

Synthesis and molecular structure of enantiopure 1-(diphenylphosphino)-2,1'-[(1-*N,N*-dimethylamino)-1,3-propanediyl]-ferrocene and its palladium dichloride complex, a new ligand for enantioselective catalysts

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Abstract

The palladium dichloride complex of (*S_c, S_m*)-1-(diphenylphosphino)-2,1'-[(1-*N,N*-dimethylamino)-1,3-propanediyl]-ferrocene (**5**-PdCl₂) has been prepared from enantiopure (*S*)-1,1'-[(1-*N,N*-dimethylamino)-1,3-propanediyl]-ferrocene (**4**) via a highly stereoselective ortho-lithiation followed by reaction with chlorodiphenyl phosphine to give amino phosphine **5**, which on treatment with (CH₃CN)₂PdCl₂ gave the complex **5**-PdCl₂. The absolute configuration of the (-)₅₈₉-enantiomer of **4** was deduced from the X-ray structure of its tartrate confirming (*S*)-configuration at the stereogenic center. A conformational analysis including X-ray structure analysis of **5** and **5**-PdCl₂ as well as empirical force field calculations on **4** and **5** together with NMR data shows strong stereochemical similarities of **5** and **5**-PdCl₂ with the widely used ligand PPFA and its palladium dichloride complex PPFA-PdCl₂.

Keywords: Iron; Aminophosphines; Palladium complex; Ferrocenes; Crystal structure; Catalyst

1. Introduction

A variety of ferrocene derivatives has already been successfully identified as ligands for enantioselective homogeneous catalysts [1,2]. Most of these ligands are derived from (1-*N,N*-dimethylaminoethyl)ferrocene (**1**) as the starting material, which is easy to resolve into its enantiomers and can conveniently be transformed into a number of 1,2-disubstituted bidentate ligands via ortho-lithiation and subsequent reaction with electrophiles [3]. Thus the synthesis of the widely used PPFA ligand 2-(1-*N,N*-dimethylaminoethyl)-1-diphenylphosphinoferrocene (**2**) was easily achieved by reaction of **1** with butyllithium and subsequent treatment of the reaction mixture with chlorodiphenylphosphine [3,4]. Further modification of the dimethylamino group led to a diversity of bidentate or potentially multidentate ferrocene ligands. Although a respectable number of highly enan-

tioselective reactions have been reported with ferrocenyl modified transition metal catalysts [1,5], ligand development appears to be limited by the small number of easily accessible enantiomerically pure starting compounds. Therefore we set out to search for enantiopure amino ferrocenes other than **1** and to test their potential as starting material for new bidentate and multidentate ligands of homogeneous enantioselective catalysts. Recently, we reported on aminoalcohols and aminophosphines based on α -*N,N*-dimethylamino [1,2] tetramethylenferrocene (**3**) and on their use in cross coupling and alkylation reactions [6–8].

In the present communication we describe synthesis and structural features of the heteroannularly bridged amine **4**, aminophosphine **5** and its palladium dichloride complex **5**-PdCl₂, which was found to be a potential Grignard cross-coupling catalyst precursor similar to the widely used PPFA-PdCl₂ complex (**2**-PdCl₂). Furthermore, structural features of **4**, **5** and **5**-PdCl₂ are compared with those of **1**, **2** and **2**-PdCl₂ both in the solid state and in solution.

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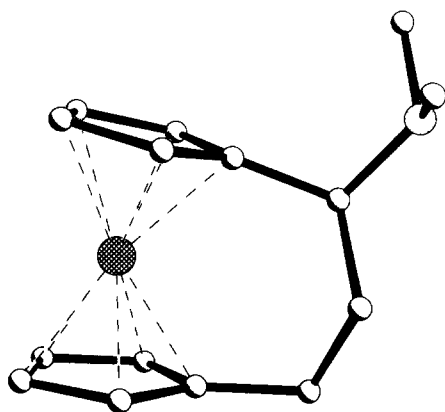


Fig. 1. Crystal structure of the (*R,R*) tartrate of (*-*)-(*S_c*)-**4** (**4-T**). Hydrogen atoms have been omitted for clarity.

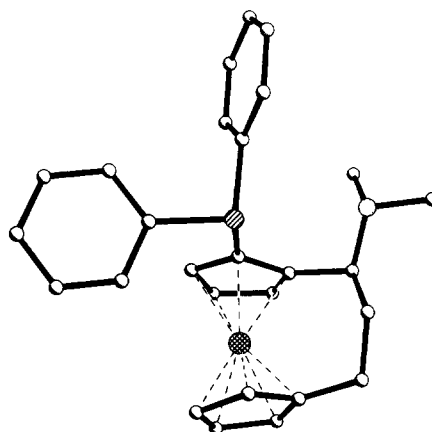


Fig. 2. Crystal structure of (*-*)-(*S_c, S_m*)-**5**.

2. Results and discussion

Racemic amine **4** is readily accessible from ferrocene aldehyde via a published five-step synthesis [9,10]. Optical resolution of **4** can be achieved by fractional crystallization of its tartrates [11]. A single-crystal X-ray structure analysis of the less soluble salt reveals an (*S*)-configuration for the (*-*)-enantiomer of **4** (Fig. 1), thus confirming the original assignment based on chemical correlation [12]. Reaction of **4** with 1.2 equivalents of *n*-butyl lithium and subsequent treatment with chlorodiphenylphosphine gave aminophosphine **5**. As for (*S*)-**1** [3], the ortho-lithiation of (*S*)-**4** is highly stereoselective; however, it leads to products with reversed configuration at the ferrocene unit. Reaction of lithiated (*S*)-**1** with chlorodiphenylphosphine results in (*S_c, R_m*)-**2**¹ (Scheme 1), while (*S*)-**4** gives aminophosphine (*S_c, S_m*)-**5** (Scheme 1) as confirmed by X-ray structure analysis (Figs. 2 and 3). Treatment of **5** with (CH₃CN)₂ PdCl₂ in benzene gave the palladium dichloride complex **5**-PdCl₂ whose molecular structure was also determined by X-ray crystallography (Fig. 4).

2.1. X-ray structures of the tartrate of **4** (**4-T**), aminophosphine **5** and its palladium dichloride complex **5**-PdCl₂

All diffraction data were collected at a low temperature (85(2) K); structures were solved with direct methods and refined with least squares as described in Section 3. For each structure analysis, the absolute structure was determined from the anomalous data [13] and agreed with the chemical evidence.

2.1.1. **4**.

The less soluble (*R,R*)-tartrate of **4** (**4-T**) crystallizes in the monoclinic space group *P2*₁, with two molecules in the unit cell. The molecular conformation of the ferrocene moiety of **4-T** is shown in Fig. 1; final atomic coordinates are listed in Table 1. Since the configuration of the tartrate monoanion is known to be (*R,R*), the assignment of (*S*)-configuration to carbon C(21) of **4-T**, and of the related (*-*)₅₈₉-enantiomer of **4** is straightforward. This is also corroborated by the anomalous dispersion data (see Section 3).

A discussion of general structural features of the ferrocenyl ammonium cation is given below. As expected [7], the tartrate monoanion shows almost identical C–O bond lengths in the carboxylate part (1.249(4) and 1.266(4) Å) whereas these bond distances differ

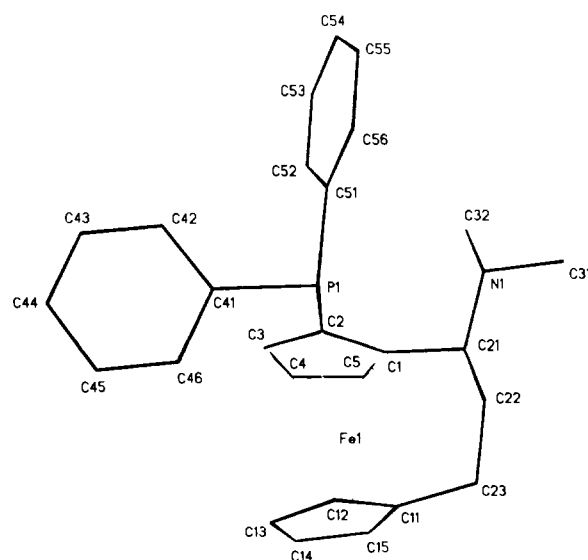
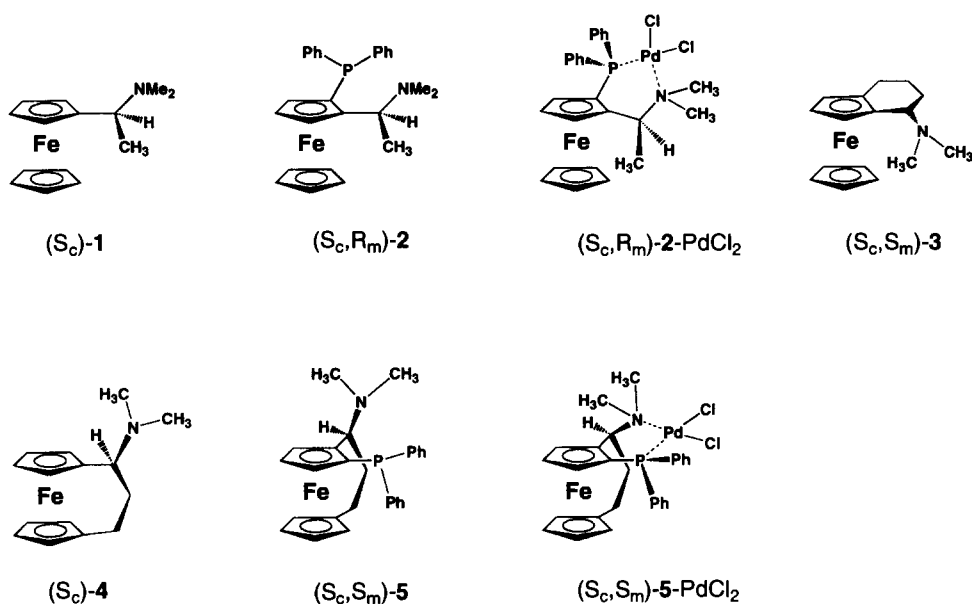


Fig. 3. Crystal structure of (*-*)-(*S_c, S_m*)-**5**, showing the atom numbering. An analogous scheme was also employed for the crystal structure of **4-T** and **5**-PdCl₂.

¹ The subscript c denotes the stereogenic center at C(21) (see Fig. 3 later) while m refers to the metallocene unit.



Scheme 1.

significantly in the hydroxycarbonyl group (C–OH, 1.313(4) Å C=O, 1.206(4) Å). The crystal packing is dominated by the formation of two intermolecular H

bonds between translationally equivalent tartrate ions (H(O(6)) ··· O(2) (1 + x, y, z), 1.65 Å) and between the ammonium hydrogen atom H(N(1)) and one of the

Table 1

Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms in the crystal structure of 4-T, where U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor, and the atomic numbering is analogous to that shown in Fig. 3

	x/a ($\times 10^{-4}$)	y/b ($\times 10^{-4}$)	z/c ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3} \text{ \AA}^2$)
Fe(1)	3448(1)	5034(1)	9383(1)	15(1)
C(1)	4640(3)	5037(5)	8030(2)	16(1)
C(2)	5243(4)	6242(4)	8607(3)	18(1)
C(3)	6035(4)	5723(4)	9525(3)	19(1)
C(4)	5961(4)	4185(4)	9504(3)	19(1)
C(5)	5106(4)	3733(4)	8587(3)	16(1)
C(11)	908(3)	5015(5)	8908(2)	18(1)
C(12)	1239(5)	6274(4)	9509(3)	20(1)
C(13)	1810(5)	5807(5)	10501(3)	24(1)
C(14)	1825(5)	4265(5)	10512(3)	22(1)
C(15)	1259(5)	3777(4)	9530(3)	20(1)
C(21)	3530(3)	5146(4)	7084(2)	16(1)
C(22)	1805(4)	4281(3)	7107(2)	19(1)
C(23)	410(3)	4989(6)	7794(2)	21(1)
N(1)	4597(3)	4754(3)	6140(2)	18(1)
C(31)	6229(4)	5647(4)	6069(2)	23(1)
C(32)	5026(4)	3177(4)	6062(2)	25(1)
C(81)	-1932(3)	10260(3)	6197(2)	18(1)
O(1)	-2421(3)	10705(3)	5342(2)	22(1)
O(2)	-2853(3)	9579(3)	6845(2)	25(1)
C(82)	-37(4)	10612(4)	6518(2)	18(1)
O(3)	898(3)	11302(3)	5722(2)	21(1)
C(83)	948(4)	9234(3)	6833(2)	18(1)
O(4)	813(3)	8146(3)	6077(2)	24(1)
C(84)	2854(3)	9659(3)	7081(2)	18(1)
O(5)	3181(3)	10496(3)	7762(2)	27(1)
O(6)	4016(3)	9045(3)	6476(2)	22(1)

Table 2
Coordinates and displacement parameters for the crystal structure of **5**, where the atomic numbering is defined in Fig. 3

	$x/a (\times 10^{-4})$	$y/b (\times 10^{-4})$	$z/c (\times 10^{-4})$	$U_{eq} (\times 10^{-3} \text{ \AA}^2)$
Fe(11)	1411(1)	-4773(2)	2875(1)	20(1)
P(11)	3272(1)	-5460(4)	3518(1)	19(1)
N(11)	3497(4)	-3252(10)	1904(4)	26(2)
C(11)	2292(4)	-3360(11)	2515(4)	19(2)
C(21)	2465(4)	-4017(12)	3250(4)	18(2)
C(31)	1909(4)	-3272(11)	3719(5)	19(2)
C(41)	1392(5)	-2192(12)	3303(5)	26(2)
C(51)	1645(5)	-2225(11)	2554(5)	24(2)
C(111)	1312(4)	-6569(12)	2042(5)	26(2)
C(121)	1454(5)	-7506(11)	2717(5)	28(2)
C(131)	872(5)	-7098(12)	3211(6)	33(2)
C(141)	356(4)	-5941(14)	2839(5)	35(2)
C(151)	613(4)	-5601(12)	2119(5)	33(2)
C(211)	2709(5)	-3834(12)	1804(5)	21(2)
C(221)	2654(5)	-5839(13)	1583(5)	25(2)
C(231)	1849(5)	-6493(13)	1401(5)	28(2)
C(311)	3952(5)	-3561(15)	1255(5)	33(2)
C(321)	3545(5)	-1343(12)	2103(5)	26(2)
C(411)	2948(5)	-6293(12)	4416(4)	23(2)
C(421)	3036(4)	-5357(13)	5086(4)	25(2)
C(431)	2791(5)	-6139(14)	5741(5)	33(2)
C(441)	2439(6)	-7812(15)	5719(5)	41(3)
C(451)	2346(6)	-8759(14)	5069(5)	39(3)
C(461)	2589(5)	-7982(11)	4420(5)	26(2)
C(511)	3946(4)	-3718(12)	3828(5)	24(2)
C(521)	4707(4)	-4209(14)	3870(4)	26(2)
C(531)	5266(5)	-2999(14)	4114(5)	35(2)
C(541)	5067(5)	-1253(14)	4305(5)	35(2)
C(551)	4313(4)	-747(13)	4275(5)	29(2)
C(561)	3760(5)	-1967(12)	4038(5)	27(2)
Fe(12)	8809(1)	-115(0)	872(1)	16(1)
P(12)	7062(1)	-865(4)	1701(1)	18(1)
N(12)	7895(4)	2328(11)	2824(4)	23(2)
C(12)	8340(4)	1602(11)	1581(4)	15(2)
C(22)	7752(4)	561(10)	1228(4)	14(2)
C(32)	7797(4)	900(12)	451(4)	18(2)
C(42)	8404(4)	2121(12)	319(5)	20(2)
C(52)	8717(4)	2603(11)	1033(5)	16(2)
C(112)	9533(4)	-1344(12)	1586(4)	20(2)
C(122)	9018(5)	-2656(11)	1270(5)	22(2)
C(132)	9109(5)	-2624(12)	479(5)	22(2)
C(142)	9672(4)	-1356(12)	308(5)	23(2)
C(152)	9944(4)	-564(13)	981(4)	27(2)
C(212)	8562(4)	1672(13)	2405(4)	20(2)
C(222)	8841(4)	-155(14)	2700(4)	28(2)
C(232)	9597(5)	-796(14)	2380(4)	28(2)
C(312)	8091(6)	2648(15)	3611(5)	33(3)
C(322)	7648(5)	4096(12)	2539(5)	25(2)
C(412)	6614(4)	-2019(12)	902(4)	19(2)
C(422)	5901(4)	-1598(11)	603(5)	20(2)
C(432)	5603(4)	-2562(13)	0(4)	20(2)
C(442)	5999(4)	-3965(12)	-308(4)	22(2)
C(452)	6721(4)	-4402(12)	-21(5)	26(2)
C(462)	7017(4)	-3468(12)	578(5)	22(2)
C(512)	6331(4)	809(11)	1895(4)	17(2)
C(522)	6220(4)	2371(11)	1478(5)	20(2)
C(532)	5628(4)	3565(12)	1634(5)	24(2)
C(542)	5144(5)	3188(12)	2208(4)	24(2)
C(552)	5252(5)	1623(13)	2622(5)	26(2)
C(562)	5833(4)	434(11)	2469(4)	20(2)
C(1X)	9732(11)	3356(34)	4959(7)	107(6)
C(2X)	10300(11)	4949(43)	5174(8)	138(6)
C(3X)	9659(16)	6603(36)	4623(12)	183(9)

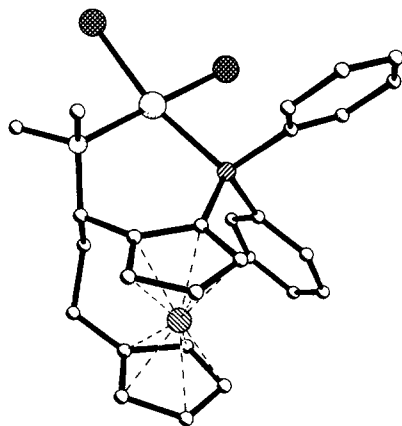
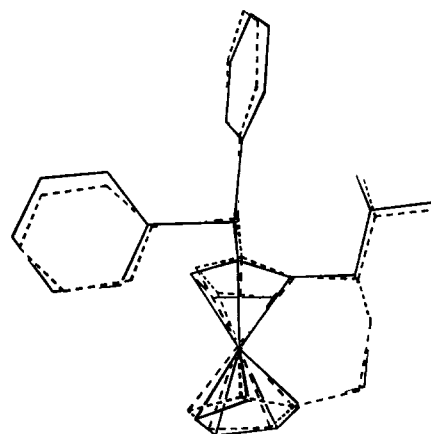
Fig. 4. Crystal structure of (+)-(S_c, S_m)-5-PdCl₂.

Fig. 5. Superposition of the two symmetry-independent molecules of the crystal structure of 5.

tartrate carboxylate oxygen atoms (H(N(1)) ··· O(1) (-x, -1/2 + y, 1 - z), 1.97 Å).

2.1.2. 5.

For the X-ray structure determination a crystal of the (-)₅₈₉-enantiomer was used. Crystals belong to the

monoclinic space group $P2_1$, with four molecules in the unit cell, i.e. two non-equivalent molecules in the asymmetric unit. These two independent molecules have a very similar conformation as shown in their superposition in Fig. 5. The molecular conformations of one of the two molecules of 5 is shown in Fig. 2. Atomic

Table 3

Coordinates and displacement parameters for the crystal structure of 5-PdCl₂, where the atomic numbering is analogous to that shown in Fig. 3

	x/a (×10 ⁻⁴)	y/b (×10 ⁻⁴)	z/c (×10 ⁻⁴)	U _{eq} (×10 ⁻³ Å ²)
Pd(1)	9839(1)	7277(0)	971(1)	16(1)
Cl(1)	11980(2)	7187(1)	3557(2)	30(1)
Cl(2)	9610(2)	5936(1)	973(2)	21(1)
Fe(1)	6625(1)	8770(1)	-4034(1)	17(1)
P(1)	7550(1)	7180(1)	-1295(1)	14(1)
N(1)	10072(5)	8530(3)	914(5)	16(1)
C(1)	7708(6)	8832(3)	-1630(6)	17(1)
C(2)	6755(6)	8130(2)	-2080(6)	16(1)
C(3)	5060(6)	8341(3)	-3014(7)	20(1)
C(4)	4978(7)	9179(3)	-3101(7)	21(1)
C(5)	6595(6)	9482(3)	-2237(6)	18(1)
C(11)	8642(6)	8899(3)	-4567(6)	21(1)
C(12)	7830(7)	8176(3)	-5221(6)	21(1)
C(13)	6194(7)	8342(3)	-6297(7)	23(1)
C(14)	5963(7)	9177(3)	-6343(7)	24(1)
C(15)	7486(7)	9519(3)	-5279(7)	23(1)
C(21)	9540(6)	8888(3)	-750(6)	17(1)
C(22)	10532(6)	8537(3)	-1694(6)	20(1)
C(23)	10312(6)	8990(3)	-3243(6)	22(1)
C(31)	9031(7)	8857(3)	1745(6)	23(1)
C(32)	11788(7)	8804(4)	1887(7)	26(1)
C(41)	7661(6)	6619(3)	-2959(5)	16(1)
C(42)	6218(6)	6503(3)	-4335(6)	21(1)
C(43)	6307(8)	6186(3)	-5718(7)	26(1)
C(44)	7826(9)	5975(4)	-5752(8)	30(1)
C(45)	9254(8)	6078(4)	-4383(8)	28(1)
C(46)	9173(6)	6395(3)	-2980(6)	21(1)
C(51)	5886(6)	6757(3)	-845(6)	17(1)
C(52)	5040(6)	7228(4)	-153(6)	21(1)
C(53)	3778(7)	6909(3)	224(7)	23(1)
C(54)	3347(6)	6132(3)	-97(6)	20(1)
C(55)	4191(7)	5653(3)	-768(7)	25(1)
C(56)	5461(7)	5972(3)	-1135(7)	22(1)

Table 4
Selected conformational parameters of **1-T**, **2**, **2-PdCl₂**, **4-T**, **5** and **5-PdCl₂**

Parameter (units)	Value for following compounds					
	1-T ^a	2	2-PdCl₂	4-T	5 ^a	5-PdCl₂
Tilt angle ^b Cp ¹ –Cp ² (°)	1.8 4.0	2.0	3.9	9.7	10.45 10.63	9.86
Distance of atom from Cp plane (Å)						
Cp ¹ –C(21)	0.079 0.012	–0.026	0.115	0.176	0.066 0.086	0.099
Cp ² –C(23)	—	—	—	0.102	0.147 0.111	0.163
Cp ¹ –N(1)	–1.461 –1.533	–1.314	–1.037	–1.127	–1.103 –1.106	–1.104
Cp ¹ –P(1)	—	0.064	–0.284	—	–0.055 –0.069	–0.283
Cp ¹ –Pd(1)	—	—	–1.383	—	—	–1.207
Cp ¹ –Cl(1)	—	—	–2.910	—	—	–2.475
Cp ¹ –Cl(2)	—	—	–1.599	—	—	–1.255
Distance P(1)–N(1) (Å)	—	3.361	3.233	—	3.362 3.401	3.275

^a Two molecules per asymmetric unit.

^b Cp¹, Cp², least-squares planes defined by carbon atoms C(1)–C(5) (Cp¹) and C(11)–C(15) (Cp²).

coordinates are given in Table 2. According to a force field study (see below), both conformations are calculated to represent minimum-energy conformations.

2.1.3. **5-PdCl₂**

Reaction of the (–)₅₈₉-enantiomer of **5** with (CH₃CN)₂PdCl₂ in benzene gave (+)₅₈₉-**5-PdCl₂**. A suitable crystal was used for X-ray structure analysis. Crystals belong to the monoclinic space group *P*2₁ with two molecules in the unit cell. Fig. 4 shows the molecular conformation of **5-PdCl₂**. Table 3 lists final atomic parameters.

As mentioned above, lithiation of (–)-(*S*)-**4**, and subsequent treatment with chlorodiphenylphosphine leads to (*S*_c, *S*_m)-**5** (Fig. 2) while the same reaction applied to (*S*)-**1** gives (*S*_c, *R*_m)-**2**. Although the relative configuration of **2** differs from that of **5**, it is certainly of interest to compare the molecular structures of **4-T**, **5** and **5-PdCl₂** with those of the very popular and widely used compounds **1-T** [14], **2** [15] and **2-PdCl₂** [16].

The general structural features of **4-T**, **5** and **5-PdCl₂** are very similar. The cyclopentadienyl (Cp) rings are essentially planar but are forced by the three-carbon bridge into a tilted arrangement with a tilt angle of about 10° (Table 4). Steric strain induced by the bridging carbon atoms not only results into tilting of the Cp rings but also leads to significant out-of-plane deformations of the benzylic carbon atoms C(21) and C(23) towards the proximal Cp side (towards the iron-coordinated side of the Cp ring). Bond lengths and bond angles in the ferrocene unit are quite normal; the average Fe–Cp bond lengths are 2.03(2), 2.03(4) and 2.03(2)

Å for **4-T**, **5** and **5-PdCl₂**; the average C_{ar}–C_{ar} bond lengths are 1.43(1), 1.42(1) and 1.43(1) Å respectively.

While in **1-T**, **2** and **2-PdCl₂** the distance of the amino nitrogen from the best plane of the Cp¹ ring (defined by carbon atoms C(1) to C(5)) is adjustable via rotation of the dimethylamino group and varies between 1.533 and 1.037 Å, it is fixed in the bridged compounds at about 1.13 Å (Table 4). Aminophosphines **2** and **5** show many similarities. In both cases the phosphorus atom is only slightly out of plane of the Cp¹ ring with the phosphorus lone pair pointing towards the proximal side (Fig. 2); the N–P distance is 3.361 Å in **2** and

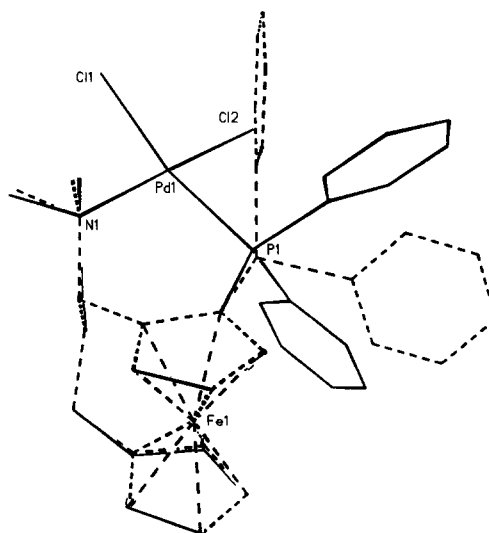


Fig. 6. Superposition of the asymmetric units of the crystal structures of **5** (---) and **5-PdCl₂** (—).

3.362 and 3.401 Å in **5**. As for **2**, complexation of **5** to **5**-PdCl₂ results in pronounced structural changes as shown in the superposition of the crystal structures of **5**-PdCl₂ and **5** (Fig. 6). In order to allow for complexation, the diphenylphosphino group has to be rotated so that the lone pair points towards the distal Cp side, which puts one phenyl ring into close proximity to the Cp² proton H(12), at a distance of 2.59 Å in **2**-PdCl₂ and 2.47 Å in **5**. This structural change can also be seen by NMR spectroscopy (see below). In both complexes, the phosphorus atom is forced out of the Cp plane towards the distal side, by 0.284 Å in **2**-PdCl₂ and 0.283 Å in **5**-PdCl₂, resulting in shorter P–N distances compared with the free ligands (Table 4). Evidently, the non-coplanarity of phosphorus and Cp also relieves some of the strain caused by the proximity between phenyl ring and H(12).

In both structures (**2**-PdCl₂ and **5**-PdCl₂), the square planar arrangement of the palladium substituents is rather distorted, the Cl–Pd–Cl plane being tilted against the N–Pd–P plane by 9.9° in **2**-PdCl₂ and 7.8° in **5**-PdCl₂. The N–Pd–P bond angles are opened up to 96.1° and 96.4° respectively. According to previous reports [17] this might enhance the reactivity of such complexes in catalytic reactions.

The close conformational similarity between the crystal structures of **2**-PdCl₂ and **5**-PdCl₂ is evident from the superposition shown in Fig. 7.

2.2. Minimum-energy conformations of **4** and **5**

To check the conformational possibilities of **4** and **5** an empirical force field study was carried out using the MMX force field implemented in the program PCMODEL [18]. In each case, minimum-energy conformations very similar to those found in the solid state could be lo-

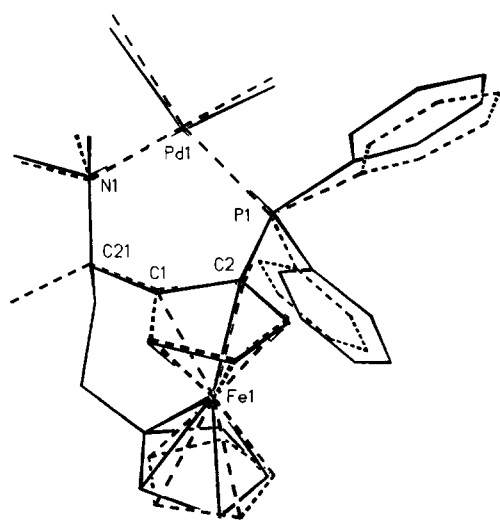


Fig. 7. Superposition (labelled atoms) of the asymmetric units of the crystal structures of **5**-PdCl₂ (—) and **2**-PdCl₂ (---).

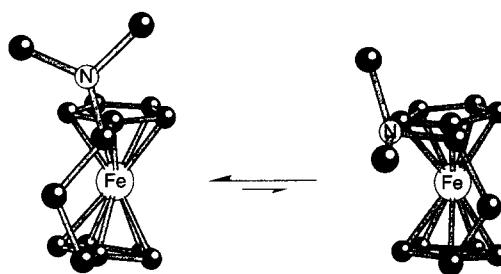


Fig. 8. Calculated molecular structures of **4** with an out-of-plane (left) and an in-plane (right) dimethylamino group.

cated. A close comparison of calculated and experimental data shows that the force field program is well suited to model this type of ferrocene except that out-of-plane deformations are underestimated. While in the crystal C(21) and C(23) are pushed towards the proximal Cp¹ side, these atoms are calculated to essentially lie in the Cp planes. As a consequence the Cp rings are calculated to be much more tilted (**5A**, 24.4°; **5B**, 24.6°) than actually found in the solid state (10.5° and 10.6°; see Table 4).

When viewed along the bond N(1)–C(21) the dimethylamino group in **4-T** can be seen to be in a staggered conformation with bond C(21)–C(1) bisecting the angle C(31)–N(1)–C(32). In **5A** and **5B**, staggered conformations are also found for the dimethylamino group but now the bond H(21)–C(21) bisecting angle C(31)–N(1)–C(32). These side-chain features are again reproduced very well by the force field used. Hence, it was of interest to search for additional conformers which might also contribute to an equilibrium in solution.

As shown in Fig. 8, a flip of the carbon bridge will cause the out-of-plane dimethylamino group to adopt an in-plane position. Calculations show that these minimum energy conformations are of higher energy than the out-of-plane arrangements, the differences being 7.9 kJ mol⁻¹ for **4**, and 24.3 and 22.2 kJ mol⁻¹ for **5A** and **5B** respectively.

2.3. Conformation of **4**, **5** and **5**-PdCl₂ in solution

Straightforward analysis of the vicinal ¹H–¹H coupling constants shows conclusively that all compounds **4**, **5** and **5**-PdCl₂ are present in solution preferably in an out-of-plane conformation. The vicinal coupling constants measured for H(21) (10.3 and 2.8 Hz for **4**, 11.3 and 2.8 Hz for **5**, and 11 and 2 Hz for **5**-PdCl₂) are indicative for one *trans* and one *gauche* interaction, possible only in an out-of-plane arrangement of the dimethylamino group. In addition the complex **5**-PdCl₂ shows a very strong upfield shift of about 2 ppm for one Cp² proton (H(12)) compared with the remaining Cp protons caused by a close interaction with one phenyl ring of the diphenylphosphino unit (Fig. 4). According

to the force field calculations, such an arrangement cannot be expected for a complex with an in-plane dimethylamino group.

The NMR results together with the empirical force field calculations clearly indicate that **5**-PdCl₂ adopts in solution a preferred conformation with the dimethylamino group in an out-of-plane arrangement. Furthermore, comparison of the molecular conformations of **5** and **5**-PdCl₂ with PPFA and its palladium dichloride complex shows many structural similarities most pronounced in the PdCl₂ complexes. It is anticipated that, like PPFA, aminophosphine **5** should be a useful ligand in homogeneous catalysis.

3. Experimental part

¹H, ¹³C and ³¹P NMR (proton-decoupled) spectra were run in CDCl₃ on a Bruker AM-400 spectrometer at 400, 100 and 162 MHz respectively. ¹³C NMR spectra were run in a *J*-modulated mode. Listed *J* values refer to phosphorus–carbon coupling constants. Chemical shifts δ , are given relative to tetramethylsilane as internal standard (¹H and ¹³C NMR) and relative to 85% H₃PO₄ (³¹P NMR). Mass spectroscopy (MS) was carried out on a Varian MAT-CH7. Optical rotations were measured with a Perkin–Elmer polarimeter 241 in CH₂Cl₂ at 20°C (*d* = 1 dm). CD spectra were recorded on a dichrograph CD6 (Jobin–Yvon) in CH₂Cl₂. Melting points were determined on a Kofler melting-point apparatus and are uncorrected. Elemental analyses were carried out at Mikroanalytisches Laboratorium der Universität Wien (J. Theiner).

3.1. 1,1'-[1-(Dimethylamino)-1,3-propanediyl]-ferrocene (**4**)

This was prepared according to modified literature procedures [9,10]. Optical resolution was performed via fractional crystallization of the diastereomeric tartrates [11].

3.2. 1-Diphenylphosphino-2,1'-[1-(*N,N*-dimethylamino)-1,3-propanediyl]-ferrocene I(-)(*S_c*, *S_m*)-**5**

In a 100 ml Schlenk tube, 720 mg (2.68 mmol) of **4** ($[\alpha]_D^{20} = -31^\circ$, (*c* = 1; MeOH)) was dissolved under argon in 15 ml of absolute diethyl ether. To the degassed solution was added dropwise 2.0 ml (3.2 mmol) of *n*-butyllithium (1.6 M in hexane). After stirring for 4 h at room temperature an orange precipitate was formed. To this suspension, 0.58 ml (3.2 mmol) of chlorodiphenylphosphine was added dropwise at 0°C and the mixture was stirred for an additional 16 h at room temperature. The yellow reaction mixture was quenched at 0°C with 15 ml of saturated aqueous

NaHCO₃ solution. The organic layer was separated and the aqueous layer was extracted with diethyl ether (4 × 15 ml). The combined organic layers were washed with 20 ml of water and dried with MgSO₄; the solvent was removed under reduced pressure to give 1.2 g of a yellow precipitate. The crude product was chromatographed on silica gel (40–63 μm; column, 3 × 50 cm) using a mixture of 0.4% triethylamine–20% methanol–79.6% chloroform as eluent, yielding 766 mg (1.69 mmol, 63%) of **5** (*R_f* = 0.57). In addition, 265 mg (0.984 mmol) of the amine **4** (*R_f* = 0.17) was recovered. Aminophosphine **5** (melting point (m.p.), 125–135°C) was used without further purification. An analytical sample of **5** (m.p., 138–140°C) was obtained by MPLC (silica gel; 25–40 μm; 40 × 4.3 cm) with MeOH:chloroform (5:95) as eluent.

¹H NMR: δ 1.83 (6H, s), 1.90 (1H, m), 2.40 (1H, m), 2.46 (H21), dd, *J* = 2.8, 11.3 Hz, 2.62 (1H, ddd, *J* = 2.5, 4.7, 14.7 Hz), 3.00 (1H, m), 3.71 (2H, m), 3.86 (1H, m), 4.08 (1H, m), 4.16 (1H, m), 4.19 (1H, m), 4.39 (1H, m), 7.29 (8H, m), 7.46 (2H, m) ppm. ¹³C NMR: δ 25.60 (C(23)), 38.38 (C(22), d, *J* = 10 Hz), 44.31 (C(31), C(32)), 66.70 (C(21)), 67.58 (Cp), 69.14 (Cp), 70.21 (Cp), 71.42 (Cp), 71.55 (Cp, d, *J* = 5.3 Hz), 74.05 (Cp, d, *J* = 5.2 Hz), 74.36 (Cp, d, *J* = 4.6 Hz), 75.60 (Cp, d, *J* = 20.1 Hz), 88.68 (Cp), 91.50 (Cp, d, *J* = 18.4 Hz), 127.53 (2Ph, d, *J* = 7.5 Hz), 127.71 (2Ph, d, *J* = 6.6 Hz), 127.70 (Ph), 128.08 (Ph), 133.51 (2Ph, d, *J* = 20.3 Hz), 134.19 (2Ph, d, *J* = 19.3 Hz), 138.89 (Ph, d, *J* = 11.8 Hz), 139.47 (Ph, d, *J* = 8.6 Hz) ppm. ³¹P NMR: δ -21.04 (s) ppm. MS: *m/e* (relative%) 453 (100, M⁺), 438 (38), 408 (70), 332 (32), 253 (27), 225 (33), 224 (96), 183 (27), 176 (18), 165 (24), 121 (19), 78 (12). $[\alpha]_D^{20}$ (*c* = 1.024) -207.8 (589), -209.1 (578), -194.3 (546) °(nm). CD (*c* = 2.3 × 10⁻³–2.3 × 10⁻⁴ mol l⁻¹): λ ($\Delta\epsilon$): 251 (-11.2), 276 sh (-8.36), 325 (-0.84), 418 (+1.31) nm.

3.3. 1-Diphenylphosphino-2,1'-[1-(*N,N*-dimethylamino)-1,3-propanediyl]-ferrocene-PdCl₂ [(+)-(*S_c*, *S_m*)-**5**-PdCl₂]

A 100 ml Schlenk tube was charged under argon with 269 mg (1.04 mmol) of (CH₃CN)₂PdCl₂ and 15 ml of dry benzene. A degassed solution of **5** (495 mg, 1.09 mmol) in 10 ml of dry benzene was added through a Teflon tube. After stirring for 12 h at room temperature a red–orange precipitate was formed. The supernatant solution was removed via a syringe and the remaining precipitate was washed twice with 10 ml of dry ether. The crude complex was dissolved in 15 ml of dry dichloromethane and to this solution was added carefully 10 ml of dry ethanol avoiding mixing of the two layers. After standing for 90 h in a slow stream of argon 479 mg (0.76 mmol, 76%) (m.p., 280°C (decomposition)), deep-red needles of **5**-PdCl₂ were formed.

^1H NMR: δ 1.85 (1H, m), 2.18 (1H, m), 2.44 (1H, m), 2.54 (H21, dd, $J = 2.0, 11.0$ Hz), 2.65 (1H, m), 2.81 (3H, s), 2.90 (1H, m), 3.33 (3H, s), 3.68 (1H, m), 3.82 (1H, m), 4.07 (1H, m), 4.26 (1H, m), 4.37 (1H, m), 4.46 (1H, m), 7.31 (5H, m), 7.57 (3H, m), 8.27 (2H, m) ppm. ^{13}C NMR: δ 24.48 (C(23)), 42.80 (C(22), d, $J = 4$ Hz), 52.38 (N-CH₃), 56.81 (N-CH₃), 68.22 (Cp, d, $J = 45.6$ Hz), 68.82 (C(21)), 70.54 (Cp, d, $J = 6.5$ Hz), 71.68 (Cp), 72.00 (Cp, d, $J = 8.3$ Hz), 72.10 (Cp, d, $J = 3.5$ Hz), 72.13 (Cp), 72.93 (Cp), 75.15 (Cp), 88.25 (Cp), 88.40 (Cp, d, $J = 18.6$ Hz), 127.85 (2Ph, d, $J = 11.7$ Hz), 128.08 (2Ph, d, $J = 11.7$ Hz), 130.49 (Ph, d, $J = 3.2$ Hz), 131.63 (Ph, d, $J = 66.3$ Hz), 133.67 (Ph, d, $J = 2.5$ Hz), 133.15 (2Ph, d, $J = 9.6$ Hz), 133.86 (Ph, d, $J = 65.3$ Hz), 136.29 (2Ph, d, $J = 11.3$ Hz) ppm. ^{31}P NMR: δ 10.51 (s), ppm. $[\alpha]_{\text{D}}^{20}$ ($c = 1.0034$) +304.0 (589), +373.7 (578), +756.4 (546) °(nm). CD: $\lambda(\Delta\epsilon)$ 244 (-17.8), 257 (+7.29), 276 (-6.77), 311 (+9.05), 344 (-3.47), 388 (-2.58), 452 (+8.04) nm.

3.4. Crystal structure analysis of 4-T

Crystals of yellow color were grown from methanol. A specimen of size $0.4 \times 0.3 \times 0.3$ mm was used for diffraction experiments, which were performed at 85(2) K on a modified STOE diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were obtained by least-squares refinement against the setting angles of 70 reflections ($3^\circ \leq \theta \leq 9^\circ$). Crystals are monoclinic, of space group $P2_1$, with two molecules (C₁₉H₂₅FeNO₆; formula weight, 419.3) per unit cell: $a = 7.559(2)$ Å, $b = 9.216(2)$ Å and $c = 13.119(3)$ Å; $\beta = 90.16(3)^\circ$; $V = 913.9(4)$ Å³; $d_c = 1.524$ g cm⁻³ (calculated from the cell constants observed at 85(2) K; $F(000) = 440$).

Intensity data (ω scan; $\Delta\omega = 1.5^\circ$) were collected for two octants of reciprocal space ($-10 \leq h \leq 10$; $-1 \leq k \leq 12$; $-1 \leq l \leq 18$; $3^\circ \leq \theta \leq 30^\circ$), yielding 2623 symmetry independent reflections, of which 2374 are significant ($I > 2\sigma(I)$). Lorentz-polarization correction and empirical adsorption correction (program DIFABS [19]) were applied to the data $\mu(\text{Mo K}\alpha) = 0.862$ mm⁻¹; ratio of minimum to maximum transmission, 0.796.

The structure was solved with direct methods and refined with least squares, using a full-matrix least squares program (SHELXL93 [19]) which minimizes the quantity $\sum \omega(F_o^2 - F_c^2)^2$ with $\omega = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$, $a = 0.038$, $b = 0.56$, using all reflections. Anisotropic atomic displacement parameters (ADP's) were refined for all non-hydrogen atoms; H atoms were included at calculated positions ("riding"); an isotropic ADP was refined for each H atom.

Refinement of 244 parameters against 2623 intensity data and 98 restraints converged at the following values

for the reliability indices: $\omega R_2 = [\sum[\omega(F_o^2 - F_c^2)^2]/\sum[\omega(F_o^2)^2]]^{1/2} = 0.0829$ (for all 2623 reflections); $R_1 = \sum \|F_o\| - |F_c|/\sum |F_o| = 0.0296$ for 2374 significant reflections and 0.0362 for all 2623 data; goodness of fit $S = [\sum \omega(F_o^2 - F_c^2)^2/(n - p)]^{1/2} = 0.956$ number n of observations, 2623; number P of parameters, 244). Features up to 0.336 electrons Å⁻³ and down to -0.368 were observed in a final difference electron density map. The absolute structure parameters [13] converged to 0.00(2) (a value of 0 indicating the correct and a value of 1 the opposite enantiomer). Atomic coordinates and equivalent isotropic displacement parameters are given in Table 1.

3.5. Crystal structure analysis of 5

Conditions and procedures analogous to the structure determination of 4-T, except where noted explicitly: orange crystals were grown from CH₂Cl₂-hexane; crystal size, $0.5 \times 0.4 \times 0.3$ mm; temperature, 84(2) K. Unit-cell parameters from 47 reflections with $4^\circ \leq \theta \leq 7^\circ$. Crystals are monoclinic, of space group $P2_1$, with four molecules (C₂₇H₂₈FeNP; formula weight, 453.35) per unit cell: $a = 17.578(4)$ Å, $b = 7.3220(10)$ Å and $c = 18.040(4)$ Å; $\beta = 91.42(3)^\circ$; $V = 2321.1(8)$ Å³; $d_{\text{calc}} = 1.359$ g cm⁻³ (calculated from the 84(2) K cell constants, with four molecules 5 plus one molecule hexane per unit cell); $d_{\text{obs}} = 1.34$ g cm⁻³ (determined at room temperature by flotation in aqueous CsCl); $F(000) = 1002$.

Intensity data ($\Delta\omega = 1.5^\circ$) were collected for two octants ($-1 \leq h \leq 22$; $-1 \leq k \leq 9$; $-23 \leq l \leq 23$; $3^\circ \leq \theta \leq 27.5^\circ$), 6161 symmetry independent reflections and 3221 significant reflections. DIFABS [19] absorption correction with $\mu(\text{Mo K}\alpha) = 0.735$ mm⁻¹ (ratio of minimum to maximum transmission, 0.623). Refinement (621 parameters; 6161 observations; 457 restraints) converged at $\omega R_2 = 0.1423$ (all 6161 reflections); $R_1 = 0.0678$ (3221 significant reflections); $R_1 = 0.1404$ (all 6161 data); $S = 0.934$ ($n = 6161$; $p = 621$). Maximum and minimum residual electron densities 0.644 and -0.555 electrons Å⁻³. Absolute-structure parameter [13], 0.03(3). Atomic coordinates are given in Table 2.

3.6. Crystal structure analysis of 5PdCl₂

Conditions and procedures analogous to the structure determination of 4-T, except where noted explicitly: red crystals were grown from CH₂Cl₂-ethanol; crystal size, $0.3 \times 0.2 \times 0.2$ mm; temperature, 85(2) K. Unit-cell parameters from 44 reflections with $3^\circ \leq \theta \leq 7^\circ$. Crystals are monoclinic, of space group $P2_1$, with two molecules (C₂₇H₂₈Cl₂FeNPPd; formula weight, 630.6) per unit cell: $a = 8.768(2)$ Å, $b = 17.065(3)$ Å and

$c = 8.978(2) \text{ \AA}$; $\beta = 112.81(3)^\circ$; $V = 1238.3(5) \text{ \AA}^3$; $d_{\text{calc}} = 1.691 \text{ g cm}^{-3}$ (at $85(2) \text{ K}$); $F(000) = 636$.

Intensity data ($\Delta\omega = 1.2^\circ$) were collected for two octants ($-1 \leq h \leq 14$; $-1 \leq k \leq 27$; $-14 \leq l \leq 14$; $3^\circ \leq \theta \leq 35^\circ$), 5821 symmetry independent reflections and 4661 significant reflections. DIFABS [19] absorption correction with $\mu(\text{Mo K}\alpha) = 1.609 \text{ mm}^{-1}$ (ratio of minimum to maximum transmission, 0.521). Refinement (297 parameters; 5821 observations; 129 restraints) converged at $\omega R_2 = 0.1293$ (all 5821 reflections); $R_1 = 0.0376$ (4661 significant reflections); $R_1 = 0.0548$ (all 5821 data); $S = 0.649$ ($n = 5821$; $p = 297$). Maximum and minimum residual electron densities, 1.091 and $-1328 \text{ electron \AA}^{-3}$. Absolute-structure parameter [13], $-0.04(3)$. Atomic coordinates are given in Table 3.

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References and note

- [1] A. Togni and T. Hayashi, (eds.), *Ferrocenes*, VCH, Weinheim, 1995.
- [2] H. Brunner and W. Zettlmeier, *Handbook of Enantioselective Catalysis with Transition Metal Compounds*, VCH, Weinheim, 1993.
- [3] D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann and I. Ugi, *J. Am. Chem. Soc.*, **92** (1970) 5389.
- [4] T. Hayashi, T. Mise, M. Fukushima, M. Kagotani, N. Nagashima, Y. Hamada, A. Matsumoto, S. Kawakami, M. Konishi, K. Yamamoto and M. Kumada, *Bull. Chem. Soc. Jpn.*, **53** (1980) 1138.
- [5] M. Sawamura and Y. Ito, *Chem. Rev.* **92** (1992) 857.
- [6] B. Jedlicka, Ch. Kratky, W. Weissensteiner and M. Widhalm, *J. Chem. Soc., Chem. Commun.*, (1993) 1329.
- [7] H. Wally, Ch. Kratky, W. Weissensteiner, M. Widhalm and K. Schlögl, *J. Organomet. Chem.*, **450** (1993) 185.
- [8] H. Wally, K. Schlögl, W. Weissensteiner and M. Widhalm, *Tetrahedron Asymm.*, **4** (1993) 285.
- [9] M. Rosenblum, A.K. Banerjee, N. Danieli, R.W. Fish and V. Schlatter, *J. Am. Chem. Soc.*, **85** (1963) 316.
- [10] P. Dixneuf and R. Dabard, *Bull. Soc. Chim. Fr.*, **7** (1972) 2847.
- [11] G. Tainturier, K. Chhor y Sok and B. Gautheron, *C.R. Acad. Sci., Sér. C* **277** (1973) 1269.
- [12] C.Y.S. Khay, G. Tainturier and B. Gautheron, *Tetrahedron Lett.*, **25** (1974) 2207.
- [13] H.D. Flack, *Acta Crystallogr., Sect. A*, **39** (1983) 876.
- [14] Y.G. Luo, R.J. Barton and B.E. Robertson, *Can. J. Chem.*, **65** (1987) 2756.
- [15] F.W.B. Einstein and A.C. Willis, *Acta Crystallogr., Sect. B*, **36** (1980) 39.
- [16] F.H. van der Steen and J.A. Kanters, *Acta Crystallogr., Sect. C*, **42** (1986) 547.
- [17] T. Hayashi, M. Konishi, Y. Kobori, M. Kumada, T. Higuchi and K. Hirotsu *J. Am. Chem. Soc.*, **106** (1984) 158.
- [18] *PCMODEL* Serena Software, Bloomington, IN, 1992.
- [19] The following computer programs were used for the crystallographic work: *SHELXL PC, Version 4.1*, Siemens Analytical Instruments, Inc., Madison, WI, 1990; G.M. Sheldrick, *SHELXL-93, a Program for Refinement of Crystal Structures from Diffraction Data*, University of Göttingen, 1993; DIFABS, N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, **39** (1983) 158.