(2)	−0.052(1)	9(2)	5(1)	4(1)	2(1)	0(1)	5(1)

(continued)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C7′	-0.785(2)	-0.691(2)	-0.103(1)	4(1)	6(1)	5(1)	0(1)	2(1)	1(1)
C1′	-0.591(1)	-0.497(1)	-0.017(1)	5(0)					
C2′	-0.523(1)	-0.522(1)	-0.053(1)	6(1)					
C3′	-0.561(1)	-0.388(1)	-0.079(1)	5(0)					
C4′	-0.652(1)	-0.280(1)	-0.060(1)	5(0)					
C5′	-0.671(1)	-0.348(1)	-0.022(1)	5(1)					
C8′	-0.827(2)	-0.839(3)	-0.086(1)	10(1)					
C9′	-1.130(1)	-0.530(1)	-0.162(1)	4(0)					
C10′	-1.268(1)	-0.577(1)	-0.146(1)	5(1)					
C11′	-1.380(1)	-0.691(1)	-0.168(1)	5(0)					
C12′	-1.353(1)	-0.760(1)	-0.204(1)	6(1)					
C13′	-1.215(1)	-0.713(1)	-0.220(1)	6(1)					
C14′	-1.103(1)	-0.598(1)	-0.198(1)	5(1)					
C15′	-1.123(1)	-0.249(1)	-0.116(1)	3(0)					
C16′	-1.266(1)	-0.200(1)	-0.147(1)	4(0)					
C17′	-1.374(1)	-0.085(1)	-0.137(1)	5(0)					
C18′	-1.338(1)	-0.019(1)	-0.097(1)	6(1)					
C19′	-1.194(1)	-0.068(1)	-0.066(1)	5(1)					
C20′	-1.087(1)	-0.183(1)	-0.076(1)	4(0)					
C21′	-0.878(1)	-0.290(1)	-0.167(1)	4(0)					
C22′	-0.918(1)	-0.135(1)	-0.178(1)	5(0)					
C23′	-0.848(1)	-0.063(1)	-0.209(1)	5(1)					
C24′	-0.738(1)	-0.148(1)	-0.227(1)	5(1)					
C25′	-0.698(1)	-0.303(1)	-0.216(1)	6(1)					
C26′	-0.768(1)	-0.374(1)	-0.185(1)	5(0)					
H1′	0.417(1)	-0.578(1)	0.009(1)	99(7)					
H2′	0.545(1)	-0.625(1)	-0.059(1)	99(7)					
H3′	0.473(1)	-0.371(1)	-0.109(1)	99(7)					
H4′	0.301(1)	-0.167(1)	-0.072(1)	99(7)					
H5′	0.266(1)	-0.294(1)	0.000(1)	99(7)					
H8A′	-0.865(2)	-0.818(3)	-0.057(1)	99(7)					
H8B′	-0.716(2)	-0.915(3)	-0.080(1)	99(7)					
H8C′	-0.930(2)	-0.895(3)	-0.109(1)	99(7)					
H10′	-1.289(1)	-0.524(1)	-0.118(1)	99(7)					
H11′	-1.487(1)	-0.727(1)	-0.156(1)	99(7)					
H12′	-1.440(1)	-0.849(1)	-0.221(1)	99(7)					
H13′	-1.194(1)	-0.766(1)	-0.248(1)	99(7)					
H14′	-0.996(1)	-0.562(1)	-0.210(1)	99(7)					
H16′	-1.294(1)	-0.251(1)	-0.178(1)	99(7)					
H17′	-1.485(1)	-0.048(1)	-0.161(1)	99(7)					
H18′	-1.421(1)	0.070(1)	-0.089(1)	99(7)					
H19′	-1.166(1)	-0.017(1)	-0.035(1)	99(7)					
H20′	-0.976(1)	-0.220(1)	-0.052(1)	99(7)					
H22′	-1.003(1)	-0.069(1)	-0.164(1)	99(7)					
H23′	-0.879(1)	0.057(1)	-0.218(1)	99(7)					
H24′	-0.683(1)	-0.093(1)	-0.251(1)	99(7)					
H25′	-0.613(1)	-0.369(1)	-0.230(1)	99(7)					
H26′	-0.738(1)	-0.495(1)	-0.176(1)	99(7)					

match so well individual atom refinements [20–22], we feel this procedure is justified (see discussion in ref. 14).

The structural parameters of Fe–C≡O in **IIa**/**IIb** (Tables III and IV) are virtually the same as those of **III**, which were already compared with literature values and found to be well behaved. The shorter Fe–C(CO) distance in **III** (1.749 Å) with respect to that found in **IIa**/**IIb** (1.811 and 1.791 Å) is in line with the longer Fe–C(COCH$_3$) distance in **III** (1.976 Å) compared to **IIa**/**IIb** (1.938 and 1.940 Å). Since the Fe–P distances in **IIa**/**IIb** (2.189 and 2.187 Å) and **III** (2.188 Å) are identical, the ligands CO and COCH$_3$ seem to compete in a push–pull mechanism for multiple bonding to Fe [12, 14]. The differences between **IIa**/**IIb** and **III** are probably due

TABLE III. Bond Lengths (Å)[a]

	Molecule **IIa**	Molecule **IIb** [b]	Average
Fe–P	2.189(6)	2.187(7)	2.188
Fe–C6	1.811(27)	1.791(29)	1.801
Fe–C7	1.938(31)	1.940(27)	1.939
Fe–Cp [c]	1.758	1.762	1.761
Fe–C1	2.148(13)	2.152(13)	2.135
Fe–C2	2.127(14)	2.130(15)	
Fe–C3	2.114(14)	2.118(14)	
Fe–C4	2.127(15)	2.131(16)	
Fe–C5	2.149(16)	2.152(16)	
P–C9	1.838(12)	1.849(12)	1.843
P–C15	1.841(11)	1.825(11)	
P–C21	1.849(11)	1.854(11)	
C6–O6	1.116(26)	1.149(27)	1.133
C7–O7	1.202(27)	1.174(26)	1.188
C7–C8	1.474(36)	1.457(36)	1.466

[a] e.s.d.s given in parentheses. Phenyl and Cp rings were refined as rigid bodies with Ph(C–C) = 1.395 Å and Cp(C–C) = 1.420 Å. All C–H = 1.08 Å. [b] Labels for molecule **IIb** are identical with molecule **IIa** but are primed in Table II. [c] Cp is the ring centroid.

TABLE IV. Bond Angles (°)[a]

	Molecule **IIa**	Molecule **IIb**	Average
C6–Fe–P	91.4(9)	91.2(8)	91.3
C7–Fe–P	91.6(8)	92.4(8)	92.0
C7–Fe–C6	92.5(1.2)	92.0(1.1)	92.3
C9–P–Fe	116.9(5)	116.8(5)	116.9
C9–P–C15	100.2(7)	100.3(7)	100.3
C9–P–C21	104.8(7)	103.9(7)	104.4
C15–P–Fe	114.7(6)	115.3(6)	115.0
C15–P–C21	103.4(7)	104.0(7)	103.7
C21–P–Fe	115.0(6)	114.6(6)	114.8
Fe–C6–O6	176.3(3.0)	174.6(2.9)	175.5
Fe–C7–O7	124.3(2.2)	124.7(2.2)	124.5
O7–C7–C8	115.9(2.9)	113.3(2.7)	114.5
Fe–C7–C8	119.7(2.0)	122.0(2.1)	120.9

[a] e.s.d.s given in parentheses.

TABLE V. Equations of Least-squares Planes and Dihedral Angles (°) Between Pairs of Planes

Plane 1: defined by Fe, C7, C8 and O7

IIa $0.8630x + 0.1021y - 0.4948z - 5.220 = 0$
IIb $-0.8525x + 0.1159y - 0.5097z - 5.667 = 0$

Plane 2: defined by C9 → C14 (phenyl ring 1)

IIa $0.4513x + 0.7119y - 0.5381z - 4.828 = 0$
IIb $-0.4420x + 0.7082y - 0.5505z - 3.080 = 0$

Plane 3: defined by C15 → C20 (phenyl ring 2)

IIa $-0.6412x + 0.7046y - 0.3040z - 5.385 = 0$
IIb $0.6384x + 0.7101y - 0.2970z + 5.593 = 0$

Plane 4: defined by C21 → C26 (phenyl ring 3)

IIa $0.6180x - 0.3046y - 0.7248z - 6.892 = 0$
IIb $-0.6212x - 0.3064y - 0.7212z - 8.143 = 0$

Plane 5: defined by C1 → C5 (Cp ring)

IIa $0.7713x - 0.4165y - 0.4813z - 6.577 = 0$
IIb $-0.7666x - 0.4186y - 0.4870z - 5.597 = 0$

Plane A	Plane B	Dihedral angle	
		IIa	**IIb**
1	2	43.25	42.31
1	3	109.33	108.09
1	4	30.59	30.49
1	5	30.54	31.44
2	3	67.92	67.41
2	4	63.13	62.96
2	5	71.91	71.91
3	4	112.99	113.58
3	5	129.92	129.94
4	5	17.76	17.12

TABLE VI. Selected Torsional Angles (°)[a]

	Molecule **IIa**	Molecule **IIb**
Cp–Fe–P–C9	161.95	161.27
–C15	−81.28	−81.26
–C21	38.36	39.46
C6–Fe–P–C9	−59.53	−59.94
–C15	57.24	57.53
–C21	176.89	178.24
C7–Fe–P–C9	33.05	32.08
–C15	149.82	149.55
–C21	−90.53	−89.74
C6–Fe–Cp–C5	−31.56	−33.05
Cp–Fe–C7–O7	−73.58	−74.49

[a] Cp is the position of the centroid of the cyclopentadiene ring.

to the formation of the hydrogen bond from the acetyl ligand to the aminophosphine NH group in **III**, which is not possible for **II**. The effect of this additional hydrogen bond in **III** is also reflected by the C=O(acetyl) distances: in **IIa**/**IIb** these distances are 1.202 and 1.174 Å and in **III** 1.208 Å.

In a previous paper [14] we remarked that the Fe–P distance in **III** (2.188 Å) was one of the shortest reported for unoxidized iron phosphines and we speculated that the presence of a hydrogen-bonded amino group may alter the electronic environment of the Fe–phosphineamine moiety enough to be responsible for the improved Fe–P bonding. Some evidence was offered in support of this tentative thesis. Now, it appears this cannot be the origin of the strong Fe–P bonding since the triphenylphosphine derivative **II** has an identical Fe–P

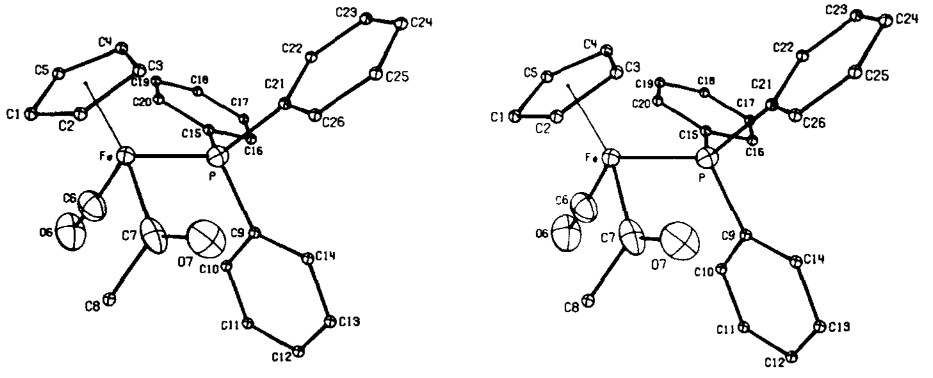

Fig. 1. Stereoscopic view of compound **II** showing the atomic labelling scheme.

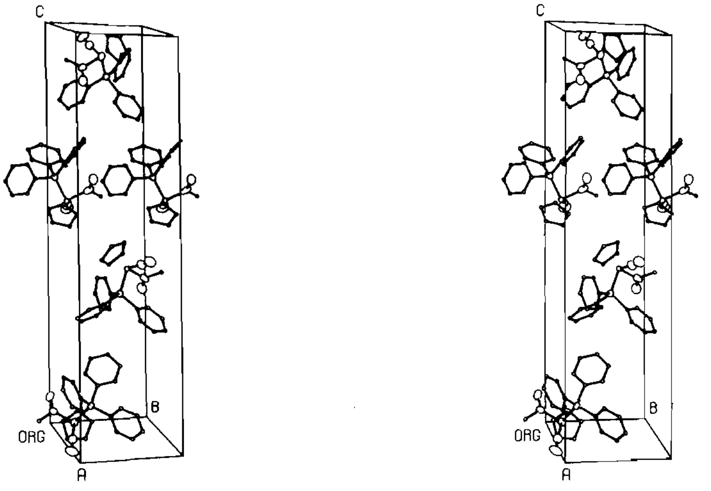

Fig. 2. Stereoscopic packing diagram of compound **II**.

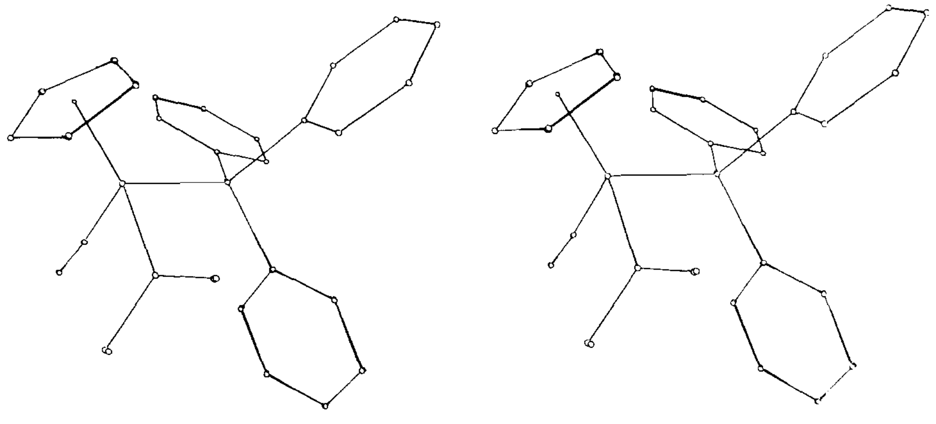

Fig. 3. BMFIT least-squares fit of molecules **IIa** and **IIb** present in the asymmetric unit.

bond length. Thus, the acceptor strength of CO and $COCH_3$ must be the origin of the improved Fe–P bonding, making $P(C_6H_5)_3$ a better donor.

Absolute Configuration

When the refinement converged using the original coordinates, the R and R_w factors had values of 0.0688 and 0.0583, respectively. Upon inversion of the coordinates and refinement to convergence, these quantities had values of 0.0623 and 0.0487, which, given the above comments, was taken to fix the absolute configuration of this molecule. The coordinates used for all subsequent data processing, listed in Table II, are those of the correct absolute

TABLE VII. BMFIT Calculated Differences (in Å) Between Atoms of Molecules **IIa** and **IIb**

Fe	Fe′	0.005	C12	C12′	0.017
P	P′	0.018	C13	C13′	0.021
O6	O6′	0.019	C14	C14′	0.014
O7	O7′	0.036	C15	C15′	0.005
C6	C6′	0.029	C16	C16′	0.008
C7	C7′	0.010	C17	C17′	0.008
C1	C1′	0.014	C18	C18′	0.017
C2	C2′	0.024	C19	C19′	0.018
C3	C3′	0.033	C20	C20′	0.008
C4	C4′	0.032	C21	C21′	0.008
C5	C5′	0.023	C22	C22′	0.008
C8	C8′	0.065	C23	C23′	0.011
C9	C9′	0.016	C24	C24′	0.013
C10	C10′	0.031	C25	C25′	0.010
C11	C11′	0.028	C26	C26′	0.006

configuration. Since both molecules in the asymmetric unit have identical labels (except for the primes) and since they have identical configurations, only one molecular stereo-diagram (Fig. 1) is given. The fact that the two molecules have nearly identical conformation is shown in the double stereo (BMFIT) diagram, Fig. 3. Using the ranking of the ligands Cp > P > C(CO) > C(acetyl) [23, 24], the correct absolute configuration at Fe is (S) for both molecules in the asymmetric unit, as expected since this is a pure enantiomer. This result establishes the change of configuration at Fe in going from $(-)_{578}$-**I** to $(+)_{578}$-**II**, according to Scheme 1.

Conformation of the Acetyl Group

Not only the bond lengths and angles of **IIa** and **IIb** (Tables III and IV) but also the conformations of **IIa** and **IIb** are essentially identical (Fig. 3). Table VII lists the largest differences encountered upon a least-squares fit in order to draw the BMFIT (Best Molecular FIT) stereo plot [19]. Since the packing environment of the two molecules is different (Fig. 2) the conformation found for **IIa** and **IIb** must represent an energy minimum over which packing forces have no control.

The C–CH_3 bond of the acetyl ligand is close to being aligned with the Fe–C(CO) bond as in other $C_5H_5Fe(CO)[P(C_6H_5)_3]COR$ compounds [9, 13, 25]. This arrangement makes the acetyl oxygen in **IIa** and **IIb** point in the direction of the phosphorus atom. Similarly, the M–COOR plane in **I** is almost aligned with the Fe–C(CO) bond [11, 12] and the Re–carbene plane in $C_5H_5Re(NO)[P(C_6H_5)_3]CHR^+$ with the Re–N(NO) bond [26–28]. Taking into account that the rotation around the Mn–acetyl bond in $Mn(CO)_4COCH_3$ was calculated to be 20 Kcal/mol [29], it can be assumed that the arrangement found in the crystal persists in solution. With this orientation of the acetyl oxygen, the stereochemical results obtained in phosphine exchange reactions with compounds of the type **II** and **III** can be explained. In these reactions solutions of optically active $C_5H_5Fe(CO)(PR_3)COCH_3$ undergo a phosphine exchange reaction with an added phosphine PR'_3. The substitution products $C_5H_5Fe(CO)(PR'_3)COCH_3$ are still optically active and have the same relative configuration at the Fe atom as the starting material $C_5H_5Fe(CO)(PR_3)COCH_3$ [30]. Retention stereochemistry was also found for the ligand substitution in C_5H_5Rh–acyl complexes [31].

As a mechanism for the epimerization and ligand exchange in the optically active complexes $C_5H_5Fe(CO)(PR_3)COCH_3$ it was suggested that the acetyl oxygen replaced the phosphine ligand in a frontside attack to form a dihapto acetyl intermediate $C_5H_5Fe(CO)(\eta^2\text{-}COCH_3)$ retaining the configuration at the Fe atom. Partial epimerization at the Fe atom in these phosphine substitution reactions was attributed to a slow rotation of the η^2-$COCH_3$ ligand prior to attack of the intermediate $C_5H_5Fe(CO)(\eta^2\text{-}COCH_3)$ by PR'_3 to give the substitution product [30]. In the X-ray structure determination of compound **III** it was found that the acetyl oxygen also was directed to the phosphine substituent, specifically by hydrogen bonding to the adjacent NH group [11]. So, the orientation of the acetyl group in compounds **IIa**, **IIb**, and **III** is in accord with the mechanism suggested to account for the retention stereochemistry in phosphine exchange reactions with respect to the Fe atom [30]. An alternative explanation of the observed retention stereochemistry at Fe would be a double inversion. In such a mechanism the acetyl oxygen would replace the phosphine ligand by backside attack at the Fe atom inverting its configuration. By another inversion the incoming new ligand would lead to the observed retention product. For such a mechanism the acetyl group would have to rotate, a process known to have a high activation energy [29]. In such a mechanism the activation energy would be required to overcome the barrier for the rotation. The present X-ray structure determination confirms the proximity of a phenyl ligand to one side of the acetyl plane, corroborating the results and the box model of Davies and its stereochemical consequences with respect to reactions of the acetyl ligand [8, 9].

References

1 H. Brunner, J. Ernst, T. Wischert and U. Thewalt, *J. Organomet. Chem., 328,* 331 (1987).

2 H. Brunner and E. Schmidt, *J. Organomet. Chem., 21,* P53 (1970).

3 H. Brunner and E. Schmidt, *J. Organomet. Chem., 36,* C18 (1972); *J. Organomet. Chem., 50,* 219 (1973).

4 H. Brunner and J. Strutz, *Z. Naturforsch., Teil B, 29,* 446 (1974).

5 H. Brunner, *Top. Curr. Chem.*, *56*, 67 (1975).

6 H. Brunner, *Adv. Organomet. Chem.*, *18*, 151 (1980).

7 H. Brunner and H.-D. Schindler, *Z. Naturforsch.*, *Teil B*, *26*, 1221 (1971).

8 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton and J. C. Walker, *Tetrahedron*, *42*, 5123 (1986).

9 S. G. Davies, I. M. Dordor-Hedgecock, R. J. C. Easton, S. C. Preston, K. H. Sutton and J. C. Walker, *Bull. Soc. Chim. Fr.*, 608 (1987).

10 C.-K. Chou, D. L. Miles, R. Bau and T. C. Flood, *J. Am. Chem. Soc.*, *100*, 7271 (1978).

11 M. G. Reisner, I. Bernal, H. Brunner and M. Muschiol, *Angew. Chem.*, *88*, 847 (1976); *Angew. Chem., Int. Ed. Engl.*, *15*, 776 (1976).

12 G. M. Reisner, I. Bernal, H. Brunner and M. Muschiol, *Inorg. Chem.*, *17*, 783 (1978).

13 S. G. Davies, I. M. Dordor-Hedgecock, K. H. Sutton, J. C. Walker, C. Bourne, R. J. Jones and K. Prout, *J. Chem. Soc., Chem. Commun.*, 607 (1986).

14 J. D. Korp and I. Bernal, *J. Organomet. Chem.*, *220*, 335 (1981).

15 G. M. Reisner, I. Bernal and G. R. Dobson, *J. Organomet. Chem.*, *157*, 23 (1978).

16 G. M. Sheldrick, 'SHELX-76', a program for crystal structure determination, Cambridge University, Cambridge, 1976.

17 I. Bernal, *Inorg. Chim. Acta*, *101*, 175 (1985).

18 C. K. Johnson, 'ORTEP 2', a Fortran ellipsoid plotting program for crystal structure illustration, *ORNL-5138*, Oak Ridge, Tenn., 1972.

19 L.-K. Liu, 'BMFIT', University of Texas, Austin, Tex. 1977 (modified at the University of Houston by J. D. Korp, 1981).

20 G. A. Melson, P. F. Stokely and R. F. Bryan, *J. Chem. Soc. A*, 2247 (1970).

21 P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 2261 (1970).

22 L. F. Dahl, R. J. Doedens, W. Hübel and J. Nielsen, *J. Am. Chem. Soc.*, *88*, 446 (1966).

23 C. Lecomte, Y. Dusausoy, J. Protas, J. Tirouflet and A. Dormond, *J. Organomet. Chem.*, *73*, 67 (1974).

24 K. Stanley and M. C. Baird, *J. Am. Chem. Soc.*, *97*, 6598 (1976).

25 G. J. Baird, J. A. Bandy, S. G. Davies and K. Prout, *J. Chem. Soc., Chem. Commun.*, 1202 (1983).

26 W.-K. Wong, W. Tam, C. E. Strouse and J. A. Gladysz, *J. Chem. Soc., Chem. Commun.*, 530 (1979).

27 W. A. Kiel, G.-Y. Lin, A. G. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein and J. A. Gladysz, *J. Am. Chem. Soc.*, *104*, 4865 (1982).

28 B. E. R. Schilling, R. Hoffmann and J. W. Faller, *J. Am. Chem. Soc.*, *101*, 592 (1979).

29 H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, *100*, 7224 (1978).

30 H. Brunner and H. Vogt, *Chem. Ber.*, *114*, 2186 (1981).

31 S. Quinn, A. Shaver and V. W. Day, *J. Am. Chem. Soc.*, *104*, 1096 (1982).