ELSEVIER

Journal of Organometallic Chemistry 540 (1997) 15–25

Journal of Organometallic Chemistry

Synthesis of Pt compounds containing chiral (2*S*,4*S*)-pentane-2,4-diyl-bis(5*H*-dibenzo[b]phosphindole) as ligand and their use in asymmetric hydroformylation of styrene derivatives

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Received 12 August 1996; revised 27 January 1997

Abstract

Unlike bis(diphenyl)phosphine derivatives in general, (2*S*,4*S*)-pentane-2,4-diyl-bis(5*H*-dibenzo[b]phosphindole), *S*,*S*-BDBPP, gives a trans oligomeric compound $[PtCl_2(S,S\text{-BDBPP})]_n$, **1**, in reaction with dichloro-Pt precursors such as $PtCl_2(PhCN)_2$, $PtCl_2(CH_3CN)_2$ and $PtCl_2(COD)$ at room temperature. Compound **1**, which could be readily isolated, slowly rearranges in solutions at room temperature to the expected cis-monomer $PtCl_2(S,S\text{-BDBPP})$, **3**. Heating or the presence of $PtCl_2(COD)$ accelerates the transformation of compound **1** to **3**. $SnCl_2$ adducts of both compounds, *trans*-$[PtCl(SnCl_3)(S,S\text{-BDBPP})]_n$, **2**, and *cis*-$PtCl(SnCl_3)(S,S\text{-BDBPP})$, **4**, as well as the known *cis*-$PtCl(SnCl_3)(S,S\text{-BDPP})$, **5**, (*S*,*S*-BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane) have been tested as catalysts in the asymmetric hydroformylation of *p*-isobutylstyrene. The phenyl analog **5** provides up to 75% *e.e.* but moderate yields to chiral 2-(4-isobutylphenyl)-2-propanal. Compared to this, the regioselectivity to the branched aldehyde is remarkably increased; however, the enantioselectivity is drastically decreased by the use of both dibenzophosphole derivatives **2** and **4**. The similarities in the selectivities provided by **2** and **4** indicate that the trans oligomer **2** transforms to the cis-monomer **4** during the catalytic process. X-ray crystal structure determination of compound **3** shows a half-chair conformation for the chelate ring with a symmetric arrangement of dibenzophosphole groups. Besides a preference for the latter achiral conformation, the planar structure of the dibenzophosphole groups can also be considered as reason for the moderate enantioselectivities provided by **4**. © 1997 Elsevier Science S.A.

Keywords: Platinum; Asymmetric hydroformylation; Ibuprofen; Dibenzophospholes

1. Introduction

Asymmetric hydroformylation of an appropriate styrene derivative is an attractive catalytic approach to the synthesis of the optically active 2-aryl-propionic acid type of anti-inflammatories [1–4]. High enantiomeric excesses in the branched aldehydes can be readily achieved by the use of platinum–tin [5–8] and rhodium [9–11] complexes of various chiral ligands. The transformation of the formed aldehyde products to the desired acids by oxidation is also a simple one-step procedure [12]. The recently developed Rh-based asymmetric hydroformylation catalysts, which utilize chiral bidentate phosphine–phosphite or diphosphite ligands are generally superior to Pt–Sn systems containing chiral diphosphines in terms of regioselectivity [1,2,9–11]. However, the moderate branched aldehyde selectivity of the latter system can also be improved by using more suitable ligands than the ones containing diphenylphosphino moieties. Chelating dibenzophosphole derivatives are known to have such an effect in carbonylations with Rh, [13] Pt [14,15] and Pd [16] complexes. For example, chiral 2,3-bis[(dibenzophospholyl)methylene]bicyclo-[2.2.2]octane [6] and 1-(t-butoxycarbonyl)-2-[(dibenzophospholyl)methylene]-4-(dibenzophospholyl)pyrrolidine

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PII S0022-328X(97)00130-7

[7] have been recently described to afford both excellent regio- and enantioselectivities in the Pt–Sn-catalyzed hydroformylation of styrene derivatives.

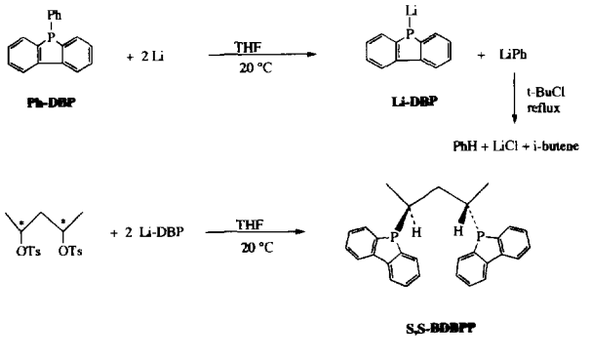
To date, BDPP (enantiomeric 2,4-bis(diphenylphosphino)pentane) is one of the chiral ligands which has given the highest enantioselectivities in the asymmetric hydroformylation of unfunctionalized styrene with the Pt–Sn system [5,17,18]. In the present paper, we show that *S,S*-BDPP readily provides high enantioselectivity, although with the expected moderate branched aldehyde selectivity in the hydroformylation of *p*-i-butylstyrene (ibuprofen precursor). It was then reasoned that by introducing dibenzophosphole instead of diphenylphosphino groups to BDPP the regioselectivity of the catalytic system could also be improved.

2. Results and discussion

2.1. Synthesis of (2S,4S)-2,4-bis(dibenzophospholyl)pentane, S,S-BDBPP

Chiral pentane-2,4-diyl-bis(5*H*-dibenzo[b]phosphindole (Scheme 1), BDBPP (abbreviation from the trivial name 2,4-bis(dibenzophospholyl)pentane) has recently been used as ligand for a mechanistic study on asymmetric hydrogenation [19]. Since there were no synthetic details given and the synthesis of BDBPP requires somewhat different reaction conditions than those of the analogous bis-diphenylphosphine derivatives, a synthetic procedure and the characterization of the ligand are included in Section 4.

In the synthesis of BDBPP and other analogous phosphole derivatives it should be regarded that the cleavage of phenyl-dibenzophosphole (Ph-DBP) proceeds differently to that of triphenylphosphine with lithium. When the reaction of Ph-DBP with lithium (Scheme 1) was monitored by ^{31}P NMR in THF, the occurrence of a single broad peak at +15 ppm was observed after several hours of stirring at room temperature. This range of chemical shift is more characteristic for the presence of a quaternary phosphine derivative than that of a monomeric phosphide. The analogous reaction of PPh_3 with Li results in the formation of $LiPPh_2$, which appears as a sharp singlet at −23.1 ppm [20,21]. The large chemical shift difference of the two phosphides is not due to a general electronic difference between dibenzophosphole derivatives and their diphenylphosphino analogs. For example, Ph-DBP, BDBPP and some of their Pt and Pd complexes show very similar chemical shifts to that of PPh_3, BDPP and their analogous Pt and Pd compounds respectively. Other than a ^{31}P NMR feature, the anomalous behavior of the reaction mixture of the cleavage of Ph-DBP with Li is also reflected in its reactivity. In contrast with the experience in the cleavage of PPh_3, the destruction of



Scheme 1. Synthesis of (2*S*,4*S*)-2,4-bis(dibenzophospholyl)pentane, BDBPP.

PhLi by-product with t-BuCl requires reflux temperatures in the alkalic phosphole mixture. Upon this process the broad peak at +15 ppm shifts to +0.5 ppm in the ^{31}P NMR spectrum. The analogous process in the cleavage of PPh_3 proceeds readily at room temperature without a change in the ^{31}P NMR signal of $LiPPh_2$. Thus, it seems that in the cleavage of Ph-DBP with Li an uncharacterized phosphide adduct is formed with the possible participation of Ph-Li. The reaction of Li-DBP after destroying Ph-Li (+0.5 ppm) is significantly slower at room temperature with the diol-ditosylate (Scheme 1) than that of $LiPPh_2$. The former requires about 5 h of reaction time for a conversion of 80%, while the latter takes place in several minutes.

2.2. Platinum complexes with S,S-BDBPP

The coordination chemistry of chelating phosphole derivatives is also different than that of the analogous compounds containing diphenylphosphino groups. Sterically hindered bis-2,5-diphenylphosphole derivatives tend to give cis- and trans-oligomeric structures instead of monomeric chelates with some transition metal complexes, i.e. the ligand acts rather as bridging than as chelating [22]. The formation of cis- [23] and trans-oligomeric [24] Pt-complexes beside the monomeric cis-$PtCl_2$ compounds have also been noted in the reactions of $PtCl_2(PhCN)_2$ with bis-dibenzophosphole derivatives closely analogous to BDBPP. It has been found that the formation of chelate complexes in the latter system can be facilitated by increasing the reaction temperature or by using polar solvents [6,23,24].

When the reaction of $PtCl_2(PhCN)_2$ or $PtCl_2(CH_3CN)_2$ with the diphosphole, BDBPP (Scheme 2) was followed by ^{31}P NMR in benzene or CH_2Cl_2 solution at room temperature, the exclusive formation of a compound other than *cis*-$PtCl_2$(BDBPP) was revealed. Although when isolated the compound **1** analyzes for the given formula, its ^{31}P NMR spectrum shows a singlet at −0.3 ppm (at significantly higher field than expected for the cis-compound) with $^{1}J_{Pt,P}$

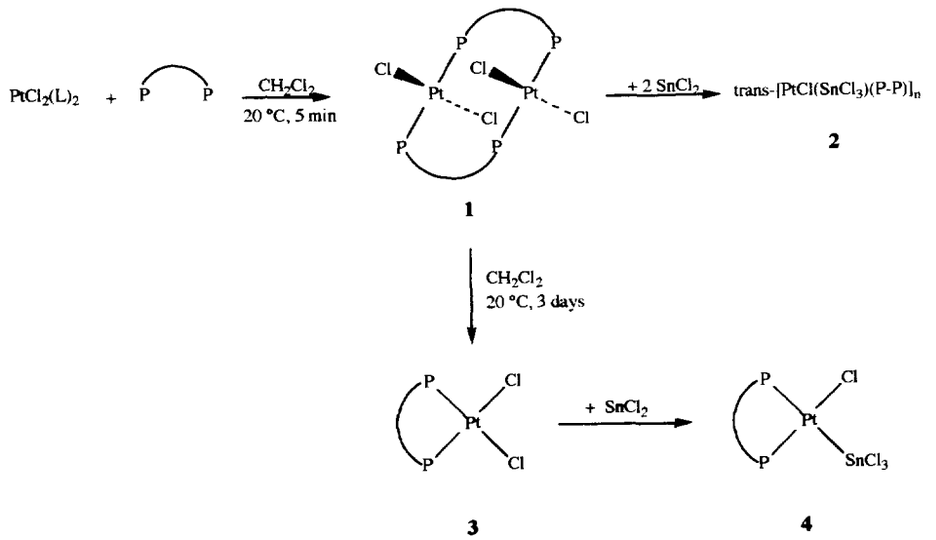
satellites of 2453 Hz. This range of $^1J_{Pt,P}$ coupling constants is typical of divalent platinum complexes which have monotertiary phosphine ligands in trans position [25]. Accordingly, compound **1** should have a trans oligomeric structure in a fashion that the two phosphorus atoms of BDBPP are coordinated to different metal centers. Another interesting NMR feature of compound **1** is the remarkable upfield (low frequency) and downfield shifts of the methyl and methine protons respectively in the ^{1}H NMR spectrum, in comparison with the values observed for the non-coordinated ligand. The sharp signal in the ^{31}P NMR spectrum and the relatively good solubility of compound **1** in $CHCl_3$ (significantly better than that of the monomeric cis-compound vide infra) indicate the presence of a single, low molecular-weight oligomer. The discrete character of compound **1** in solutions was confirmed by HPLC analysis. On this basis, we propose a dimer structure for compound **1** (Scheme 2), despite the fact that no molecular peak could be detected by direct mass spectroscopy (MS) from solid **1** due to premature decomposition.

Trans oligomer **1** reacts with 2 equiv. of $SnCl_2$ to form an oligomeric compound, **2**, (Scheme 2) which when isolated analyzes for Pt(Cl)($SnCl_3$)(BDBPP). Unlike the isolated monomer analog (vide infra), compound **2** is not soluble in most common solvents. The solid state ^{31}P CPMAS spectrum shows a singlet centered at 11.2 ppm, which is slightly broader than the usual range of J_{PtP} couplings. For this reason an adequate J_{PtP} coupling could not be delivered for compound **2**. One possible reason for the observed line broadening is that the oligomeric compound is not homogeneous but statistical in the distribution of the Cl and $SnCl_3$ ligands, i.e. it contains Pt centers with none, one and two $SnCl_3$ groups.

Compound **1** appears to be a kinetic product, as it rearranges quantitatively to *cis*-$PtCl_2$(BDBPP), **3** (^{31}P NMR *d* 8.3 ppm, $^1J_{Pt,P}$ = 3258 Hz) upon 2–3 days stirring in CH_2Cl_2 at room temperature (Scheme 2). The subsequently isolated cis-compound can then be reacted with $SnCl_2$ to form *cis*-Pt(Cl)($SnCl_3$)(BDBPP), **4**. Similar to what has been found with analogous oligomers [23,24], heating accelerates the rearrangement of **1** to **3**. For example, ^{31}P NMR showed only the presence of **3** after refluxing a solution of compound **1** in $CHCl_3$ for 1 h or longer. Interestingly, the analogous rearrangement of $SnCl_2$ adduct **2** to **4** is a significantly slower process, probably due to the poor solubility of **2** in most of the common solvents.

Since the coupling constant of $^1J_{Pt,P}$ = 3258 Hz for compound **3** is a relatively small value for a monomeric cis-Pt-dichloro-diphosphine complex [25] some additional measurements were carried out to confirm whether **3** is not also an oligomer. HPLC from a $CHCl_3$ solution of **3** showed the presence of a single compound at a different elution time than what has been found for compound **1**. Direct mass spectroscopy revealed that compound starts fragmenting the monomeric molecular ion before anything else upon heating. This is in sharp contrast with the behavior of compound **1**, which fragments the ligand and some Pt-complexes (decomposes) first. Consequently, the monomeric structure seemed to be inherent for cis-compound **3**, which was later confirmed by X-ray crystal structure determination.

$PtCl_2(PhCN)_2$ and $PtCl_2(CH_3CN)_2$ in solutions are known to undergo rapid cis–trans isomerization [26]. In order to estimate whether the formation of trans-oligomer **1** is due to a cis–trans pre-equilibration, i.e. to the ready availability of *trans*-$PtCl_2(PhCN)_2$ and *trans*-$PtCl_2(CH_3CN)_2$ respectively, *S,S*-BDBPP was tested with the fixed cis-compound, $PtCl_2$(COD). In the latter case, by carrying out the reaction at room temper-



Scheme 2. Pt complexes with *S,S*-BDBPP (P–P).

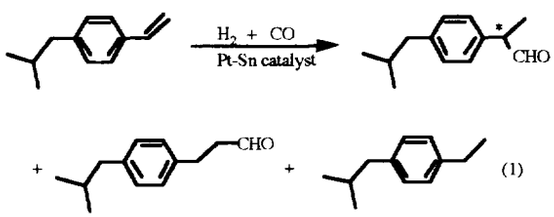
ature in $CDCl_3$ the formation of trans-oligomer **1** has also been observed. However, by the time a ^{31}P NMR spectrum could be recorded (ca. 10 min) about 50% of the phosphorus content was found already in compound **3**. The ratio of compound **3** to compound **1** was 9/1 after 1 h, and only the cis-monomer could be detected after 2 h of reaction time. Similar results were obtained when the isolated trans-oligomer **1** was brought together after dissolving in $CDCl_3$ with less than equivalent amounts (0.1–0.5 equiv.) of $PtCl_2COD$. On the other hand, the addition of $PtCl_2(PhCN)_2$ in less or more than stoichiometric ratio to the similar solution of compound **1** had no accelerating effect on the transformation of **1** to **3**, which required again more than 2 days for completion at room temperature.

Thus, it appears that the presence of a precursor with trans position of the chloro groups is not a condition for the formation of the trans-oligomer. The rate increase in the presence of $PtCl_2COD$ can only be explained by assuming that the latter compound acts as a catalyst in the transformation of **1** to **3**. However, the mechanism of the rearrangement of **1** to **3** and the exact catalytic role of $PtCl_2COD$ therein remain yet to be revealed.

2.3. Hydroformylation experiments

The enantioselectivity in the hydroformylation of styrene by using Pt–Sn complexes of the diphosphine analog, *S,S*-BDPP, is strongly influenced by the reaction temperature [5,18]. At low temperatures (20–40 °C) (*S*)-(+)-2-phenylpropanal predominates in up to 85% *ee*, while at temperatures above 100 °C the *R* enantiomer prevails with a maximum of 28% *ee*. A further increase in enantioselectivity in this direction by increasing the temperature is limited by the increasing racemization rates [5,8,27]. The reversal of product configuration as a function of reaction temperature, which is also the feature of some analogous systems, can be attributed to kinetic effects [27,28].

The results of the hydroformylation of *p*-i-butylstyrene (Eq. (1)) by the use of Pt–Sn complexes containing *S,S*-BDBPP and *S,S*-BDPP are summarized in Table 1. The optical purities of the formed branched aldehydes in two experiments have been both determined by direct NMR shift technique and by polarimetry after oxidation to the acid derivatives on the basis of the known absolute rotation of optically pure ibuprofen. The absolute rotation value of the optically pure ibuprofen-aldehyde was then calculated (after measuring the rotation of the aldehyde mixtures) and used as basis to estimate the optical purity of the branched aldehydes directly by polarimetry. Contrary to literature experience [7,8], we failed to get a diastereomeric separation at any of the ^1H NMR signals of ibuprofen-aldehyde in NMR shift experiments by using $Eu(hfc)_3$ or $Eu(tfc)_3$, in spite of the considerable shifts of some signals. Even by the use of the more powerful shift reagent $Eu(dmc)_3$ [29] the enantiotopic methine protons required selective decoupling from the vicinal methyl protons to obtain well-separated signals.



(1)

The hydroformylation results of *p*-i-butylstyrene (Eq. (1)) with $Pt(Cl)(SnCl_3)(S,S\text{-BDPP})$, **5**, follow the expectation that the *p*-substitution on styrene should have little effect on the activity and selectivity of the catalyst. At room temperature an enantioselectivity of 74.8% was achieved to *S*-2-(4-i-butylphenyl)-2-propanal,while at 100 °C the *R* product was obtained in low *ee*. Consistent with the literature data on non-substituted styrene [5,18], the ibuprofen-aldehyde selectivity decreases by

Table 1
Enantioselective hydroformylation of 4-i-butylstyrene [a]

Catalyst	Reaction temperature (°C)	Reaction time (h)	Conversion (%)	Hydrogenation (%)	Regioselectivity (*b/n*) [b]	Enantioselectivity (%*ll*) [c]	$[\alpha]_D^{20}$ [d] (deg)
5	20	336	53.2	0.1	0.42	74.8 (*S*)	+186.0 (*c* 3.57)
5	100	2	51.7	2.1	0.29	8.2 (*R*)	−20.4 (*c* 3.65)
5 [e]	100	2	54.0	10.4	0.50	13.8 (*R*)	−34.2 (*c* 3.42)
4	20	336	25.6	6.0	8.2	25.7 (*S*)	+63.8 (*c* 3.54)
4	100	3	32.5	15.3	2.4	3.9 (*S*)	+9.7 (*c* 3.48)
2	100	3	7.7	3.6	2.5	1.8 (*S*)	+4.3 (*c* 0.72)

[a] Reaction conditions: subst/Pt = 1000/1, 0.01 mmol of Pt in 30 ml of toluene, 70 bar of CO/H_2 (1/1).
[b] Ratio of branched to linear aldehydes.
[c] Absolute configuration in parentheses.
[d] Optical rotation of branched aldehyde in benzene.
[e] Subst/Pt = 200/1, 0.05 mmol of Pt in 30 ml of CH_2Cl_2.

Table 2
Enantioselective hydroformylation of styrene by using compound **4** as catalyst [a]

Reaction temperature (°C)	Reaction time (h)	Conversion (%)	Hydrogenation (%)	Regioselectivity (b/n) [b]	Enantioselectivity (%*ee*) [c]
70	27	90	26.8	6.14	18.8 (*S*)
80	23	73	32.8	4.65	17.8 (*S*)
100	8	27	46.7	3.84	11.6 (*S*)
130	5	50	48.9	3.21	5.1 (*S*)

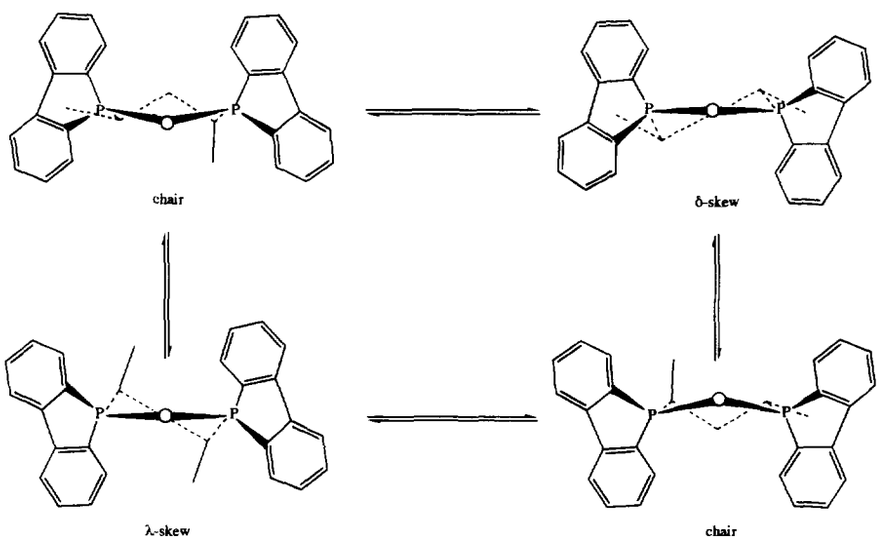
[a] Reaction conditions: subst/Pt = 2000/1, 0.05 mmol of Pt in 50 ml of toluene, 70 bar of CO/H_2 (1/1).
[b] Ratio of branched to linear aldehydes.
[c] Absolute configuration in parentheses.

increasing the temperature and also somewhat higher enantio- and regioselectivity is obtained in CH_2Cl_2 than in toluene as solvent.

As can be seen in Table 1, the moderate branched aldehyde selectivity with **5** is indeed remarkably improved by using the dibenzophosphole analog **4** instead. For example, a b/n (branched to linear aldehydes) ratio of 8.2 could be achieved with compound **4** at room temperature compared to the analogous 0.42 value with compound **5**. Unfortunately, the introduction of dibenzophospholyl groups has an unfavorable effect on the enantioselectivity and the low enantioselectivities with **4** are not due to a strong temperature dependence (see also Table 2). Furthermore, the chemoselectivity of the latter catalyst is also much lower than that of the diphenylphosphino analog **5** owing to increased hydrogenation activity. The trans-oligomeric compound **2** and **1** in the presence of $SnCl_2$ give selectivity data similar to those obtained with the monomeric cis-compound **4**, but with low activities. This might indicate that under catalytic conditions the trans-oligomeric compounds fragment to monomeric cis-compounds which drive the catalytic process. In several experiments, which are summarized in Table 2, compound **4** has been tested in the hydroformylation of non-substituted styrene with similar results.

2.4. X-ray structure of cis-monomer 3

It is well-known that the presence or dominance of an unfavorable chelate conformation can also be the reason for the low enantioselectivities by the use of metal complexes of chiral chelating ligands [30–33]. Like the analogous bis(diphenylphosphino) derivative [31], the six-member chelate ring of optically pure BDBPP can also take four chelate conformations. As shown in Scheme 3, these are two identical chair, a δ and a λ twisted boat (skew) conformations, possessing one equatorial–one axial, two equatorial and two axial Me groups respectively. Among the possible conformations only the twisted boat ones provide chiral arrangements for the aryl groups (thus a space-filling which alters quadrate to quadrate around the metal) which is necessary for the ultimate success of asymmetric induction. By the analogy of BDPP chelates [31], from the two chiral conformations of compound **3**, which have



Scheme 3. Possible chelate conformations in complexes containing *S,S*-BDBPP.

opposite (enantiomeric) aryl group arrangements, the λ-skew conformation can be considered the higher energy species.

Yellowish block-shaped single crystals of compound **3** were obtained from dichloromethane. The thermal ellipsoid plot of the refined X-ray structure and data of some selected bonds are shown in Fig. 1 and Table 3 respectively. The Pt coordination is slightly distorted square-planar, as can be seen from the Cl–Pt–P angles of 174.83(7)° and 175.57(6)° for Cl(1) and Cl(2) respectively. The Pt–Cl and Pt–P distances of compound **3** are in the same range as previously observed in the analogous Pt–dppp complex [34].

The chelate ring of compound **3** possesses a half-chair conformation, which provides a symmetric arrangement for dibenzophospholyl groups (Fig. 1). It is obvious that such an aryl group arrangement, despite the fact that the complex itself is chiral, sterically can hardly express any enantiotopic discrimination for a coordinating prochiral olefin. However, one should be careful in adopting crystallographic evidence for solution chemistry (crystal packing effects). One of the demonstrative examples for this is the chelate of the above-discussed phenyl analog. In Rh(NBD) [33] and $PdCl_2$ [35] complexes of chiral BDPP the chair conformation was also revealed by crystal structure determination, while NMR studies [32,35] and catalytic results [18,31,33,36] indicated the presence of the δ-skew conformation in solutions.

^1H and ^{31}P NMR spectra of compound **3** in $CDCl_3$ solution at room temperature show magnetically equivalent Me groups and phosphorus atoms respectively. Accordingly, the chelate ring of the compound should possess either a stable δ-skew conformation or a fast equilibrium between conformers with a time-averaged C_2 symmetry. For the latter case, a conformational lability with a preference for the achiral chair conformation can easily be the reason for the moderate performance of the Pt-BDBPP precursor. For the former case, it can be considered that the planar arrangement of dibenzophosholyl groups (Scheme 3) provides perhaps less steric discrimination for the coordinating substrate than a typical face–edge arrangement of phenyl groups

Table 3
Selected bond distances and angles of compound **3**

Bond length (Å)		Bond angle (deg)	
Pt(1)–Cl(1)	2.3475(17)	Cl(1)–Pt(1)–Cl(2)	89.26(5)
Pt(1)–Cl(2)	2.3408(16)	Cl(1)–Pt(1)–P(1)	86.60(6)
Pt(1)–P(1)	2.2145(16)	Cl(1)–Pt(1)–P(2)	174.83(7)
Pt(1)–P(2)	2.2109(18)	Cl(2)–Pt(1)–P(1)	175.57(6)
P(1)–C(1)	1.794(7)	P(1)–Pt(1)–P(2)	97.39(6)
P(1)–C(12)	1.804(8)	Pt(1)–P(1)–C(1)	117.8(2)
P(1)–C(13)	1.857(7)	Pt(1)–P(1)–C(12)	115.0(3)
P(2)–C(16)	1.829(8)	C(1)–P(1)–C(13)	104.8(3)
P(2)–C(18)	1.815(6)	Pt(1)–P(2)–C(18)	118.8(2)
P(2)–C(29)	1.813(7)	Pt(1)–P(2)–C(29)	114.9(2)
C(1)–C(6)	1.390(9)	C(16)–P(2)–C(18)	102.9(3)
C(6)–C(7)	1.434(11)	P(1)–C(13)–C(14)	110.8(4)
C(7)–C(12)	1.407(10)	P(2)–C(16)–C(17)	111.8(6)
C(13)–C(14)	1.538(10)	P(1)–C(13)–C(15)	112.9(5)
C(13)–C(15)	1.493(10)	P(2)–C(16)–C(15)	111.4(5)
C(15)–C(16)	1.558(10)	C(13)–C(15)–C(16)	114.8(5)
C(16)–C(17)	1.499(12)	C(14)–C(13)–C(15)	112.3(6)
C(18)–C(23)	1.406(9)	C(15)–C(16)–C(17)	109.6(6)
C(23)–C(24)	1.460(11)		
C(24)–C(29)	1.402(9)		

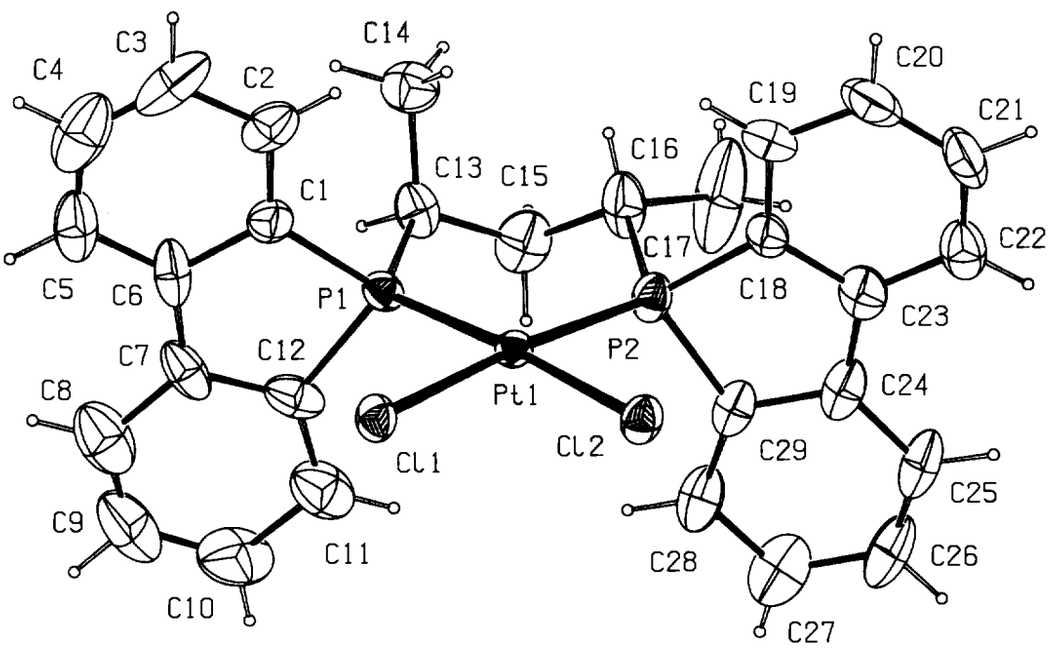


Fig. 1. Thermal ellipsoid (ORTEP) plot of the refined X-ray structure of compound **3**.

in the analogous BDPP derivative. From recent findings that the analogous complex containing the more bulky binaphthophosphole derivative shows several stable conformers below 50 °C [24], the explanation involving a conformational equilibrium seems to be more likely for **3**.

3. Conclusion

It has been shown that *S,S*-BDPP as a ligand provides reasonably good enantioselectivity, albeit with moderate regioselectivity in the Pt–Sn-catalyzed hydroformylation of 4-isobutylstyrene. It is somewhat unfortunate with this ligand that high enantioselectivities are achieved only at low reaction temperatures, thus at low catalyst activities. The dibenzophosphole analog *S,S*-BDBPP, despite its positive effect on the branched aldehyde selectivity, is not a favorable choice of ligand for the enantioselective hydroformylation of styrene derivatives. Similar findings have also been made with the dinaphthophosphole derivative [24].

4. Experimental details

(2*R*,4*R*)-2,4-Pentanediol (Aldrich), (*S,S*)-BDPP (Strem), anhydrous $SnCl_2$ (Aldrich), $Eu(dcm)_3$ (Fluka) and $PtCl_2$ (Aldrich) were purchased and used as-obtained. $PtCl_2(COD)$ [37], $PtCl_2(PhCN)_2$ [38], $PtCl_2(CH_3CN)_2$ [38], Pt(Cl)($SnCl_3$)[(*S,S*)-BDPP] [18], (2*R*,4*R*)-2,4-pentanedilolditosylate [36] and *p*-i-butylstyrene [8] were synthesized by literature procedures. Styrene was obtained from Aldrich. The syntheses of phenyl-5*H*-dibenzo[b]phosphindol, (*S,S*)-BDBPP and the Pt-diphosphine complexes were carried out under nitrogen atmospheres by using freshly distilled, oxygen-free solvents. Since relatively small amounts of catalyst precursors were used in the hydroformylation experiments, it was essential to exclude oxygen and peroxides from the system to get reproducible results. This was done either by using solvent and substrate, which were freshly distilled under N_2 or by an equally sufficient method, by bubbling N_2 into the solution of the substrate for at least 15 min. In the latter case the substrate was distilled only once then kept cold on 100 ppm hydroquinone under N_2. Liquid NMR spectra were recorded on a Bruker AMX-300 and a Bruker ARX-400 instrument at an equivalent ^1H frequency of 300 MHz and 400 MHz respectively. ^{31}P CPMAS spectra were recorded on a Varian 400 WB instrument. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. The optical purity of 2-phenyl-2-propanal was determined by polarimetry based on the literature values for the enantiopure aldehyde [15]. Direct mass spectra were recorded on a Kratos MS80 RF instrument by using a temperature program of 10 °C min^{-1} from 80 to 450 °C. HPLC measurements were carried with a Hewlett-Packard pump (HP 1090) by using an HP1040 DAD UV detection unit at $\lambda = 300$ nm.

4.1. Synthesis of Ph-DBP

Phenyl-5*H*-dibenzo[b]phosphindol was synthesized from PPh_4Br and $LiNMe_2$ by closely following the procedure of Cornforth et al. [39]. Contrary to what was noted by the authors, we did not find any phosphine-oxide in the crude product after work-up, but ca. 20% of another impurity, which was identified as PPh_3. The latter could be readily removed by crystallizing the crude phosphine mixture from ether (30 g/200 ml) and washing the separated white crystalline material with a small amount of cold methanol. *Caution: since $LiNMe_2$ is an extremely pyrophoric material, absolute precaution should be taken to exclude oxygen when it is brought into contact with ether (solvent).* For this reason, we weighed the required amount of $LiNMe_2$ into a Schlenk-tube in a dry-box. After connecting the Schlenk-tube to a nitrogen line, dry ether was added into the Schlenk through a septum with a syringe.

4.2. Synthesis of (S,S)-BDBPP

An amount of 6 g (23 mmol) Ph-DBP was dissolved in a volume of 50 ml of dry THF. To the colorless solution, 350 mg (50.6 mmol) Li was added in small pieces and the mixture was stirred at room temperature. The color of the mixture turned deep brown-red in several minutes upon stirring. After 5 h of stirring, the small amount of unreacted Li was removed with a spatula and a volume of 2.50 ml (23 mmol) dry t-butylchloride was added to the solution. The solution was then refluxed for a short while (ca. 10 min). During reflux, gas and heat development was observed (due to the exothermic reaction, heating was required only until the reflux temperature was reached) and the solution turned light orange-red. After refluxing, the solution was cooled to room temperature. An amount of 4.73 g (11.5 mmol) (2*R*,4*R*)-2,4-pentanediol-ditosylate was added in small portions and the solution was allowed to stand overnight at room temperature, upon which its color went light yellow gradually. (^{31}P NMR indicates that 5 h of reaction time is sufficient for ca. 80% conversion to (*S,S*)-BDBPP.) Then, a volume of 50 ml of degassed water was added to the solution and most of the THF was removed from the solution under reduced pressure. Upon evaporation, an off-white solid separated. The residual aqueous solution was decanted, the solid was washed with some more water (ca. 20 ml) and recrystallized twice from 60 ml of hot ethanol, yielding 2.7 g (54%) of a white crystalline solid. M.p. 85–86 °C, $[\alpha]^{20} = -30.2°$ and $-19.0°$ in *c* 3.85 and *c* 1.0 solu-

tion in $CHCl_3$ respectively. Anal. calcd. for $C_{29}H_{26}P_2$: C 79.81; H, 5.96; P,14.22. Found: C, 79.06; H, 5.87; P, 13.95. ^{1}H NMR (300 MHz, $CDCl_3$): 7.91 d ($^3J_{HH}$ = 7.7 Hz, 4H), 7.26–7.58 m (not res., 12H), 2.01 sext. ($^2J_{PH} = {}^3J_{HH}$ = 7.0 Hz, 2H), 1.32 quint. ($^3J_{PH} = {}^3J_{HH}$ = 7 Hz, 2H), 0.71 dd ($^3J_{PH}$ = 13.3 Hz, $^3J_{HH}$ = 7.0 Hz, 6H). ^{31}P NMR (121 MHz, $CDCl_3$): 1.07 s.

4.3. Synthesis of $[PtCl_2(S,S\text{-BDBPP})]_2$ trans-oligomer, 1

A 5 ml amount of toluene was added to a mixture of 1 mmol each of $PtCl_2(CH_3CN)_2$ (348 mg) and *S,S*-BDBPP (436 mg) with stirring at room temperature. A clear yellow solution formed for a short while then a yellow precipitate separated. The mixture was further stirred for 20 min and filtered. The filtrate was washed with 20 ml of hexane and dried under vacuo yielding 520 mg of a yellow powder. Anal. calcd. for $[C_{29}H_{26}Cl_2P_2Pt]_2$: C, 49.57; H, 3.70; P, 8.83. Found: C, 49.57; H, 3.79; P, 8.46. ^{1}H NMR (400 MHz, CD_2Cl_2): 8.02, 7.89 br. s, br. s (4H), 7.50 q (J = 7.1 Hz, 2H), 7.46 q (J = 6.1 Hz, 2H), 7.39 t (J = 7.2 Hz, 4H), 7.29 t (J = 7.2 Hz, 2H), 6.75 t (J = 6.8 Hz, 2H), 3.27 br.sext ($^3J_{HH}$ = 6.6 Hz, 2H), 1.80 m (J = 9.3 Hz, 2H), 0.07 br. d ($^3J_{HH}$ = 6.6 Hz, 6H). ^{31}P NMR ($CDCl_3$, 121 MHz): −0.3 s (J_{PtP} = 2453 Hz, satellites). MS (temperature, mass, intensity, structure): 178–218 °C, 288, 1%, $Cl(C_5H_{10})P(C_{12}H_8)$; 245–311 °C, 183, 100%, $P(C_{12}H_8)$; 248–311 °C, 436, 9%,$(C_{12}H_8)P(C_5H_{10})P(C_{12}H_8)$; 255–370 °C, 218, 11%, $ClP(C_{12}H_8)$; 300–450 °C, 702, 0.1%, $PtCl_2$BDBPP.

4.4. Synthesis of $[PtCl(SnCl_3)(S,S\text{-BDBPP})]_n$ trans-oligomer, 2

An amount of 0.35 mmol (66 mg) of anhydrous $SnCl_2$ was added to the yellow suspension of 0.35 mmol (244 mg) of compound **1** in 5 ml of CH_2Cl_2, upon which the mixture turned orange-red immediately. The suspension was stirred for 2 h at room temperature and, after adding 10 ml of pentane, was filtered. The filtrate was washed with some additional amount of pentane and dried under vacuo. Yield: 210 mg of an orange-red powder, which is sparingly soluble in common solvents. Anal. calcd. for $C_{29}H_{26}Cl_4P_2SnPt$: C, 39.03; H, 2.91; P, 6.95. Found: C, 37.89; H, 3.05; P, 6.72. ^{31}P CPMAS NMR (162.8 MHz, 293 K, spinning rate: 7.0 K s^{-1}): 11.3 br. s.

4.5. Synthesis of cis-$PtCl_2(S,S\text{-BDBPP})$, 3

A 10 ml amount of $CHCl_3$ was added to a mixture of 0.82 mmol each of $PtCl_2(PhCN)_2$ (387 mg) and *S,S*-BDBPP (358 mg) with stirring. The formed yellow solution was refluxed for 1 h, upon which the solution went lighter in color and some yellowish-white crystals began to separate. After cooling, 20 ml of pentane was added and the formed precipitate was filtered. The solid was washed with 10 ml of pentane and dried under vacuo, yielding 490 mg of a slightly yellowish-white powder. Anal. calcd. for $C_{29}H_{26}Cl_2P_2Pt$: C, 49.57; H, 3.70; P, 8.83. Found: C, 49.36; H, 3.58; P, 8.50. ^{1}H NMR (300 MHz, $CDCl_3$): 7.94 q (J = 7.2 Hz, 4H), 7.87 t (J = 6.3 Hz, 4H), 7.58 t (J = 7.3 Hz,4H), 7.51 q (J = 7.2 Hz, 4H), 2.27 m (not res., 4H), 0.90 dd ($^3J_{PH}$ = 15.4 Hz, $^3J_{HH}$ = 6.7 Hz, 6H). ^{31}P NMR ($CDCl_3$): 8.3 s (J_{PtP} = 3258 Hz, satellites). MS (temperature, mass, intensity, structure): 287–367 °C, 702, 0.1%, $PtCl_2$BDBPP; 290–425 °C, 288, 0.1%, $Cl(C_5H_{10})P(C_{12}H_8)$; 337–362 °C, 183, 100%, $P(C_{12}H_8)$; 337–450 °C, 218, 2%, $ClP(C_{12}H_8)$; 340–450 °C, 436, 0.3%, $(C_{12}H_8)P(C_5H_{10})P(C_{12}H_8)$.

4.6. Synthesis of cis-$PtCl(SnCl_3)(S,S\text{-BDBPP})$, 4

The compound was prepared by reacting compound **3** with $SnCl_2$ analogous to the literature procedure [18]. Beige solid (orange-yellow in solutions). Anal. calcd. for $C_{29}H_{26}Cl_4P_2PtSn$: C, 39.03; H, 2.91; P, 6.95. Found: C, 38.25; H, 2.98, 6.64. ^{31}P NMR ($CDCl_3$, 121 MHz): 15.6, −0.7 d, d (J_{PtP1} = 2556 Hz, J_{PtP2} = 3120 Hz (trans to Cl), satellites, J_{PP} = 20.8 Hz).

4.7. HPLC measurements

5 μl saturated solutions of compounds **1** or **3**, each in chloroform, were injected into a 50 × 5 mm^2 Nucleosil 120-5C18 HPLC column at room temperature by using the following HPLC conditions: flow rate, 2.0 ml min^{-1} for 60 min; eluent A, 10 mmol aqueous H_3PO_4 solution (0 min 75%, 60 min 0%); eluent B, acetonitrile. At these conditions compounds **1** and **3** eluted at 21 and 11 min respectively, giving relatively sharp peaks ($\omega_{1/2}$ < 4 min).

4.8. Hydroformylation experiments

An amount of 0.01 mmol Pt precursor was weighed into a Teflon-coated Berghof Hastalloy C reactor (volume 75 ml) under air. After closing, the reactor was flushed with a gentle stream of N_2 and the oxygen-free solution of 10 mmol (1.8 g) *p*-i-butylstyrene in 30 ml toluene was added in under N_2. The reactor was heated to the desired temperature with internal magnetic stirring and then pressurized to 70 bar by a mixture of CO/H_2 = 1/1. After cooling and venting after a run, the yellow solution was removed and quickly analyzed by GC. Fractional distillation to remove *p*-i-butylstyrene and *p*-i-butyl-ethylbenzene was done prior to the determination of the optical purity of the branched aldehyde. A similar procedure was employed in the hydroformyla-

tion of styrene, except that 0.05 mmol Pt precursor and 100 mmol styrene in 50 ml toluene were used instead.

4.9. Determination of optical purity and absolute rotation of 2-(4-i-butyl-phenyl)-2-propanal

A portion of the aldehyde mixture was oxidized by $KMnO_4$ and the acid mixture formed was subsequently extracted as given in Ref. [8] and Ref. [40] respectively. The optical purity was then determined by measuring the rotation of the acid mixture and calculating on the basis of the known, $[\alpha]_D^{20} = +60°$ (*S*) (*c* 2; EtOH) [41], absolute rotation of ibuprofen. Since the isolated yield of the acids after oxidation was only about 67–70% and the acid mixture contained a significant amount of the non-chiral linear acid as ballast, an alternative method was needed to estimate the optical purity and absolute rotation of ibuprofen-aldehyde. For this purpose, the NMR shift technique was used with $Eu(dmc)_3$, similar to the literature procedure [15] described for 2-phenyl-2-propanal. A portion of the aldehyde mixture containing 2 mg of optically active 2-(4-i-butyl-phenyl)-2-propanal was dissolved in 0.5 ml of $CDCl_3$ and after adding 25 mg of $Eu(dcm)_3$ ^1H NMR spectra were recorded at room temperature. The diastereomeric separation was the largest at the methine pseudo-quartets (next to CHO) with a relatively small value of 17 Hz. Thus, for a clear separation the methine quartets needed to be decoupled from the vicinal methyl protons. The optical purity was then determined by the integrated ratio of well-separated H-decoupled methine singlets. In two parallel experiments with branched aldehydes, which were later calculated to have average optical purities of 74.8% and 25.7%, the two methods gave less than 2% differences. On the basis of the known optical purities and optical rotations which were measured directly after fractional distillation, absolute optical rotation values were calculated for the two aldehydes of different optical purity. Since the difference in the thus-obtained values was less than 2%, an average value of $[\alpha]_D^{20} = +248°$ (*c* 3.5; benzene) could be taken for the absolute rotation of *S*-(+)-2-(4-i-butyl-phenyl)-2-propanal. (Error range is at least ±3%). In order to estimate whether the absolute rotation is strongly concentration dependent, the rotations of the two aldehyde solutions were measured after diluting to 1/5. A value of $[\alpha]_D^{20} = +243.8°$ (*c* 0.7; benzene) was thus obtained for the diluted solutions.

4.10. Structure determination and refinement of compound 3

A transparent yellowish block-shaped crystal was mounted on top of a glass-fiber (by using the inert-oil technique) and placed in the cold nitrogen stream of an Enraf-Nonius CAD4T diffractometer for data collection at 150 K (rotating anode, 50 kV, 50 mA, graphite-monochromated Mo Kα radiation, ω-scan mode). Unit cell parameters were determined from a least squares treatment of the SET4 setting angles of 25 reflections with $11.44 < \theta < 13.40°$. The unit cell parameters were checked for the presence of higher lattice symmetry [42]. A total of 17 533 reflections were collected and merged into a unique data set of 6988 reflections (R_i = 0.0374). Data were corrected for Lp, for a linear decay (0.2%) of the three intensity control reflections during the 34.7 h of X-ray exposure time and for absorption (using the DIFABS method [43]; correction range 0.750–1.322). The structure was solved with Patterson methods (DIRDIF [44]) and subsequent Fourier analyses. Refinement on F^2 with all unique reflections was carried out by full matrix least squares techniques. H-atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters; H-atoms with isotropic thermal parameters related to the U_{eq} of the carrier atoms. The unit cell contains two symmetry-related cavities of 307 Å^3, each containing three severely disordered molecules of dichloromethane. These solvent molecules could not be located from

Table 4
Crystal data and details of the structure determination of compound 3

Crystal data	
Formula	$C_{29}H_{26}Cl_2P_2Pt \cdot \frac{3}{2}CH_2Cl_2$
Mol. wt.	829.86
Crystal system	orthorhombic
Space group	$P2_12_12_1$ (No. 19)
a, *b*, *c* (Å)	10.4029(12), 14.076(2), 20.816(2)
V (Å^3)	3048.1(6)
Z	4
D_{calc} (g cm^{-3})	1.808
F(000)	1620
μ (cm^{-1})	54.0
Crystal size (mm^3)	0.50 × 0.50 × 0.70
Data collection	
Temperature (K)	150
θ_{min}, θ_{max}	0.98, 27.5
Radiation	Mo Kα (monochrom.), 0.71073 Å
$\Delta\omega$ (deg)	0.95 + 0.35 tan θ
Hor. and vert. aperture (mm)	1.94 + 0.97 tan θ, 4.00
Linear decay (%)	0.2
Reference reflections	2 1 −3, −3 −2 −1, −2 −4 −2
Data set	*h* −13:13; *k* −18:18; *l* −27:18
Total data	17533
Total unique data	6988; R_{int} = 0.0374
Refinement	
No. of refl. and params.	6988, 309
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0235P)^2 + 2.41P]$ where $P = (F_o^2 + 2F_c^2)/3$
Final *R*1, *wR*2, *S*	0.0322, 0.0648, 1.036
$(\Delta/\sigma)_{av}$ and max. in final cycle	0.000, 0.001

Table 5
Final coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms of compound **3**

Atom	x	y	z	U_{eq} (Å^2)
Pt(1)	0.18688(2)	0.01697(1)	0.23848(1)	0.0286(1)
Cl(1)	0.2948(2)	−0.07111(10)	0.15935(7)	0.0408(5)
Cl(2)	0.27583(15)	−0.08208(11)	0.31711(7)	0.0422(5)
P(1)	0.1148(2)	0.10708(11)	0.15906(7)	0.0333(5)
P(2)	0.1008(2)	0.09834(12)	0.31850(8)	0.0405(6)
C(1)	0.0509(7)	0.0487(5)	0.0894(3)	0.042(2)
C(2)	−0.0504(7)	−0.0153(5)	0.0856(3)	0.056(2)
C(3)	−0.0879(10)	−0.0506(7)	0.0265(5)	0.087(4)
C(4)	−0.0265(11)	−0.0264(7)	−0.0258(5)	0.093(5)
C(5)	0.0746(9)	0.0348(6)	−0.0258(3)	0.068(3)
C(6)	0.1157(8)	0.0742(5)	0.0336(3)	0.052(3)
C(7)	0.2188(7)	0.1397(5)	0.0449(3)	0.054(3)
C(8)	0.2988(12)	0.1809(6)	−0.0010(4)	0.084(4)
C(9)	0.3918(12)	0.2361(9)	0.0173(6)	0.097(5)
C(10)	0.4153(10)	0.2595(7)	0.0812(5)	0.090(4)
C(11)	0.3357(9)	0.2206(6)	0.1303(4)	0.073(3)
C(12)	0.2378(7)	0.1613(5)	0.1102(4)	0.051(3)
C(13)	−0.0004(7)	0.2046(4)	0.1762(3)	0.045(2)
C(14)	−0.1398(6)	0.1707(5)	0.1671(4)	0.058(3)
C(15)	0.0207(7)	0.2493(4)	0.2404(4)	0.063(3)
C(16)	−0.0212(8)	0.1872(5)	0.2987(3)	0.064(3)
C(17)	−0.0511(13)	0.2500(8)	0.3549(4)	0.155(6)
C(18)	0.0279(6)	0.0338(4)	0.3846(3)	0.0397(19)
C(19)	−0.0737(7)	−0.0301(6)	0.3820(3)	0.066(3)
C(20)	−0.1218(7)	−0.0659(6)	0.4406(4)	0.070(3)
C(21)	−0.0687(9)	−0.0362(7)	0.4979(3)	0.070(3)
C(22)	0.0299(8)	0.0277(6)	0.5008(3)	0.056(3)
C(23)	0.0831(7)	0.0634(5)	0.4429(3)	0.050(3)
C(24)	0.1876(9)	0.1316(4)	0.4350(3)	0.051(3)
C(25)	0.2627(8)	0.1725(5)	0.4835(3)	0.061(3)
C(26)	0.3575(10)	0.2357(6)	0.4682(4)	0.071(4)
C(27)	0.3858(10)	0.2572(5)	0.4040(4)	0.072(4)
C(28)	0.3146(9)	0.2183(4)	0.3549(3)	0.056(3)
C(29)	0.2155(7)	0.1561(4)	0.3712(3)	0.043(2)

U_{eq} equals one-third of the trace of the orthogonalized U tensor.

difference Fourier maps unambiguously and were taken into account in the structure factor and refinement calculations by direct Fourier transformation of the electron density in the cavities, following the BYPASS method [45] as implemented in PLATON [46] (as the 'SQUEEZE' option). The absolute structure was checked by refinement of the Flack parameter, resulting in 0.0027(73). Weights were introduced in the final refinement cycles, convergence was reached at $R1 = 0.0322$, $wR2 = 0.0648$. A final difference Fourier analysis shows no features outside the range -0.94:0.64 e Å^3.

Crystal data and numerical details of the structure determination are given in Table 4. Final atomic coordinates and equivalent isotropic thermal parameters of **3** are listed in Table 5. Neutral atomic scattering and anomalous dispersion factors were taken from Ref. [47]. All calculations were performed with SHELXL93 [48] and the PLATON [46] package (geometrical calculations and illustrations) on a DEC-5000 cluster.

Acknowledgements

Support of this work was provided by DSM Research, Geleen, Netherlands, which is gratefully acknowledged. We thank the technical assistance of Harrie Linssen in liquid NMR, Wim Barendswaard in CP MAS NMR, Gerard Kwakkenbos in MS and Ynze Mengerink (all from DSM Research) in HPLC measurements.

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