Bull Soc Chim Fr (1997) 134, 315-331
© Elsevier, Paris

TADDOLs on their way to late transition metal complexes – synthesis and crystal structure of *N*- and *S*-containing TADDOL-derived compounds

Dieter Seebach[1]*, Albert K Beck[1], Michiya Hayakawa[1], Georg Jaeschke[1], Florian NM Kühnle[1], Ivo Nägeli[1], Anthony B Pinkerton[1], P Beat Rheiner[1], Rudolf O Duthaler[2], Petra M Rothe[2], Wolfgang Weigand[3], Ralf Wünsch[3], Stefan Dick[3], Reinhard Nesper[4], Michael Wörle[4], Volker Gramlich[5]

[1] *Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstr 16, CH-8092 Zürich;*
[2] *Zentrale Forschungslaboratorien, CIBA-Geigy AG, Postfach CH-4002 Basel, Switzerland;*
[3] *Institut für Anorganische Chemie der Universität München, Meiserstr 1, D-80333 München, Germany;*
[4] *Laboratorium für Anorganische Chemie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Universitätstr 6;*
[5] *Laboratorium für Kristallographie der Eidgenössischen Technischen Hochschule, ETH-Zentrum, Sonneggstr 5, CH-8092 Zürich, Switzerland*

(Received 21 October 1996; accepted 16 November 1996)

Summary — As a part of our research program aimed at the synthesis of TADDOL-derived ligands with heteroatoms other than oxygen as chelating units, we describe here new or improved routes to amino TADDOL-analogs (**4**, **5**, **17–19**, **21**, **22**, **26**, **34** and **35**) and thio-TADDOL-analogs (**27–30** and **32**). The sulfinato-thiolato Pt-complex **44** was prepared by an oxidative insertion of Pt into the S–S-bond of the corresponding thiosulfinate **29**. Furthermore, the X-ray crystal structures of some of the new compounds (**2–5**, **28**, **29**, **32**, **42** and **44**) are presented and discussed.

TADDOL derivative / chiral ligand / X-ray structure / platinum complex

Résumé — **Synthèse et structure de dérivés azotés et sulfurés du TADDOL destinés à la formation de complexes de métaux de transition lointains.** Dans le cadre de notre programme de recherche, nous nous sommes orientés vers la synthèse de dérivés du TADDOL possédant d'autres hétéroatomes que l'oxygène en tant qu'unité chélatante ; nous décrivons ici des voies de synthèse optimisées ou bien nouvelles, conduisant aux analogues amino-TADDOL (**4**, **5**, **17–19**, **21**, **22**, **26**, **34** et **35**) et thio-TADDOL (**27–30** et **32**). Le complexe sulfinato-thiolato platine **44** a été préparé par insertion oxydative du Pt dans la liaison S–S du thiosulfinate correspondant **29**. Par ailleurs, les analyses structurales par rayons X de plusieurs de ces nouveaux composés (**2–5**, **28**, **29**, **32** et **44**) sont aussi présentées et discutées.

dérivé du TADDOL / ligand chiral / analyse structurale par rayons X / complexe de platine

Introduction

Since we first reported the preparation of α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) **1** in 1983 [1, 2], this class of ligands has found numerous applications in catalytic and stoichiometric enantioselective reactions [3]. Following the concept of hard and soft acids and bases by Pearson [4], the TADDOLs, acting as chelating alkoxy ligands, prefer complexation with hard main group or early transition metals, namely Mg, Al, Ti and Zr. The resulting chiral Lewis-acid complexes turn out to be successful in the mediation of the addition of C-nucleophiles to aldehydes and nitroolefins [5–9], in cyanohydrin [10] and Grignard additions [11], in Diels-Alder reactions [12–14], in [2 + 2] [15, 16] and [3 + 2] cycloadditions [17, 18], ene reactions [19], aldol additions [20], reductions of ketones [21], catalytic iodocarbocyclisation [22] and transesterifications [23–25]. A feature common to most of these reactions is the activation of a carbonyl or nitro group by the oxophilic metal center. The creation of a chiral ligand sphere around the metal by the TADDOLate allows for discrimination of enantiotopic faces in a substrate or of enantiotopic carbonyl groups in a *meso* compound. The enantioselectivities have been rationalized on the basis of X-ray crystal structures of numerous TADDOL-ligands [26] of several tetracoordinated [5, 20, 27] and of two hexacoordinated Ti-TADDOLates [22, 28], which show a propeller-type arrangement of the diarylhydroxymethyl groups in most cases. The success

---

* Correspondence and reprints

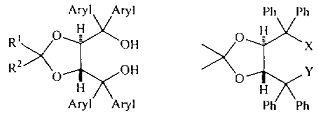
Table I. TADDOL-analogs **2–27**, bearing functional groups different from OH at the positions X and/or Y.

N°	*X*	*Y*	*Reference*	*X-ray*
1	OH	OH	[1]	[26]
2	Cl	Cl	[33], this paper	This paper
3	N_3	N_3	[33]	This paper
4	NH_2	NH_2	[33], this paper	This paper
5	$NH(CH_3)$	$NH(CH_3)$	[33, 34], this paper	This paper
6	$N(CH_3)_2$	$N(CH_3)_2$	[33]	–
7	$NHCOCF_3$	$NHCOCF_3$	[33]	–
8	NHCHO	NHCHO	[34]	–
9	NCS	NCS	[33], this paper	–
10	SH	SH	This paper[a]	–
11	$OPPh_2$	$OPPh_2$	[31]	[31]
12	OCH_3	OCH_3	[36], this paper	[5]
13	OH	OCH_3	This paper	–
14	OH	OAc	[37], this paper	–
15	OH	Cl	[33], this paper	–
16	OH	N_3	[33]	–
17	OH	NH_2	[33], this paper	–
18	OH	$NH(CH_3)$	[33], this paper	–
19	OH	$N(CH_3)_2$	[33], this paper	–
20	OH	$NH(CH_2Ph)$	[33]	–
21	OH	$NH(SO_2CF_3)$	This paper	–
22	OH	$NH(C_2H_5)$	This paper	–
23	OH	SH	[38]	–
24	OH	SCH_3	[38]	–
25	OH	$S(O)CH_3$	[38]	–
26	Cl	$N(CH_3)_2$	This paper	–
27	SH	$N(CH_3)_2$	This paper	–

[a] Isolated as a mixture with **28** (scheme 1).

of this structural subunit, which is also present in a wide variety of other ligands, has recently been the subject of a review article entitled *The magic diarylhydroxymethyl group* [29]. The propeller-type arrangement of the phenyl groups in the TADDOL derivatives strongly resembles that found in the structures of numerous bis-diphenylphosphino ligands (for example DIOP, BINAP, TADDOP) [30, 31].

A general goal – or should we say dream – of chemists is to find an auxiliary, which is, by slight variation of a parent compound, applicable to as many different types of enantioselective reactions as possible [32]. Besides binaphthol derivatives (BINOL), which are isolated in enantiomerically pure form only after an enantiomer separation step, TADDOLs are the most promising. The latter are readily available in two steps and in enantiomerically pure form from dimethyl tartrate by acetalization or ketalization and subsequent Grignard addition. In contrast to the binaphthyl derivatives, however, the structure of the TADDOLs **A** can be greatly varied by introducing different groups (R^1, R^2) in the 2-position of the dioxolane ring and by varying the aryl groups [26]. The prospect of obtaining TADDOL-derivatives, with 'soft' donor atoms instead of oxygen, which are suitable for the complexation of late transition metals, has prompted us to start a program aimed at the synthesis of analogs containing nitrogen, sulfur and phosphorus atoms. As a result of this project, we have recently reported the synthesis of TADDAMIN-derivatives **4–8** [33, 34], of bicyclic phosphonites **33** [33] of TADDOP **11** [31], and first applications of these in enantioselective synthesis [31, 34, 35]. For a list containing all known TADDOL-derivatives bearing at least one functional group other than OH on the chelating unit, see table I (**2–27**) and scheme 1 (**28–35**). The synthetic efforts described herein led to new or improved routes to the amino-derivatives **4**, **5**, **17–19**, **21**, **22**, **26**, **34** and **35** and to the thio-TADDOL-analogs **27–30** and **32**. Furthermore, we are now able to describe the insertion of Pt into the S-S bond of the thiosulfinate **29** which led to the Pt complex **44**.



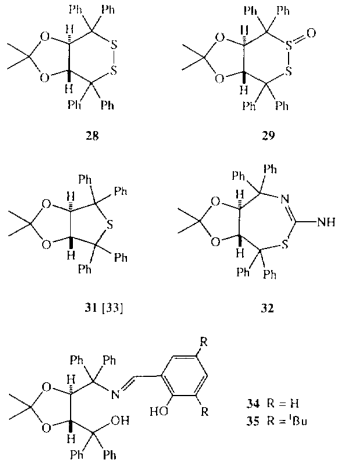
A 1-27

(For specification, see table I)

Formula 1

Synthetic results

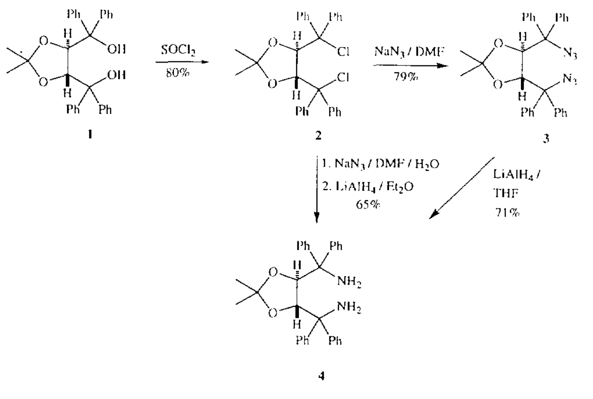
In a previous approach, we chose dichloride **2**, obtained from TADDOL **1**, as a key intermediate for the replacement of the oxygen by different heteroatoms [33]. An improved procedure for the preparation of **2** is described in the experimental section. Substitution of the chlorides by N_3^- and subsequent reduction of the diazide **3** with $LiAlH_4$ gave the TADDAMIN **4**. The isolation of the diazide **3** turns out to be somewhat dangerous due to the formation of volatile, explosive side products



Scheme 1

which condense in the receiver flask during evaporation of the solvent. To circumvent this isolation step, the transformation was carried out following a modified procedure: dichloride **2** was dissolved in DMF, but instead of using crystalline NaN_3, the nucleophile was added as an aqueous solution. This increased the amount of available azide ions in the reaction mixture, and consequently the reaction proceeded considerably faster (5 h vs 3 d at 80 °C). The mixture was extracted with Et_2O and the dried ethereal solution was added dropwise to a $LiAlH_4$ suspension in the same solvent (scheme 2). Using this procedure, the TADDAMIN **4** can be prepared easily on a large scale and in good yield (65% over two steps starting from TADDOL **1**).

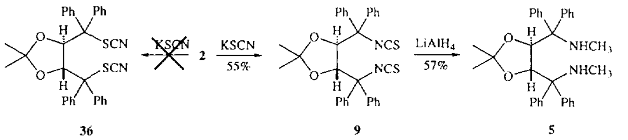
The TADDAMIN **4** can be further transformed to the *N,N′*-dimethyl derivative **5** by direct methylation with CH_3I [33] or via the bisformyl derivative **8** [34]. This TADDAMIN **5** has been employed as a chiral Li-amide base in the enantioselective addition of ketones to nitroolefins [34].



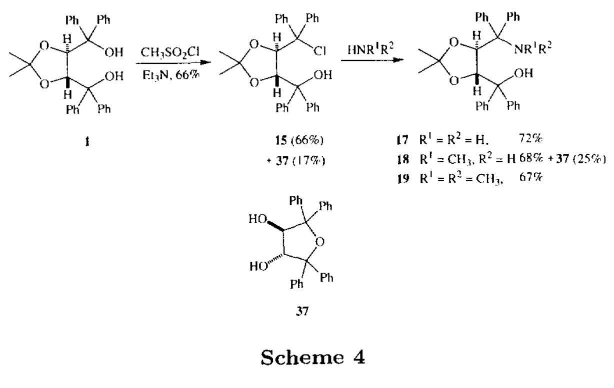
Scheme 2

A shorter route to the diamine **5** is the reaction of the dichloride **2** with KSCN. In contrast to our original assignment [33], thiocyanate reacts at the N-terminus and not at the S-terminus, which leads to the bis-isothiocyanate **9** (rather than the bis-thiocyanate **36**). Reduction of **9** with $LiAlH_4$ yields the bis-methylated TADDAMIN **5** (scheme 3).

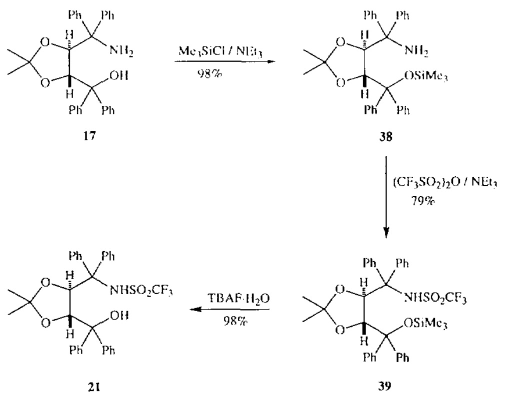
The increasing number of successful applications of C_1-symmetrical bidentate chelating ligands [39–44] has prompted us to improve the preparation of the monoamino-TADDOL derivatives **17–19** [33], whereby the selectively accessible monochloride **15** (preparable as a mixture with tetrahydrofuran **37**) is still the intermediate. Slight variation of the reaction conditions leads to its formation in higher yield. However, the major improvement is the direct replacement of Cl by NH_2, HNMe or $N(CH_3)_2$ (scheme 4): instead of by substitution with NaN_3 and subsequent reduction and alkylation, the aminoalcohols **17–19** have now been found to be formed by direct treatment with excess NH_3 or the corresponding amines under high pressure conditions. It should be mentioned that in the case of the preparation of **18** the tetrahydrofuran **37** could be removed and isolated in a yield of 25% as a byproduct.



Scheme 3



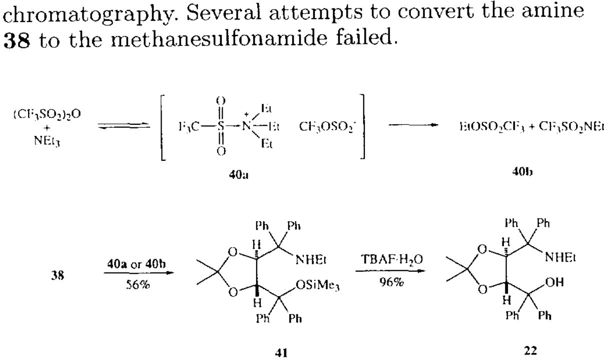
Scheme 4



Scheme 5

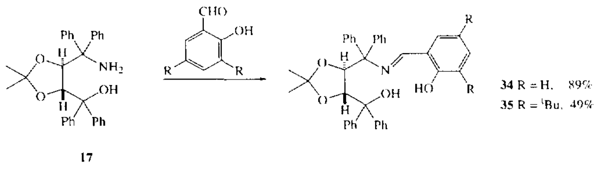
To reduce the pK_a of the amino functionality in **17** and thus to increase the affinity to early transition metals, we tried to prepare the trifluorosulfonamide **21** from **17**. Our initial attempts involved the addition of trifluorosulfonic acid anhydride (TFSAA) followed by NEt_3 to the aminoalcohol **17**, but only starting material was isolated. This and minor side products, arising from elimination of the hydroxy group or cyclization to a pyrrolidine, indicated preferential formation of the hydrolytically unstable trifluoromethylsulfonyl ester. Furthermore, a highly strained bicyclic pyrrolidine was formed, when **17** was treated with tosyl chloride/4-(dimethylamino)pyridine at 80 °C [33]. Indeed, protection of the hydroxy group in **17** (→ silyl ether **38**), slow addition of NEt_3 to a solution of **38** and TFSAA in CH_2Cl_2, deprotection and recrystallization gave the desired product **21** in 76% yield (scheme 5).

The sequence in which the reagents are added to the silyl ether **38** is crucial for the outcome of the reaction: addition of TFSAA to a solution of **38** and Et_3N at −75 °C gave, after desilylation, the ethylamino-TADDOL derivative **22** in 54% yield (scheme 6). We suppose that the formation of the alkylating agents **40a** or **40b** leads to the ethylamino TADDOL derivative **41**, which can be isolated in 56% yield after flash chromatography. Several attempts to convert the amine **38** to the methanesulfonamide failed.



Scheme 6

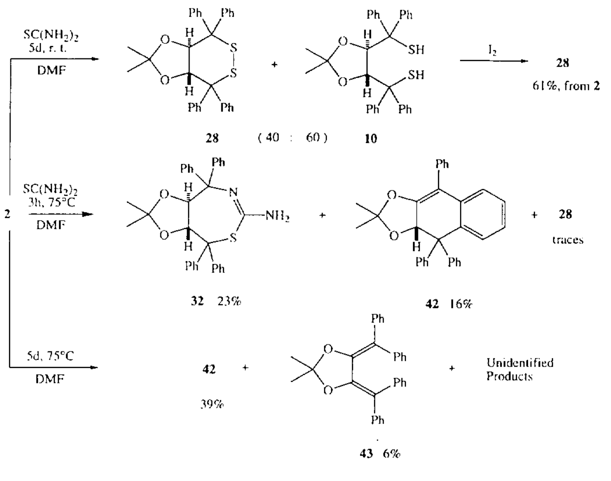
The differentiation of the two 'chelating arms' of the TADDOL offers the opportunity to introduce an additional coordinating atom, ie, to prepare tridentate TADDOL-derived ligands. Such an additional subunit may be used for fine-tuning of the respective ligands [45-48]. Thus, starting from TADDOL **1**, the new ligands **34** and **35** were obtained by monochlorination and nucleophilic substitution with NH_3 (described above) and subsequent imine condensation with various salicylic aldehydes in a total of three steps (scheme 7). Investigations on the potential of these ligands in enantioselective catalysis are under way.



Scheme 7

Once we had established the synthesis of nitrogen- and phosphorus-containing compounds derived from TADDOL **1** and studied their application as chiral ligands, the introduction of sulfur as the coordinating heteroatom appeared to be the next obvious step. In spite of the favourable coordination properties, only a few metal complexes with sulfur containing ligands have been employed in catalytic synthesis [40, 42, 44, 49–53] and it was therefore considered promising to enter this field of transition metal chemistry. All previously reported attempts to replace both OH groups of TADDOL **1** by SR failed: only monosubstituted products were isolated in low yield [38], or, starting from the dichloride **2**, both Cl-atoms were replaced by one sulfur atom leading to the highly strained bicyclic product **31** [33]. To prevent this cyclisation by an intramolecular substitution we chose thiourea as a synthetic equivalent of HS^-. Starting from dichloride **2**, a 40:60 mixture of disulfide **28** and dithiol **10** was thus obtained after alkaline hydrolysis. The iodine oxidation of this mixture led to the disulfide **28** as a single product in 61% yield (scheme 8). However, attempts to carry out the opposite transformation, reductive cleavage of the disulfide bond in **28** to the dithiol **10**, have so far failed. Raising the temperature to 75 °C during the substitution step led to completely different products: only traces of **28** could be detected by ^1H NMR spectroscopy, whereas the bicyclic compound **32** was isolated as the main product in 23% yield after flash chromatography. In addition, the tricyclic dihydronaphthalene derivative **42**, which is a product of chloride elimination and Friedel–Crafts alkylation, was formed, and its structure established by X-ray crystallography (fig 9). By analogy to the *p*-methoxyphenyl-TADDOL [54], **42** is formed via a cationic mechanism not involving thiourea: indeed, compound **42** is the major component of a reaction mixture resulting from heating a solution of the dichloride **2** in DMF. Besides **42**, the bis-elimination product **43** and further unidentified components were detected by ^1H NMR spectroscopy (scheme 8).

In principle, metal complexes of the dithiol **10** could also be prepared from the disulfide directly. To this end, we attempted to insert Pt into the disulfide bond of **28**, but, unfortunately, the corresponding experiments failed (possibly due to the strength of the dithi-



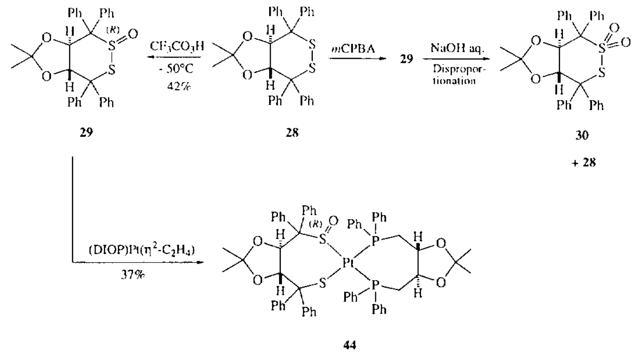
Scheme 8

ane S–S bond!?) [55]. Since S–S bonds of thiosulfinates have been reported to be about 20–30 kcal/mol weaker than those of the corresponding disulfides [56] and thiosulfonates [56–58], we oxidized **28** to the thiosulfinate **29** using *meta*-chloroperbenzoic acid as oxidant. The isolation of **29** turned out to be difficult due to its rapid disproportionation to the disulfide **28** and the thiosulfonate **30** during work-up under basic conditions. Satisfying results were, however, obtained using CF_3CO_3H at −50 °C [59, 60]. This reaction led selectively to a single diastereoisomer **29**. The oxygen on one of the sulfur atoms of the chair 1,2-dithiane ring in this product was expected to be in an axial position, due to stereoelectronic effects [61–64]. This has been proven by X-ray crystal structure analysis (fig 6). In preliminary work [65–68], it was shown that the oxidative addition of acyclic thiosulfinates to platinum(0) complexes $(R_3P)_2Pt(C_2H_4)$ led to bimetallic thiolate-bridged sulfenato complexes; cyclic thiosulfinates also react readily via insertion of platinum(0) into the S–S bond, to give chelate complexes containing sulfenato-thiolato compounds. Indeed, the thiosulfinato-TADDOL derivative **29** reacted smoothly with (*R*,*R*)-DIOP-Pt(C_2H_4) [69] in toluene at room temperature to yield the sulfinato-thiolato-Pt complex **44** in an oxidative addition reaction (scheme 9). Its all-(*R*) configuration was established by X-ray crystal structure determination.

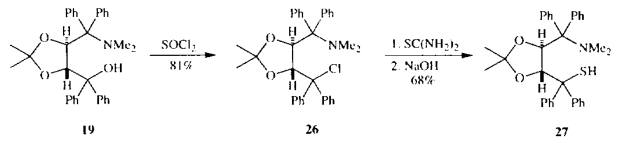
Since compound **19**, containing one OH and one $N(CH_3)_2$ group, was now easily accessible by the method described above, we tried to replace the hydroxy group by a thiol functionality following the thiourea procedure which had proved to be successful in the synthesis of the disulfide **28**. Treatment of **19** with $SOCl_2$ yielded the corresponding monochloride **26** in 81% yield. Substitution of the chloride by treatment with thiourea and alkaline hydrolysis led to the dimethylamino-thiol **27** in good yield (scheme 10). The potential of this ligand in asymmetric catalysis procedures, such as the addition of cuprates to enones, is currently under investigation.

Structural investigations: a new TADDOL conformation and bicyclic TADDOL derivatives

As pointed out in previous publications [5, 54], the most important features determining the structures of TADDOLs and TADDOL derivatives are: the preference for an antiperiplanar arrangement of the hetero atoms along the O–C(Ph)$_2$–CH–O subunit; and the hydrogen bond, which is usually formed between the hydroxy groups of the diphenyl methanol moieties. The crystal structures of the TADDAMIN 4 and the *N*,*N*′-dimethyl TADDAMIN **5**, in which the hydroxy groups are replaced by amino and methylamino groups



Scheme 9



Scheme 10

respectively (fig 1 and 2), display the same features as previously observed for the oxygen analogs. Both structures contain two crystallographically independent, but almost identical molecules in the unit cell, and they show a remarkably good agreement with the structure of the CCl_4 clathrate of TADDOL **1** [26]. In both cases, the dioxolane ring displays an envelope conformation with one of the C–H carbons out of plane. The phenyl substituents occupy quasi-equatorial and quasi-axial positions on the seven-membered ring formed by the C–C bonds of the acetal ring, both of the diphenyl methylamino groups and a N–H···N hydrogen bond. The distances between the heteroatoms (2.96–3.07 Å) are slightly longer than those found in TADDOLs (ca 2.6 Å) or in the dimethyl ether derivative **12** (2.9 Å) [5], but they correspond to the literature values for *N*-donor *N*-acceptor hydrogen bonds [70, 71].

In contrast, the structures of the dichloride **2** and of the diazide **3** display a hitherto unknown conformation (fig 3 and 4). While the heteroatoms in one half of the molecule have the usual antiperiplanar arrangement along the X–C(Ph)$_2$–CH–O subunit, those in the other half show a torsion angle of 63.1° for the dichloride and 61.2° for the diazide, which positions one X-atom above the dioxolane ring, synclinal to one of the dioxolane O-atoms (the generally preferred conformation of ethane moieties X–CR$_2$–CR$_2$–Y, cf the generalized gauche effect [61]). Similar torsion angles have so far been observed only in the structure of the tetra-(*ortho*-methoxy)-TADDOL [54] and in the solvent-free and guest-free crystals of the hexaphenyl-TADDOL [72]. In these structures, however, hydroxy groups are placed above and below the dioxolane ring, which puts two of the benzene rings on top of each other such that an (attractive?) π–π-interaction may be able to contribute to the stability of this conformation. Such a π–π-interaction is absent in the two new structures: only one side of the dichloride and of the diazide structure exhibits a gauche conformation whereas the antiperiplanar arrangement is conserved on the other side. Since both torsion angles are present in the same molecule, the energy difference between them in the absence of a hydrogen bond must be smaller than previously assumed [5] and the new conformation may be due to packing effects. In fact, the dimethyl ether derivative **12** is the only structure having the typical TADDOL conformation without a

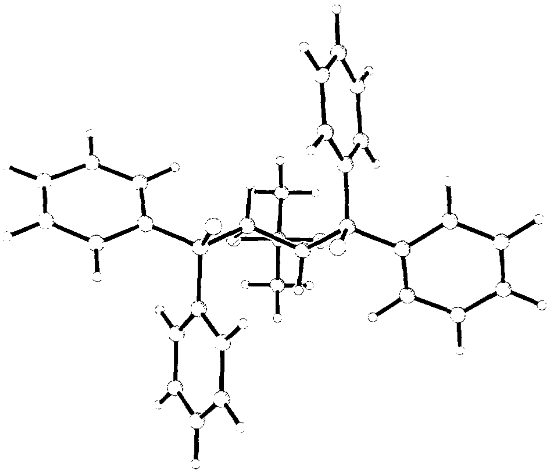


Fig 1. Ball-and-stick representation of the X-ray crystal structure of TADDAMIN **4**. Oxygen atoms are marked with little lines, nitrogen atoms are dotted.

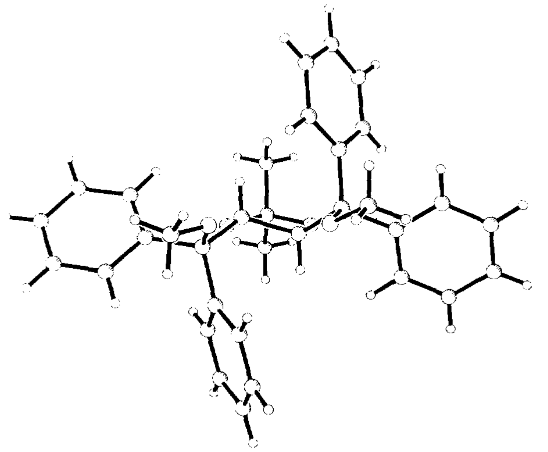


Fig 2. Ball-and-stick representation of the X-ray crystal structure of *N,N'*-dimethyl TADDAMIN **5**. Labelling of N and O atoms as in figure 1.

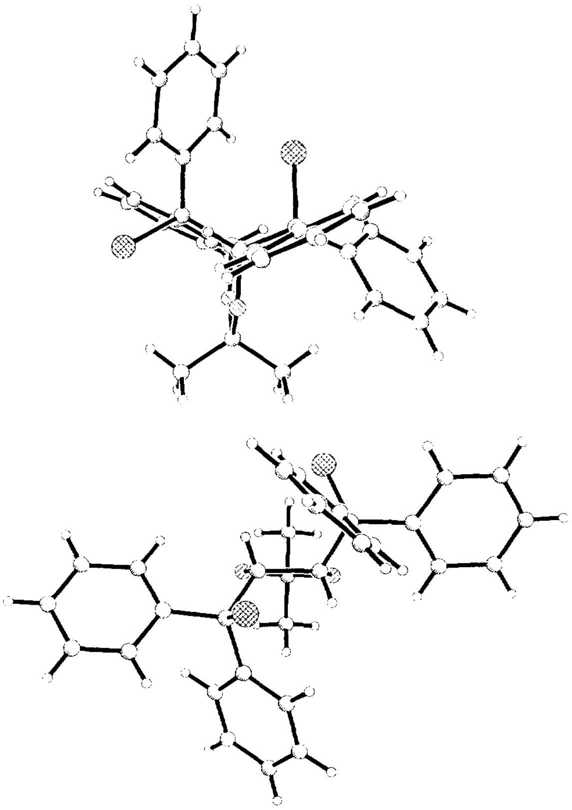


Fig 3. Side view (**a**) and front view (**b**) of the X-ray crystal structure of dichloride **2**. Oxygen atoms are marked by little lines, chlorine atoms are checkered.

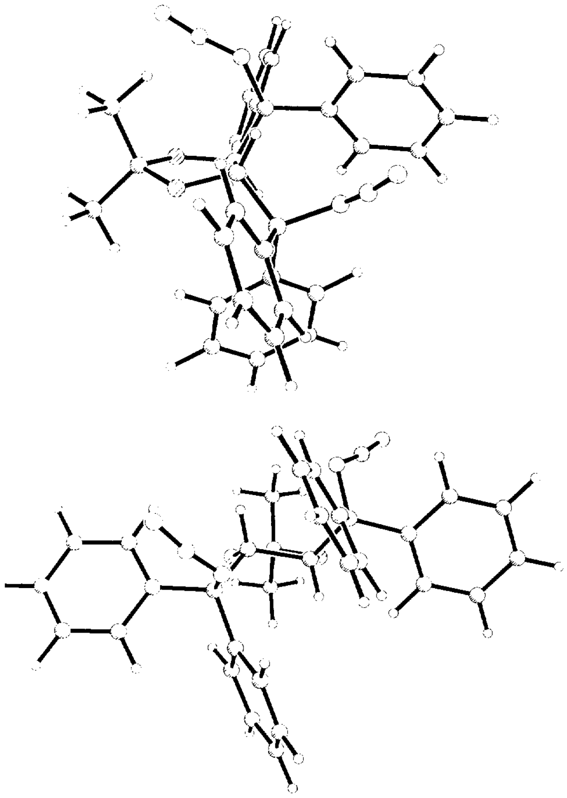


Fig 4. Side view (a) and front view (b) of the X-ray crystal structure of diazide **3**. Labelling of N and O atoms as in figure 1.

bridging or complexing atom holding the two XH atoms of the Ph_2CXH moieties in their respective positions.

We were also able to isolate single crystals suitable for X-ray analysis of the S-containing derivatives **28**, **29**, **32** and **44**. In all three bicyclic structures, ie, the disulfide **28**, the thiosulfinate **29** and the thiourea derivative **32**, the TADDOL backbone remains unchanged (fig 5–7). In **28** the diphenyl moieties are connected by a disulfide bridge of 2.05 Å length, which leads to a six-membered ring in an almost perfect chair conformation, even though this implies a torsion angle of 54.3° around the S–S bond which is rather small compared to the one in acyclic disulfides such as $H_3C–S–S–CH_3$ (88°) [73]. The phenyl groups adopt equatorial and axial positions on this dithiane ring such that the propeller-type arrangement typical for TADDOLs [5] is conserved. The thiosulfinate **29** is also present as a 1,2-dithiane six-membered ring chair conformation, with the oxygen in an axial position. The S–O bond is approximately parallel to two C–Ph and two dioxolane C–H bonds. The typical arrangement, with the phenyl substituents in a quasi-axial and quasi-equatorial position, is also found in the crystal structure of **32**. But in this case, the phenyl bearing C-atoms are connected by a S–C(=NH)–N bridge. This results in a seven-membered ring in chair conformation which is slightly distorted by the trigonal carbon atom.

Two different views of the X-ray crystal structure of the 1-sulfenato-4-thiolato Pt(II) complex **44** are shown

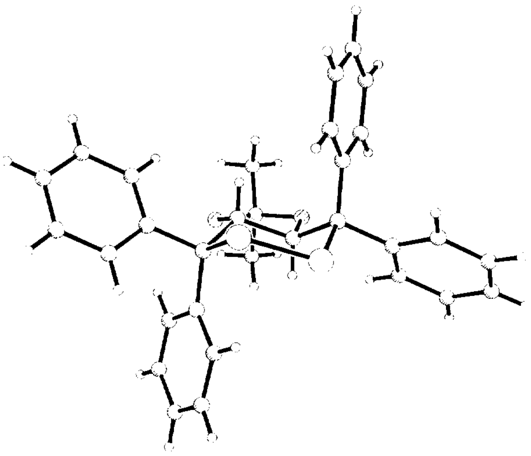


Fig 5. Ball-and-stick representation of the X-ray crystal structure of disulfide **28**. Oxygen is indicated by parallel lines, sulfur by a large empty circle.

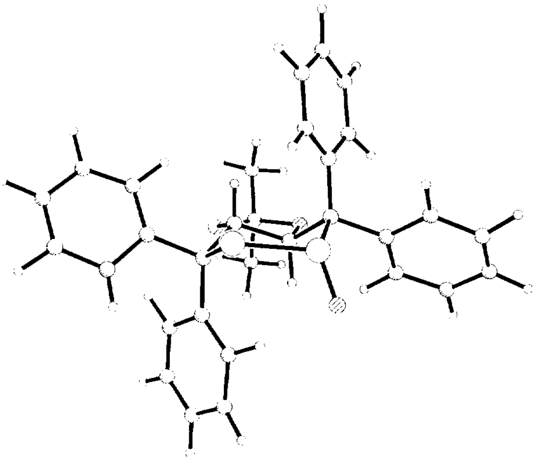


Fig 6. Ball-and-stick representation of the X-ray crystal structure of thiosulfinate **29**. Labelling of O and S atoms as in figure 5.

in figure 8. While the upper diagram shows the complex without H atoms, the lower one is drawn without the eight phenyl rings leaving only the ipso-C atoms to provide a better view. Complex **44** shows considerable distortion of the square planar coordination at the platinum(II) center: an angle of 21° is found between the planes of the P–Pt–P and the S–Pt–S atoms. This value is comparable to the one observed in the platinum complex $(Ph_3P)_2Pt[S(CH_2)_4S(O)]$ where the tetrahedral distortion of 16.1° is slightly smaller [65]. Key bond lengths in complex **44** are 2.44 Å for the Pt–P bond, which is *trans* to the sulfoxide S atom, and 2.26 Å for the other Pt–P bond. The first value shows the strong *trans* influence of the sulfenato ligand.

In the crystal structure of the tricyclic compound **42**, the dioxolane and one of the phenyl rings of TADDOL **1** are fused to give a dihydronaphthalene system with a dimethyl-methylenedioxy and three phenyl substituents on the non-aromatic ring (fig 9). This crystal structure

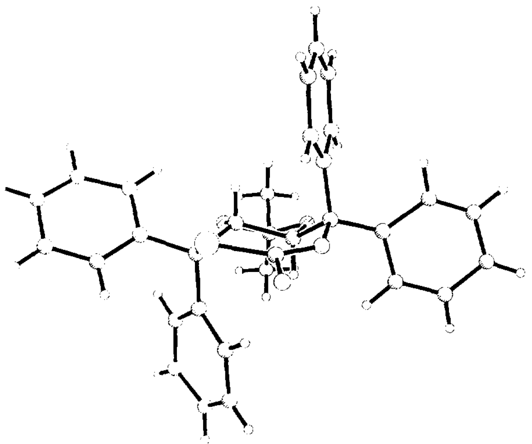


Fig 7. Ball-and-stick representation of the X-ray crystal structure of the thiourea derivative **32**. The hydrogen atoms of the amino group are omitted. For marking of N, O and S see figures 1 and 5.

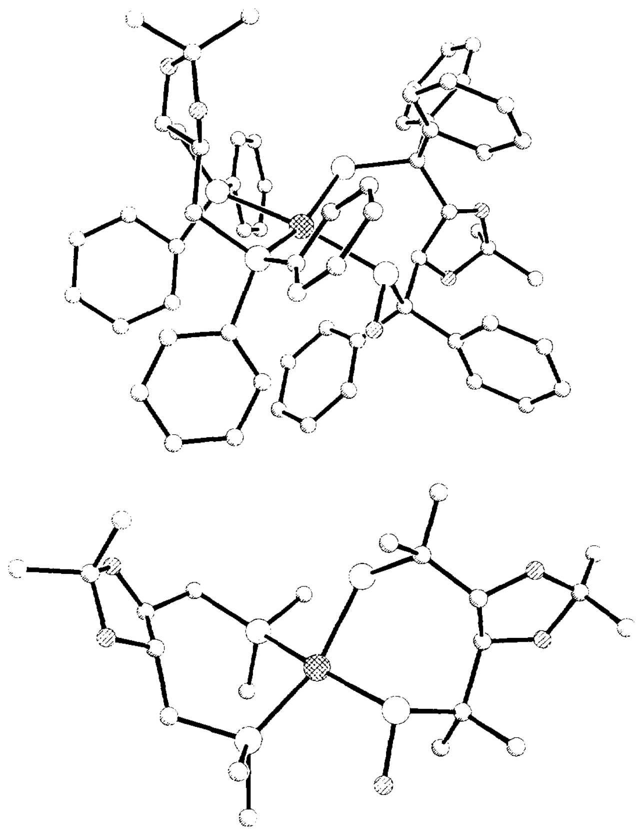


Fig 8. Two views of the X-ray crystal structure of complex **44**, including the benzene rings (**a**) and including only the ipso carbon atoms of the phenyl groups (**b**). Labelling of the heteroatoms: O striped, P dotted, S empty and Pt checkered.

further confirms our previous structural assignment of the related *p*-methoxyphenyl-TADDOL derived analog [54].

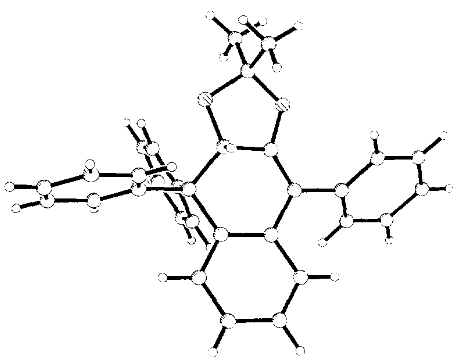


Fig 9. Ball-and-stick representation of the X-ray crystal structure of the dihydronaphthalene derivative **42**. Oxygen atoms are indicated by stripes.

Conclusion

We have shown that new symmetrical and unsymmetrical nitrogen and sulfur derivatives of TADDOL **1** are readily available by substitution of the benzhydrylic OH group(s). Thus, novel chiral ligands with two and three heteroatoms are accessible for chelation of main group and transition metal centers. With the sulfur-containing compounds, reactions occurring in the ligand sphere around late transition metal centers should thus become amenable to enantioselective modifications. Also, the tridentate compounds **34** and **35** are candidates for occupying a triangular face in a metal ligand sphere. The X-ray crystal structures, reported herein, of some of the new TADDOL derivatives will be helpful for mechanistic discussions of reactions involving the new ligands.

Experimental section

General

All reactions were carried out under an Ar or N_2 atmosphere in oven- or flame-dried glassware. Solvents used for reactions and crystallisations were purchased from Fluka (puriss). Dry THF and Et_2O was freshly distilled from K or Na under Ar atmosphere. Toluene was freshly distilled from LAH. Solvents used for extraction and flash chromatography were distilled as follows: AcOEt from P_2O_5, Et_2O from KOH/$FeSO_4$, hexane and pentane from Sikkon, MeOH was purchased from Fluka (puriss). Reactions under high pressure were performed using an Autoclave Engineer AE 316-ss stainless steel autoclave (1000 or 300 mL). Thin-layer chromatographic separations were run on Merck silica gel 60-F_{254} analytical plates; FC was performed on Fluka silica gel 60. Melting points were determined on a Büchi-510 apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 polarimeter at room temperature (10 cm, 1 mL cell).

^1H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded, unless otherwise specified, in $CDCl_3$ with TMS ($\delta = 0$) as internal standard on Bruker AC 250, Bruker AMX 400, Varian-Gemini 200, Varian-Gemini 300, Jeol GSX 270 or Jeol EX 400 spectrometers. Chemical shifts are given in ppm. FAB-MS were recorded on a VG-ZAB2-SEQ apparatus in a 3-nitrobenzyl alcohol matrix in m/z (% of the highest peak). IR spectra were recorded on Perkin Elmer 283, Perkin Elmer IR 841, Perkin Elmer 1600 FT-IR and Nicolet ZDX 5 FT-IR apparatus.

Preparation of dichloride **2** *and ethers* **12** *and* **13**

- *(4R,5R)-4,5-Bis-[(chloro-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane* **2**

A solution of NEt_3 (42 mL, 300 mmol) in CH_2Cl_2 (360 mL) was added dropwise to a refluxing mixture of TADDOL **1** [26] (27.9 g, 60 mmol) and thionyl chloride (13.1 mL, 180 mmol) in CH_2Cl_2 (360 mL) over 3 h. After an additional 15 min, the dark brown mixture was cooled to 10 °C, poured into precooled (10 °C) $NaHCO_3$ solution (1000 mL) and stirred vigorosly for 4 h at room temperature. The organic layer was separated, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Trituration of the crude product (36.8 g) with MeOH (180 mL) for 30 min gave **2** as a brown solid (24.7 g, 82%). An analytical pure sample was produced by addition of activated charcoal powder (0.05 g) to an Et_2O solution (20 mL) of **2** (0.25 g, 0.5 mmol). Filtration and evaporation of the solvent yielded a residue which, after trituration with pentane (3 mL), gave dichloride **2** as a light yellow solid (0.14 g).

Mp 171–172 °C ([33] decomposition 165–170 °C).

$[\alpha]_D^{RT} = -11.1$ ($c = 1.00$, $CHCl_3$) ([33] $[\alpha]_D^{RT} = -11.2$; $c = 1.00$, $CHCl_3$).

The analytical data (NMR, IR, EA) matched those of the literature [33].

Caution: Longer trituration of **2** in MeOH (> 45 min) followed by flash chromatography on silica gel (toluene) leads to dimethyl- (**12**) and monomethyl-ether (**13**) derivatives (analytical data see below).

- *(4R,5R)-4,5-Bis-[(methoxy-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane* **12**

Mp 186.6–187.8 ([36] Mp 182–184.5 °C).

$[\alpha]_D^{RT} = -89.7$ ($c = 1.00$, $CHCl_3$) ([36] $[\alpha]_D^{RT} = -84.7$; $c = 1.00$, $CHCl_3$).

IR (KBr): 3 100, 3 070, 3 020, 2 980, 2 950, 2 870, 1 610, 1 500, 1 450, 1 380, 1 370, 1 340, 1 325, 1 250, 1 115, 1 075, 1 060, 1 040, 890, 770, 755, 710 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ 0.88 (s, 6H, 2 CH_3), 3.02 (s, 6H, 2 OCH_3), 4.90 (s, 2H, 2 CH), 7.30–7.48 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.5, 52.7, 78.7, 84.3, 109.0, 126.7, 127.0, 127.2, 127.4, 129.8, 130.1, 142.1, 142.6.

Anal calc for $C_{33}H_{34}O_4$: C, 80.13; H, 6.93. Found: C, 80.40; H, 7.16.

- *(4R,5R)-5-[(Methoxy-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **13**

Mp 169.8–170.4 °C.

$[\alpha]_D^{RT} = -27.0$ ($c = 1.00$, $CHCl_3$).

IR ($CHCl_3$): 3 064, 3 008, 2 942, 1 496, 1 447, 1 381, 1 372, 1 169, 1 088, 1 049, 882, 639 cm^{-1}.

^1H NMR ($CDCl_3$, 200 MHz): δ 0.95 (s, 3H, CH_3), 1.06 (s, 3H, CH_3), 3.00 (s, 3H, OCH_3), 4.27 (d, $J = 8.3$ Hz, 1H, CH), 4.62 (d, $J = 8.3$ Hz, 1H, CH), 6.37 (s, 1H, OH), 7.22–7.69 (m, 20H, arom H).

Preparation of diamines **4** *and* **5** *and bis-isothiocyanate* **9**

- *(4S,5S)-2,2-Dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine* **4**

A solution of NaN_3 (12.2 g, 188 mmol) in H_2O (45 mL) was added dropwise to a solution of **2** (23.7 g, 47 mmol) in DMF (230 mL) and the mixture was then heated at 80 °C for 5 h. After cooling to room temperature, Et_2O (700 mL) and H_2O (460 mL) were added. The organic, brown layer was washed twice with H_2O (460 mL), dried over $MgSO_4$ and added to a suspension of LAH (14.3 g, 376 mmol) in Et_2O (460 mL) over 1 h. After 2.5 h, excess LAH was destroyed by slow addition of saturated Na_2SO_4 in H_2O (120 mL) until gas evolution stopped. The yellow suspension was filtered and the residue was washed with Et_2O (360 mL). After drying over $MgSO_4$ and removal of the solvent under reduced pressure, the crude product (19.8 g) was purified via trituration by refluxing with hexane (100 mL) for 1 h. Recrystallization in CH_3CN (160 mL) gave **4** as a colorless solid (14.1 g, 65%).

Mp 198–200 °C ([33] Mp 200–201 °C).

$[\alpha]_D^{RT} = -45.2$ ($c = 1.00$, $CHCl_3$) ([33] $[\alpha]_D^{RT} = -43.0$; $c = 0.68$, $CHCl_3$).

The analytical data (NMR, IR, EA) matched those of the literature [33].

- *(4S,5S)-2,2,N,N′-Tetramethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine* **5**

A solution of isothiocyanate **9** (0.55 g, 1 mmol) in Et_2O (70 mL) was added dropwise to a suspension of LAH (0.19 g, 5 mmol) in Et_2O (15 mL) over 40 min at room temperature. After stirring for 3 h excess LAH was destroyed by careful addition of H_2O (35 mL) and 10% H_2SO_4 (3 mL), the aqueous layer was filtered and extracted twice with Et_2O (50 mL). The combined organic layers were then dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the crude product (0.42 g) by flash chromatography on silica gel (toluene/ethyl acetate (9:1)) gave **5** as a colorless solid (0.28 g, 57%).

Mp 200–203 °C ([33] Mp 201–203 °C; [34] Mp 195–197 °C).

R_f: 0.27 (CH_2Cl_2/pentane (3:7)).

$[\alpha]_D^{RT} = -48.4$ ($c = 1.00$, $CHCl_3$) ([33] $[\alpha]_D^{RT} = -49.2$; $c = 0.52$, $CHCl_3$; [34] $[\alpha]_D^{RT} = -45.3$; $c = 1.00$, $CHCl_3$).

The analytical data (NMR, IR, EA) matched those of the literature [33, 34].

- *(4S,5S)-4,5-Bis-[(isothiocyanato-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane* **9**

A solution of **2** (5.03 g, 10 mmol) and KSCN (4.86 g, 50 mmol) in DMF (200 mL) was heated at 80 °C for 14 h. After cooling to room temperature, Et_2O (300 mL) and H_2O (300 mL) were added. The organic layer was washed twice with H_2O (200 mL), dried over $MgSO_4$ and removed under reduced pressure. Trituration of the crude product (5.14 g) with CH_3CN (25 mL) for 30 min gave **9** as a light brown solid (3.72 g, 68%). Further purification of **9** was achieved by flash chromatography on silica gel (pentane/CH_2Cl_2 8:2).

Mp 202–203 °C ([33] Mp 196–197 °C).

R_f: 0.85 (CH_2Cl_2).

$[\alpha]_D^{RT} = 12.9$ ($c = 1.00$, $CHCl_3$) ([33] $[\alpha]_D^{RT} = 12.6$; $c = 0.27$, $CHCl_3$).

The analytical data (NMR, IR, EA) matched those of the literature [33].

Preparation of **14** *and* **15**

- *(4R,5R)-5-[(Hydroxy-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-acetic acid methyl ester* **14**

A solution of TADDOL **1** [26] (4.67 g, 10 mmol) in Et_2O (30 mL) was treated with MeLi (20 mmol [excess acetyl chloride does not lead to the diacetate derivative!]) at −78 °C for 1 h. Acetyl chloride (0.78 mL, 11 mmol) was then added, the mixture was warmed to room temperature and stirred for an additional 5 h. After hydrolysis with saturated $NaHCO_3$ and additon of CH_2Cl_2 (300 mL), the organic layer was washed with H_2O, saturated NaCl and dried over $MgSO_4$. The solvent was then partially removed under reduced pressure until crystallization began. This resulted in the formation of **14** as a colorless solid (4.57 g, 90%).

Mp 219.6–220.8 °C.

$[\alpha]_D^{RT} = -97.3$ ($c = 1.09$, $CHCl_3$).

IR (KBr): 3 480, 3 050, 3 020, 2 980, 2 930, 2 880, 1 720, 1 590, 1 490, 1 445, 1 370, 1 250, 890, 750, 650 cm^{-1}.

^1H NMR ($CDCl_3$, 300 MHz): δ 0.81 (s, 6H, $2CH_3$), 1.93 (s, 3H, $C(O)CH_3$), 2.76 (s, 1H, OH), 4.72 (d, $J = 7.3$ Hz, 1H, CH), 5.54 (d, $J = 7.3$ Hz, 1H, CH), 7.20–7.44 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.8, 27.2, 27.3, 77.4, 77.5, 78.8, 81.2, 86.2, 109.9, 126.8, 127.2, 127.4, 127.5, 128.2, 128.7, 128.9, 129.7, 139.8, 143.2, 147.1, 168.7.

• *(4R,5R)-5-[(Chloro-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **15**

A solution of TADDOL **1** [26] (50.0 g, 107 mmol) in CH_2Cl_2 (500 mL) was treated under Ar atmosphere with NEt_3 (22.3 mL, 160 mmol) over 5 min. The mixture was stirred for an additional 5 min and then methanesulfonyl chloride (25.1 mL, 321 mmol) in CH_2Cl_2 (100 mL) was added dropwise over 45 min. After an additional 3 h H_2O (200 mL) was added, the organic layer separated and washed with 10% HCl (600 mL), saturated $NaHCO_3$ (600 mL), twice with H_2O (600 mL), and finally with saturated NaCl (600 mL). It was then dried over $MgSO_4$ and the solvent removed under reduced pressure at room temperature to give a mixture of **15** and **37** (41.8 g, 66% **15**, 17% **37** by ^1H NMR analysis). The crude mixture can be used without further purification in subsequent steps.

Extended drying of the crude mixture under HV at room temperature (to remove sulfonic acid residues) gave significant conversion of **15** to **37**. Attempted purification by flash column chromatography leads to decomposition of **15**. Recrystallization (Et_2O/hexane 1:5) leads to analytically pure **15**.

Mp 135–137 °C.

$[\alpha]_D^{RT} = -18.1$ ($c = 0.4$, $CHCl_3$).

IR (KBr): 3 590, 3 000, 2 992, 2 920, 1 600, 1 595, 1 500, 1 385, 1 365, 1 150, 1 245, 1 160, 1 085, 1 065, 970, 870, 845, 750, 700, 620, 580 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz): δ 1.05 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.98 (s, 1H, OH), 5.29 (d, $J = 6.9$ Hz, 1H, CH), 5.55 (d, $J = 6.9$ Hz, 1H, CH), 7.19–7.76 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 28.0, 28.3, 78.5, 81.9, 83.3, 112.3, 127.1, 127.2, 127.4, 127.5, 127.7, 127.8, 127.9, 128.0, 128.4, 128.6, 130.1, 142.9, 144.0, 145.8.

MS (FD): m/z 484 (M^+, 4), 448 (3), 301 (37), 183 (100).

Anal calc for $C_{31}H_{29}O_3Cl$: C, 76.77; H, 6.03; Cl, 7.31. Found: C, 76.39; H, 6.02; Cl, 7.53.

Preparation of aminoalcohols **17–19** *and of byproduct* **37**

• *(4R,5S)-5-[(Amino-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **17**

The chloro-TADDOL **15** (56.4 g, 116.2 mmol) was placed in an autoclave (1000 mL) purged with Ar. After cooling to −78 °C, NH_3 (280 g, 16.44 mol) was condensed into the autoclave and the reaction mixture was then heated to 85 °C at 40 bar. After stirring for 7 h, excess NH_3 was vented, and the crude product was dissolved in CH_2Cl_2 (500 mL). The organic layer was neutralized with 1 N HCl and washed twice with H_2O (200 mL) and saturated NaCl (150 mL) then dried over $MgSO_4$ and the solvent was removed under reduced pressure. Recrystallization of the crude product from isopropanol (200 mL) gave **17** as a colorless solid (34.6 g, 72%). Mp 210–211 °C ([33] Mp 211–212 °C).

$[\alpha]_D^{RT} = -58.1$ ($c = 0.2$, $CHCl_3$) ([33] $[\alpha]_D^{RT} = -59.9$; $c = 1.12$, $CHCl_3$).

The analytical data (NMR, IR, EA) matched those of the literature [33].

• *(4R,5S)-2,2-Dimethyl-5-[(methylamino-diphenyl)-methyl]-α,α-diphenyl-1,3-dioxolane-4-methanol* **18**

The chloro-TADDOL **15** (67.8 g, 139.8 mmol) was placed in an autoclave (1000 mL) purged with Ar. After cooling to −30 °C, CH_3NH_2 (235 g, 7.57 mol) was condensed into the autoclave. The reaction mixture was warmed up, stirred for 30 min at room temperature and then for 3 h at 100 °C at constant pressure (about 20 bar). After cooling to room temperature, excess CH_3NH_2 was vented, and the residue was dissolved in CH_2Cl_2. The organic layer was neutralized with 1 N HCl, washed twice with H_2O (200 mL) and saturated NaCl (150 mL) and then dried over $MgSO_4$ and the solvent was removed under reduced pressure. Two recrystallizations of the crude product from isopropanol (200 mL) gave **37** (14.26 g, 25%, colorless solid) beside **18** as a colorless solid (45.59 g, 68%).

Mp 195–196 °C ([33] Mp 189–191 °C).

The analytical data (NMR, IR, EA) matched those of the literature [33].

• *(3R,4R)-2,2,5,5-Tetraphenyl-tetrahydrofuran-3,4-diol* **37**

Mp 120 °C.

$[\alpha]_D^{RT} = -212$ ($c = 1.04$, $CHCl_3$).

IR (KBr): 3 410, 3 081, 3 019, 2 945, 1 600, 1 498, 1 448, 1 420, 1 400, 1 315, 1 255, 1 180, 1 144, 1 022, 900, 798, 769, 700, 620, 510 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz): δ 1.88 (dd, 2H, OH), 4.45 (dd, 2H, CH), 7.22–7.61 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 79.4, 85.1, 126.3, 127.1, 127.4, 127.8, 128.2, 141.8, 145.5.

MS (FAB): m/z 407 ($M^+ - H$), 167.

Anal calc for $C_{28}H_{24}O_3 \cdot 0.5\ H_2O$: C, 80.55; H, 6.04. Found: C, 80.80; H, 6.10.

• *(4R,5S)-5-[(Dimethylamino-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **19**

The chloro-TADDOL **15** (20.74 g, 43.2 mmol) was placed in an autoclave (300 mL) purged with Ar. After cooling to −30 °C, $(CH_3)_2NH$ (50.0 g, 1.11 mol) was condensed into the autoclave. The reaction mixture was warmed up, stirred for 30 min at room temperature and then for 5 h at 90 °C at constant pressure (about 11 bar). After cooling to room temperature, excess $(CH_3)_2NH$ was vented, and the crude product was dissolved in CH_2Cl_2. The organic layer was neutralized with 1 N HCl, washed twice with H_2O (70 mL) and saturated NaCl (50 mL) then dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification of the crude product by flash chromatography on silica gel (hexane/ethyl acetate (4:1)) and recrystallization from isopropanol gave **19** as a colorless solid (14.29 g, 67%).

The analytical data (NMR, IR, EA) matched those of the literature [33].

Preparation of **21** *from* **17** *(intermediates* **38** *and* **39***)*

- *(4S,5R)-5-[(Diphenyl-trimethylsilanyloxy)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanamine* **38**

Me_3SiCl (1.03 g, 9.46 mmol) was added to a solution of **17** (2.02 g, 4.34 mmol) in CH_2Cl_2 (30 mL) under Ar atmosphere. NEt_3 (1.34 mL, 9.7 mmol) in CH_2Cl_2 (5 mL) was then added over 20 min. After 18 h, the organic layer was washed with H_2O (50 mL) and saturated NaCl (50 mL) then dried over $MgSO_4$ and the solvent was removed under reduced pressure. Recrystallization from isopropanol gave **38** as a colorless solid (2.01 g, 85%).

Mp 75–76 °C.

$[\alpha]_D^{RT} = -63.1$ ($c = 0.3$, $CHCl_3$).

IR (KBr): 3 380, 3 310, 3 070, 2 990, 1 600, 1 495, 1 448, 1 365, 1 255, 1 180, 1 065, 1 045, 920, 865, 760, 700, 660, 630 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz): δ −0.83 (s, 9H, $Si(CH_3)_3$), 0.79 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 2.35 (s, 2H, NH_2), 3.98 (d, J = 6.9 Hz, 1H, CH), 4.28 (d, J = 6.9 Hz, 1H, CH), 7.04–7.60 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 1.0, 25.9, 26.2, 61.4, 75.5, 80.9, 81.5, 106.2, 125.4, 125.6, 125.8, 126.1, 126.3, 126.5, 126.7, 127.0, 127.1, 128.0, 128.9, 129.0, 140.1, 142.2, 143.1.

MS (FD): m/z 538 (M^+ + H, 60), 431 (40), 255 (75), 237 (80), 182 (100).

Anal calc for $C_{34}H_{39}O_3NSi$: C, 75.94; H, 7.31; N, 2.60. Found: C, 75.79; H, 7.38; N, 2.60.

- *(4S,5R)-N-[({5-[(Diphenyl-trimethylsilanyloxy)-methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}-diphenyl) methyl]-trifluoromethanesulfonamide* **39**

A solution of **38** (2.33 g, 4.15 mmol) in CH_2Cl_2 (450 mL) was treated with trifluoromethanesulfonic anhydride (0.82 mL, 5.02 mmol) in CH_2Cl_2 (15 mL) under N_2 at −78 °C. After dropwise addition of NEt_3 (0.73 mL, 5.30 mmol) in CH_2Cl_2 (60 mL) over 5 h, the colorless mixture was allowed to warm up to room temperature and stirred overnight. The resulting light red solution was then washed three times with H_2O (50 mL), twice with saturated NaCl (50 mL), dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product (2.73 g) was purified by flash chromatography on silica gel (Et_2O/hexane/CH_2Cl_2 (2:4:1)) to give **39** as colorless powder (2.18 g, 79%). For a large scale preparation of **39**, recrystallization from isopropanol is also possible.

^1H NMR ($CDCl_3$, 250 MHz): δ 1.05 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 4.23 (d, J = 6.9 Hz, 1H, CH), 4.39 (d, J = 6.9 Hz, 1H, CH), 7.12–8.18 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 2.2, 26.5, 26.8, 69.1, 80.9, 81.3, 81.5, 108.6, 125.9, 126.3, 126.5, 126.7, 127.0, 127.1, 127.3, 127.4, 127.7, 127.9, 128.0, 128.2, 128.6, 129.5, 130.0, 130.1, 130.3, 130.8, 131.2, 136.8, 139.0, 139.7, 141.5 (the CF_3-quartet could not be detected).

^{19}F NMR ($CDCl_3$, external $CFCl_3$, 235.4 MHz): δ −75.71.

- *(4S,5R)-Trifluoro-N-[({5-[(hydroxy-diphenyl)-methyl]-2,2-dimethyl-1,3-dioxolan-4-yl}-diphenyl)-methyl]methanesulfonamide* **21**

A solution of **39** (2.01 g, 3.0 mmol) in THF (30 mL) was treated with $(Bu)_4NF{\cdot}3H_2O$ (2.05 g, 6.5 mmol) in small portions. After 18 h the yellow mixture was washed with 1N HCl (20 mL), saturated $NaHCO_3$ (20 mL) and NaCl solution. The organic layer was then dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Crystallization of the crude product from t-BuOMe gave **21** as t-BuOMe-clathrate (1.76 g, 85%). Purification by flash chromatography on silica gel (Et_2O/hexane/CH_2Cl_2 (2:4:1)) is also possible. An analytical sample of the Et_2O-clathrate of **21** was obtained by recrystallization from Et_2O.

Mp 243–244 °C.

$[\alpha]_D^{RT} = -58.8$ ($c = 0.3$, $CHCl_3$).

IR (KBr): 3 474, 3 069, 2 988, 2 907, 1 499, 1 448, 1 379, 1 207, 1 146, 1 086, 1 059, 1 034, 941, 876, 770, 737, 702, 638, 604, 569, 509 cm^{-1}.

^1H NMR ($CDCl_3$, 250 MHz): δ 0.72 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 1.18 (t, $2CH_3$, Et_2O), 3.63 (q, $2CH_2$, Et_2O), 3.82 (s, OH), 4.21 (d, J = 6.9 Hz, 1H, CH), 4.62 (d, J = 6.9 Hz, 1H, CH), 7.11–7.68 (m, 20H, arom H), 9.56 (s, 1H, NH).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 15.1, 26.8, 27.0, 65.7, 69.5, 78.8, 79.7, 81.5, 109.4, 119.0 (q, J = 318.4 Hz, CF_3), 127.0, 127.3, 127.4, 128.0, 128.1, 128.2, 128.4, 128.5, 128.8, 130.1, 130.8, 138.1, 138.4, 140.5, 145.0.

^{19}F NMR ($CDCl_3$, external $CFCl_3$, 235 MHz): δ −77.95.

MS (FAB): m/z 597 (M^-, 15), 596 (50), 266 (15), 133 (100).

Anal calc for $C_{32}H_{30}O_5NF_3S{\cdot}1\ Et_2O$: C, 64.36; H, 6.00; N, 2.09. Found: C, 64.36; H, 5.94; N, 2.20.

Preparation of **22** *from* **38** *(intermediate* **41***)*

- *(4S,5R)-5-[(Diphenyl-trimethylsilanyloxy)methyl]-N-ethyl-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanamine* **41**

A solution of **38** (1.67 g, 3.1 mmol) in CH_2Cl_2 (100 mL) was treated with NEt_3 (0.52 mL, 3.8 mmol) in CH_2Cl_2 (10 mL) under Ar at −75 °C. Trifluoromethanesulfonic anhydride (0.59 mL, 3.6 mmol) in CH_2Cl_2 (20 mL) was then added dropwise over 1.5 h. After warming up slowly to room temperature and strirring overnight, the reaction mixture was washed with H_2O (3 × 30 mL) and saturated NaCl solution. It was then dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude red brown product (1.83 g) was purified by flash chromatography (twice) on silica gel (Et_2O/hexane/CH_2Cl_2 (1:3:1)) to give **41** as light yellow crystals (0.98 g, 56%).

^1H NMR ($CDCl_3$, 250 MHz): δ −0.11 (s, 9H, $Si(CH_3)_3$), 0.91 (t, 3H, NEt), 1.03 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.90 (q, 2H, NEt), 3.12 (t, 1H, NH), 4.09 (d, J = 6.9 Hz, 1H, CH), 4.28 (d, J = 6.9 Hz, 1H, CH), 7.03–7.90 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 2.6, 16.4, 27.0, 27.2, 37.7, 67.3, 80.1, 82.5, 82.9, 106.3, 126.2, 126.5, 126.7, 126.9, 127.0, 127.4, 128.1, 128.9, 130.2, 130.3, 141.7, 143.6, 144.9.

- *(4R,5S)-5-[(Ethylamino-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **22**

A solution of **41** (0.98 g, 1.73 mmol) in THF (30 mL) was treated with $(Bu)_4NF{\cdot}3H_2O$ (0.56 g, 1.8 mmol) in small portions. After 18 h at room temperature the yellow mixture was washed with 1N HCl (10 mL), saturated $NaHCO_3$ (10 mL) and saturated NaCl. The organic layer was then dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Recrystallization of the residue from Et_2O/CH_2Cl_2 (1:2) gave **22** as colorless crystals (0.83 g, 98%).

^1H NMR ($CDCl_3$, 250 MHz): δ 0.71 (s, 3H, CH_3), 1.02 (t, 3H, NEt), 1.28 (s, 3H, CH_3), 1.63 (s, 1H, NH), 1.7–2.1 (m, 2H, NCH_2CH_3), 4.12 (d, J = 6.9 Hz, 1H, CH), 4.31 (d, J = 6.9 Hz, 1H, CH), 7.02–7.82 (m, 20H, arom H), 9.02 (s, 1H, OH).

^{13}C NMR ($CDCl_3$, 63 MHz): δ 14.9, 26.4, 27.5, 37.5, 67.6, 75.5, 78.2, 83.0, 107.8, 126.8, 126.9, 127.2, 127.5, 127.6, 127.8, 128.1, 128.9, 130.6, 140.6, 144.1, 144.5, 146.7.

MS (FAB): m/z 494 ($M^+ + H$, 100), 237 (60), 210 (35), 179 (75).

Preparation of aminothiol **27** *from* **19** *(intermediate* **26***)*

• *(4S,5R)-5-[(Chloro-diphenyl)methyl]-N,N,2,2-tetramethyl-α,α-diphenyl-1,3-dioxolane-4-methanamine* **26**

Aminoalcohol **19** (4.24 g, 8.60 mmol) was dissolved in CH_2Cl_2 (50 mL) and $SOCl_2$ (0.765 mL, 10.5 mmol) was added. The mixture was stirred at reflux for 30 min. It was then poured into saturated $NaHCO_3$ solution and stirred for 5 min. The organic layer was separated and the aqueous solution was extracted twice with CH_2Cl_2 (100 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give **26** (3.55 g, 81%). The crude product was used without further purification.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.75 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.64 (s, 6H, $N(CH_3)_2$), 4.91 (d, J = 7.1 Hz, 1H, CH), 5.25 (d, J = 7.1 Hz, 1H, CH), 7.05–7.80 (m, 20H, arom H).

• *(4R,5S)-5-[(Dimethylamino-diphenyl)methyl]-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanethiol* **27**

Thiourea (25.0 g, 329 mmol) was added to a solution of chloride **26** (2.10 g, 4.10 mmol) in DMF (80 mL) and the mixture was stirred at room temperature for 3 d. 1N NaOH (80 mL) was added and the mixture was stirred for 1 h. H_2O (150 mL) was added and the aqueous layer was extracted twice with Et_2O (150 mL). The combined organic layers were washed with H_2O (300 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (pentane/Et_2O (5:1)) to give **27** as a colorless solid (1.43 g, 68%).

Mp 162–163 °C (hexane).

$[\alpha]_{\mathrm{D}}^{\mathrm{RT}} = -54.1$ (c = 0.98, ethyl acetate).

IR ($CDCl_3$): 3 060, 2 990, 2 936, 2 845, 2 252, 1 598, 1 495, 1 380, 1 371, 1 334, 1 168, 1 067, 1 034, 1 006, 909, 854, 650 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.65 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.75 (s, 3H, NCH_3), 2.25 (s, 3H, NCH_3), 4.53 (d, J = 7.9 Hz, 1H, CH), 5.04 (d, J = 7.9 Hz, 1H, CH), 6.84–7.65 (m, 17H, arom H), 8.08–8.40 (m, 3H, arom H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.3, 27.2, 40.4, 40.7, 73.8, 76.5, 83.8, 106.6, 126.0, 126.3, 126.7, 126.9, 127.3, 127.6, 127.8, 129.4, 130.6, 132.0, 132.7, 135.1, 136.7, 138.0, 142.6, 148.5.

MS: m/z 510 ($M^+ + H$, 1), 447 (1), 432 (1), 431 (1), 269 (2), 267 (1), 266 (5), 265 (24), 212 (4), 211 (43), 210 (100), 207 (13), 198 (11), 179 (28), 178 (17), 167 (15), 165 (16).

Anal calc for $C_{33}H_{35}NO_2S$: C, 77.76; H, 6.92; N, 2.75; S, 6.28. Found: C, 77.59; H, 7.06; N, 2.79; S, 6.16.

Preparation of dithiol **10**, *disulfide* **28**, *of oxidation products* **29** *and* **30** *and of complex* **44**

• *(3aR,7aR)-2,2-Dimethyl-4,4,7,7-tetraphenyl-tetrahydro-1,2-dithiino[4,5-d][1,3]dioxole* **28**

Thiourea (80 g, 1.05 mol) was added to a solution of dichloride **2** (8.00 g, 15.9 mmol) in DMF (400 mL) and the mixture was stirred for 5 d at room temperature. 3 N NaOH (400 mL) was added and the mixture was stirred for 3 h. The aqueous layer was extracted three times with Et_2O (400 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to yield a mixture of **28** and **10** (40:60). This residue was dissolved in Et_2O (100 mL), I_2 (2.42 g, 9.54 mmol) was added and the mixture was stirred for 15 min. 10% Na_2SO_3 (50 mL) was added and the aqueous layer was extracted twice with Et_2O (100 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was triturated for 10 min in MeOH (20 mL) to yield **28** as a colorless solid (4.81 g, 61%).

Mp 235–238 °C (Et_2O).

$[\alpha]_{\mathrm{D}}^{\mathrm{RT}} = -109.5$ (c = 0.99, ethyl acetate).

IR (KBr): 3 040, 2 985, 2 564, 1 590, 1 492, 1 441, 1 371, 1 231, 1 159, 1 051, 877, 749, 692 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.30 (s, 6H, 2CH_3), 4.70 (s, 2H, 2CH), 7.15–7.40 (m, 16H, arom H), 7.90–8.00 (m, 4H, arom H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 26.9, 65.6, 78.1, 106.3, 127.3, 127.5, 128.0, 128.5, 131.4, 138.1, 142.4.

MS: m/z 496 (M^+, < 1), 344 (1), 237 (22), 179 (100), 178 (71), 167 (41), 165 (56), 152 (20), 77 (21), 28 (42).

Anal calc for $C_{31}H_{28}O_2S_2$: C, 74.96; H, 5.68; O, 6.44; S, 12.91. Found: C, 75.03; H, 5.80; O, 6.68; S, 12.79.

• *(4R,5R)-2,2-Dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanethiol* **10**

The analytic data of **10** were determined from a mixture of **28** and **10** (40:60).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.98 (s, 6H, 2CH_3), 5.30 (s, 2H, 2CH), 7.10–7.60 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 50 MHz): δ 28.1, 60.1, 83.9, 110.5, 126.9, 127.0, 127.9, 129.2, 130.4, 145.0, 146.8.

• *(3aR,5R,7aR)-2,2-Dimethyl-4,4,7,7-tetraphenyl-tetrahydro-1,2-dithiino[4,5-d][1,3]dioxole 5-oxide* **29**

A freshly prepared solution of trifluoroacetic anhydride (0.20 mL, 1.4 mmol) and 30% H_2O_2 (47 μL, 0.4 mmol) in CH_2Cl_2 (20 mL) was added over 1 h to a solution of disulfide **28** (200 mg, 0.4 mmol) in CH_2Cl_2 (30 mL) at −50 °C. The reaction mixture was slowly warmed up to −30 °C and stirred for 2 h. The solvent was then removed under reduced pressure at room temperature. The residue was washed with ice water (20 mL), filtered and dried at HV. Recrystallization from pentane/CH_2Cl_2 gave **29** as a colorless solid (86 mg, 42%).

Mp 148–151 °C.

IR ($CHCl_3$): 3 064, 3 008, 2 926, 1 496, 1 445, 1 383, 1 374, 1 087, 1 034, 890, 656 cm^{-1}.

^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.84 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 4.91 (d, J = 9.1 Hz, 1H, CH), 5.14 (d, J = 9.1 Hz, 1H, CH), 7.19–7.55 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 65 MHz): δ 26.0, 27.2, 72.9, 74.3, 77.1, 79.5, 108.0, 127.0, 127.5, 127.6, 127.8, 128.0, 128.3, 128.5, 128.7, 130.3, 131.4, 133.2, 137.6, 138.9, 143.5.

Anal calc for $C_{31}H_{28}O_3S_2$: C, 72.63; H, 5.50; S, 12.51. Found: C, 72.37; H, 5.38; S, 12.44.

• *(3aR,7aR)-2,2-Dimethyl-4,4,7,7-tetraphenyl-tetrahydro-1,2-dithiino[4,5-d][1,3]dioxole 5,5-dioxide* **30**

A solution of *meta*-chloroperbenzoic acid (55%, 160 mg, 0.5 mmol) in CH_2Cl_2 (20 mL) was added dropwise over 2 h to a solution of disulfide **28** (200 mg, 0.4 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture (containing *meta*-chlorobenzoic acid, **29** and traces of **28**) was poured into precooled (0 °C) 2 N NaOH (about 50 mL) and stirred vigorosly for 20 min. The organic layer was then separated, dried over $MgSO_4$ and the solvent removed under reduced pressure. The colorless residue contained still traces of *meta*-chlorobenzoic acid and a mixture of **28**, **29** and thiosulfonate **30** (20:60:20).

The analytic data of **30** were determined from this mixture.

^{1}H NMR ($CDCl_3$, 270 MHz): δ 0.94 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 4.18 (d, J = 7.1 Hz, 1H, CH), 5.07 (d, J = 7.1 Hz, 1H, CH), 7.19–7.68 (m, 20H, arom H).

^{13}C NMR ($CDCl_3$, 63 MHz, signals of the aromatic carbon atoms are omitted): δ 26.7, 67.5, 75.1, 77.8, 89.1, 110.4.

• *(2R,3R)-2,3-Isopropylidenedioxy-1,1,4,4-tetraphenylbutane-1-(R)-sulfenato-4-thiolato-platin-[(4′R,5′R)-DIOP]-complex* ***44***

Thiosulfinate **29** (100 mg, 0.2 mmol) was added to a solution of (DIOP)Pt(η^2-C_2H_4) [69] (140 mg, 0.2 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 16 h and then the toluene partially (about 7 mL) removed under reduced pressure. After addition of hexane (20 mL), the residue formed was centrifuged and washed twice with hexane/Et_2O (5 mL, 1:1). Recrystallization from hexane/CH_2Cl_2 at −20 °C gave **44** as yellow crystals (89 mg, 37%).

Mp 141–143 °C.

IR (KBr): 3 054, 3 010, 2 926, 1 631, 1 495, 1 484, 1 436, 1 382, 1 241, 1 216, 1 162, 1 128, 1 100, 1 055, 1 001, 747, 699 cm^{-1}.

^{1}H NMR (CD_2Cl_2, 270 MHz): δ 0.84 (s, 3H, CH_3), 0.90 (s, 6H, $2CH_3$), 1.31 (s, 3H, CH_3), 1.95–2.01 (m, 1H, P-CH*H*), 2.45–2.55 (m, 1H, P-CH*H*), 2.87–2.91 (m, 1H, P-CH*H*), 3.41–3.46 (m, 1H, P-CH*H*), 3.98–4.03 (m, 1H, P-CH_2-C*H*), 4.34–4.41 (m, 1H, P-CH_2-C*H*), 4.91 (d, J = 9.1 Hz, 1H, CH), 5.14 (d, J = 9.1 Hz, 1H, CH), 7.04–7.78 (m, 40H, arom H).

^{13}C NMR (CD_2Cl_2, 100 MHz): δ 25.9, 26.6, 26.8, 27.1, 74.4, 75.1, 77.8, 77.9, 81.1, 81.8, 109.2, 110.1, 125.7, 126.1, 126.3, 126.5, 126.6, 127.1, 127.5, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4, 128.5, 128.6, 128.8, 129.0, 129.1, 129.2, 129.5, 130.0, 130.1, 130.2, 130.4, 130.7, 131.4, 131.5, 131.8, 131.9, 132.2, 132.3, 132.4, 132.9, 133.0, 133.1, 133.2, 134.4, 134.5, 145.2, 149.3.

^{31}P NMR (CD_2Cl_2, external H_3PO_4 (85%), 109 MHz): δ −2.59, −0.56; $^1J(^{195}Pt^{31}P)$ 2119/3405 Hz; $^2J(^{31}P^{31}P)$ 29.6 Hz.

Anal calc for $C_{62}H_{60}O_5P_2PtS_2$: C, 61.73; H, 5.01; S, 5.31. Found: C, 60.22; H, 4.67; S, 4.88.

Preparation and identification of thiourea derivative ***32*** *and byproducts* ***42*** *and* ***43***

• *(3aR,8aS)-2,2-Dimethyl-4,4,8,8-tetraphenyl-3a,4,8,8a-tetrahydro-1,3-dioxolo[4,5-f][2,4]thiazepin-6-amine* ***32***

Thiourea (10.0 g, 132 mmol) was added to a solution of dichloride **2** (1.00 g, 1.99 mmol) in DMF (10 mL) at 75 °C and the mixture was stirred for 3 h at the same temperature. 1N NaOH (10 mL) was added and the solution was stirred for further 5 min at room temperature. H_2O (50 mL) was added and the aqueous layer was then extracted twice with Et_2O (125 mL). The combined organic layers were washed with H_2O (100 mL), dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel (pentane/Et_2O (3:1)) to give **42** (114 mg, 16%) and **32**, (232 mg, 23%) both as colorless solids.

Mp 233–234 °C (Et_2O).

R_f: 0.65 (Et_2O).

$[\alpha]_D^{RT} = -27.4$ (c = 0.30, ethyl acetate).

IR (KBr): 3 461, 3 360, 3 056, 2 984, 1 636, 1 564, 1 492, 1 442, 1 367, 1 232, 1 167, 1 072, 1 020, 988, 752 cm^{-1}.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 4.47 (d, J = 8.7, 1H, CH), 5.08 (d, J = 8.7 Hz, 1H, CH), 7.07–7.42 (m, 16H, arom H), 7.50–7.79 (m, 4H, arom H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ 26.2, 27.4, 76.1, 79.8, 80.9, 108.0, 127.3, 127.5, 127.6, 127.7, 127.9, 128.2, 128.4, 129.0, 129.3, 131.3, 140.7, 141.2, 142.3.

MS: m/z 506 (M^+, 31), 406 (17), 241 (43), 240 (72), 208 (59), 207 (100), 182 (64), 180 (50), 179 (85), 178 (74), 167 (28), 165 (62), 137 (69), 104 (46), 77 (30).

Anal calc for $C_{32}H_{30}O_2N_2S$: C, 75.86; H, 5.97; N, 5.53; S, 6.33. Found: C, 76.04; H, 5.72; N, 5.53; S, 6.23.

• *(3aS)-2,2-Dimethyl-4,4,9-triphenyl-3a,4-dihydronaphtho[2,3-d][1,3]dioxole* ***42*** *and 4,5-dibenzhydrylidene-2,2-dimethyl-1,3-dioxolane* ***43***

A solution of **2** (1 g, 1.99 mmol) in DMF (25 mL) was stirred at 80 °C for 5 d. Et_2O (100 mL) were added and the solution was washed twice with H_2O (200 mL). The aqueous layer was extracted with Et_2O (100 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (pentane/ether (50:1)) to give **42** (280 mg, 33%) and the byproduct **43** as a yellow solid (50 mg, 6%).

■ *42*

Mp 195.8–196.4 °C.

R_f: 0.45 (Et_2O/pentane (1:50)).

$[\alpha]_D^{RT} = -205.5$ (c = 1.0, $CHCl_3$).

IR (KBr): 3 061, 3 008, 2 940, 2 860, 1 686, 1 595, 1 495, 1 468, 1 445, 1 386, 1 348, 1 308, 1 266, 1 147, 1 102, 1 076, 997, 862, 630 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.37 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 5.98 (s, 2H, CH), 6.64–6.67 (m, 1H, arom H), 6.97–7.01 (m, 1H, arom H), 7.12–7.18 (m, 7H, arom H), 7.20–7.26 (m, 2H, arom H), 7.28–7.40 (m, 8H, arom H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 25.6, 25.8, 57.7, 77.2, 80.0, 105.3, 114.9, 125.1, 125.3, 126.6, 126.7, 126.9, 127.4, 128.1, 128.2, 129.1, 129.6, 131.7, 135.4, 138.0, 138.4, 140.3, 143.5, 151.1.

MS: m/z 430 (M^+, 26), 346 (5), 345 (39), 344 (100), 343 (8), 268 (5), 267 (25), 266 (9), 265 (24), 263 (5), 252 (9), 165 (6), 163 (5), 133 (5).

Anal calc for $C_{31}H_{26}O_2$: C, 86.48; H, 6.09. Found: C, 86.40; H, 6.36.

■ *43*

Probably, this compound has an axially chiral structure. The samples isolated here show, however, no optical activity.

Mp 145.8–147.2 °C.

R_f: 0.55 (Et_2O/pentane (1:50)).

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.52 (s, 6H, $2CH_3$), 6.68–6.70 (m, 4H, arom H), 6.84–6.94 (m, 6H, arom H), 7.13–7.25 (m, 10 H, arom H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 26.2, 110.8, 120.4, 126.0, 126.5, 127.4, 127.8, 130.2, 131.0, 140.3, 140.4, 143.8.

MS: m/z 430 (M^+, 31), 345 (32), 344 (43), 343 (58), 267 (32), 266 (43), 265 (66), 252 (39), 194 (73), 178 (41), 167 (51), 166 (50), 165 (100), 154 (43), 136 (35), 105 (55).

Preparation of salicylic aldehyde imines **34** *and* **35**

- *(4S,5R)-5-{[(2-Hydroxybenzylidene)amino-diphenyl]methyl}-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **34**

A solution of the aminoalcohol **17** (5.00 g, 10.8 mmol), salicyl aldehyde (2.26 mL, 21.6 mmol) and *p*-toluenesulfonic acid (0.10 g) in toluene (150 mL) was refluxed for 20 h, with azeotropic removal of water using a Dean–Stark trap. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was dissolved in Et_2O (150 mL) and the organic layer was washed twice with water (150 mL), once with saturated NaCl (150 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was recrystallized from MeOH (150 mL) to give **34** (5.50 g, 89%).

Mp 127–130 °C.

$[\alpha]_D^{RT} = -9.0$ ($c = 0.50$, $CHCl_3$).

IR ($CHCl_3$): 3 558, 3 061, 3 007, 1 625, 1 581, 1 494, 1 446, 1 381, 1 280, 1 165, 1 067, 1 045, 1 017, 970, 874 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ 0.83 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 5.08 (d, $J = 6.8$ Hz, 1H, CH), 5.15 (d, $J = 6.8$ Hz, 1H, CH), 6.82–6.86 (m, 1H, arom H), 7.05–7.36 (m, 23H, arom H), 7.94 (s, 1H, N=CH).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.2, 28.2, 76.1, 77.9, 82.0, 82.1, 110.8, 117.1, 118.8, 119.3, 127.1, 127.2, 127.3, 127.5, 127.9, 128.5, 128.8, 130.7, 132.3, 132.8, 142.7, 143.5, 144.1, 144.7, 160.9.

MS: m/z 1 140 ($2M^+$, 13), 570 (M^+, 100), 287 (45), 237 (32), 179 (50), 105 (57).

Anal calc for $C_{38}H_{35}O_4N$: C, 80.12; H, 6.19; N, 2.46. Found: C, 80.18; H, 5.92; N, 2.36.

- *(4S,5R)-5-{[(3,5-di-tert-butyl-2-hydroxybenzylidene)amino-diphenyl]methyl}-2,2-dimethyl-α,α-diphenyl-1,3-dioxolane-4-methanol* **35**

A solution of the aminoalcohol **17** (3.00 g, 6.48 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (1.82 g, 7.78 mmol) and *p*-toluenesulfonic acid (0.06 g) in toluene (120 mL) was refluxed for 48 h, with azeotropic removal of water using a Dean–Stark trap. The mixture was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was dissolved in Et_2O (150 mL) and the organic layer was washed twice with water (150 mL), once with saturated NaCl (150 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was recrystallized from MeOH (150 mL) to give **35** (2.18 g, 49%).

Mp 234–235 °C.

$[\alpha]_D^{RT} = 14.0$ ($c = 0.57$, $CHCl_3$).

IR ($CHCl_3$): 3 527, 3 061, 3 008, 2 964, 1 622, 1 494, 1 446, 1 381, 1 371, 1 272, 1 248, 1 172, 1 066, 880, 832 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ 0.83 (s, 3H, CH_3), 0.86 (s, 3H, CH_3), 1.26 (s, 9H, $C(CH_3)_3$), 1.52 (s, 9H, $C(CH_3)_3$), 5.09 (d, $J = 7.0$ Hz, 1H, CH), 5.12 (d, $J = 7.0$ Hz, 1H, CH), 6.88 (d, $J = 2.4$ Hz, 1H, arom H), 7.17–7.41 (m, 21H, arom H), 7.96 (s, 1H, N=CH).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 27.7, 27.8, 29.4, 31.5, 34.1, 35.1, 75.8, 77.8, 81.9, 82.2, 110.5, 118.4, 126.9, 127.0, 127.1, 127.3, 127.4, 127.5, 127.8, 127.9, 128.6, 128.8, 128.9, 130.7, 136.8, 140.3, 142.7, 143.5, 144.3, 146.8, 158.0, 169.5.

MS: m/z 682 (M^+, 23), 398 (100), 237 (31), 179 (77), 167 (62), 105 (91).

Anal calc for $C_{46}H_{51}O_4Ns$: C, 81.02; H, 7.54; N, 2.05. Found: C, 80.85; H, 7.49; N, 2.03.

Crystal structure analyses

- *(4R,5R)-4,5-Bis[(chloro-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane (***2***, $C_{31}H_{28}Cl_2O_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on an Picker–Stoe four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Colorless platelet, 0.2 × 0.3 × 0.3 mm, monoclinic, space group $P2_1$, $a = 8.992(12)$ Å, $b = 10.561(14)$ Å, $c = 14.23(2)$ Å, $\beta = 103.22(12)$, $V = 1316(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.270$ g cm^{-3}, $\mu = 0.273$ mm^{-1}, $F(000) = 528$. Number of reflections measured 2638 (ω scan, $3 < 2\theta < 40°$, $T = 298$ K); 2458 unique reflections, of which 2411 with $I > 2\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXTL PLUS was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.044$ ($wR = 0.050$), maximum in the last difference fourier synthesis 0.55 e Å^{-3}, number of variables 315.

- *(4S,5S)-4,5-Bis[(azido-diphenyl)methyl]-2,2-dimethyl-1,3-dioxolane (***3***, $C_{31}H_{28}N_6O_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on a Stoe Stadi four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Monoclinic, space group $P2_1$, $a = 9.924(6)$ Å, $b = 10.928(8)$ Å, $c = 13.151(7)$ Å, $\beta = 105.8(1)$, $V = 1372.35$ Å^3, $Z = 2$, $\rho_{calc} = 1.250$ g cm^{-3}, $F(000) = 544$. Number of reflections measured 5133 (2560 unique reflections, 2θ–ω scan, $3 < 2\theta < 50°$, $T = 298$ K) of which 3376 with $I > 3\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXL-76 was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.045$ ($wR = 0.043$).

- *(4S,5S)-2,2-Dimethyl-α,α,α′,α′-tetraphenyl-1,3-dioxolane-4,5-dimethanamine (***4***, $C_{31}H_{32}N_2O_2$)*

The determination of the cell parameters and the collection of the reflection intensities were performed on a Stoe Stadi four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Orthorhombic, space group $P2_12_12_1$, $a = 15.301(2)$ Å, $b = 18.184(4)$ Å, $c = 18.555(2)$ Å, $V = 5162.6$ Å^3, $Z = 8$, $\rho_{calc} = 1.195$ g cm^{-3}, $F(000) = 1984$. Number of reflections measured 7601 (2θ–ω scan, $3 < 2\theta < 45°$, $T = 298$ K), 3712 unique reflections of which 3073 with $I > 3\sigma(I)$ were used for the structure determination (direct methods, SHELXS-86). SHELXL-76 was used for the structure refinement. The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.049$ ($wR = 0.047$).

- *(4S,5S)-N,N',2,2-Tetramethyl-α,α,α',α'-tetraphenyl-1,3-dioxolane-4,5-dimethanamine (**5**, $C_{33}H_{36}N_2O_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on an Enraf–Nonius CAD4 four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Colorless cube, 0.3 × 0.3 × 0.5 mm, triclinic, space group $P1$, $a = 8.278(5)$ Å, $b = 11.732(3)$ Å, $c = 16.041(4)$ Å, $\alpha = 93.77(29)$, $\beta = 104.96(39)$, $\gamma = 110.67(4)$, $V = 1386(10)$ Å^3, $Z = 2$, $\rho_{\mathrm{calc}} = 1.180$ g cm^{-3}, $\mu = 0.073$ mm^{-1}, $F(000) = 528$. Number of reflections measured 4272 (ω scan, $4 < 2\theta < 50°$, $T = 295$ K); 4272 unique reflections, of which 3525 with $I > 3\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXL-93 was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.036$ ($wR^2 = 0.088$), maximum in the last difference fourier synthesis 0.23 e Å^{-3}, number of variables 665.

- *(3aR,7aR)-2,2-Dimethyl-4,4,7,7-tetraphenyl-tetrahydro-1,2-dithiino[4,5-d][1,3]dioxole (**28**, $C_{31}H_{28}O_2S_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on an Enraf–Nonius CAD4 four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Colorless platelet, 0.2 × 0.4 × 0.5 mm, orthorhombic, space group $P2_12_12_1$, $a = 9.576(6)$ Å, $b = 9.644(2)$ Å, $c = 28.475(6)$ Å, $V = 2630(2)$ Å^3, $Z = 4$, $\rho_{\mathrm{calc}} = 1.255$ g cm^{-3}, $\mu = 0.229$ mm^{-1}, $F(000) = 1048$. Number of reflections measured 2359 (ω scan, $4 < 2\theta < 48°$, $T = 298$ K); 2359 unique reflections, of which 1728 with $I > 2\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXL-93 was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.031$ ($wR^2 = 0.064$), maximum in the last difference fourier synthesis 0.23 e Å^{-3}, number of variables 316.

- *(3aR,5R,7aR)-2,2-Dimethyl-4,4,7,7-tetraphenyl-tetrahydro-1,2-dithiino[4,5-d][1,3]dioxole 5-oxide (**29**, $C_{31}H_{28}O_3S_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on an Enraf–Nonius CAD4 four-circle diffractometer (graphite monochromatized CuK_α radiation, $\lambda = 1.5418$ Å). Colorless platelet, 0.15 × 0.2 × 0.3 mm, orthorhombic, space group $P2_12_12_1$, $a = 9.86(2)$ Å, $b = 9.994(3)$ Å, $c = 30.65(3)$ Å, $V = 3020(7)$ Å^3, $Z = 4$, $\rho_{\mathrm{calc}} = 1.314$ g cm^{-3}, $\mu = 3.474$ mm^{-1}, $F(000) = 1248$. Number of reflections measured 2565 (ω scan, $3 < 2\theta < 60°$, $T = 253$ K); 2565 unique reflections, of which 1919 with $I > 2\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXL-93 was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.079$ ($wR^2 = 0.213$), maximum in the last difference fourier synthesis 0.59 e Å^{-3}, number of variables 352. The high R-factor is due to a disordered CH_2Cl_2 molecule in the asymmetric unit.

- *(3aR,8aS)-2,2-Dimethyl-4,4,8,8-tetraphenyl-3a,4,8,8a-tetrahydro-1,3-dioxolo[4,5-f][2,4]thiazepin-6-amine (**32**, $C_{31}H_{29}N_2O_2S$)*

Determination of the cell parameters and collection of the reflection intensities were performed on a Picker–Stoe four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Colorless cube, 0.3 × 0.3 × 0.6 mm, monoclinic, space group $P2_1$, $a = 9.117(13)$ Å, $b = 13.945(13)$ Å, $c = 12.20(2)$ Å, $\beta = 102.94(11)$, $V = 1511(3)$ Å^3, $Z = 2$, $\rho_{\mathrm{calc}} = 1.278$ g cm^{-3}, $\mu = 0.315$ mm^{-1}, $F(000) = 606$. Number of reflections measured 2557 (ω scan, $3 < 2\theta < 40°$, $T = 298$ K); 1485 unique reflections, of which 1279 with $I > 2\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXTL PLUS was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.131$ ($wR = 0.130$), maximum in the last difference fourier synthesis 0.79 e Å^{-3}, number of variables 378. The high R-factor is due to a disordered CH_2Cl_2 molecule in the asymmetric unit.

- *(3aS)-2,2-Dimethyl-4,4,9-triphenyl-3a,4-dihydronaphtho[2,3-d][1,3]dioxole (**42**, $C_{31}H_{26}O_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on an Picker–Stoe four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Colorless prism, 0.3 × 0.4 × 0.5 mm, hexagonal, space group $P6_5$, $a = 22.09(2)$ Å, $c = 9.539(6)$ Å, $V = 4031(6)$ Å^3, $Z = 6$, $\rho_{\mathrm{calc}} = 1.183$ g cm^{-3}, $\mu = 0.072$ mm^{-1}, $F(000) = 1512$. Number of reflections measured 4251 (ω scan, $3 < 2\theta < 40°$, $T = 298$ K); 1371 unique reflections, of which 1206 with $I > 2\sigma(I)$ were used for the determination (direct methods, SHELXS-86). SHELXTL PLUS was used for structure refinement (full-matrix least-squares). The temperature factors of the non-H-atoms were refined anisotropically, the H-atoms were added to the molecule with constant isotropic temperature factors on idealized positions and refined according to the riding model (afix 3). The refinement converged at $R = 0.045$ ($wR = 0.062$), maximum in the last difference fourier synthesis 0.13 e Å^{-3}, number of variables 291. Four rest electron density peaks which may be due to a disordered solvent molecule were included in the refinement.

- *(2R,3R)-2,3-Isopropylidenedioxy-1,1,4,4-tetraphenylbutane-1-(R)-sulfenato-4-thiolato-platin-[(4'R,5'R)-DIOP]-complex (**44**, $C_{62}H_{60}O_5P_2PtS_2$)*

Determination of the cell parameters and collection of the reflection intensities were performed on a Siemens R3m/V four-circle diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.7107$ Å). Yellow prism, 0.08 × 0.3 × 0.07 mm, orthorhombic, space group $P2_12_12_1$, $a = 12.851(3)$ Å, $b = 18.818(4)$ Å, $c = 29.485(6)$ Å, $V = 7130(8)$ Å^3, $Z = 4$, $\rho_{\mathrm{calc}} = 1.127$ g cm^{-3}, $\mu = 2.130$ mm^{-1}, $F(000) = 2448$. The crystal rapidly decomposed during data collection which was stopped after the intensity of a check reflection had dropped to 40% of its original value. Intensity data were scaled on a check reflection and corrected for PL. Number of reflections measured 6879 (ω scan, $5 < 2\theta < 50°$, $T = 298$ K); 6879 unique reflections, of which 2851 with $|F_o| > 3\sigma|F_o|$ were used for structure determination by direct methods and full-matrix least-squares refinement (SHELXTL PLUS). Due to the small number of reflections all phenyl rings were refined as rigid groups. Temperature factors of Pt, S and P were refined anisotropically, and all other non-H-atoms isotropically. H-atoms were placed in idealized positions with common isotropic temperature factors for groups of atoms. The refinement converged at $R_g = 0.132$, maximum in the last difference fourier synthesis 2.42 e $Å^{-3}$. The absolute configuration of the model was chosen according to the known stereochemistry of the ligand. The unusually high R-factor is due to wrong reflection intensities induced by the decomposition of the crystal that could not be eliminated by scaling to a check reflection.

Acknowledgments

The authors wish to thank the Fonds der Chemischen Industrie for a Kekulé Stipendium, granted to Georg Jaeschke, and the Fulbright Foundation, USA, for a Fulbright Grant awarded to Anthony B Pinkerton. We gratefully acknowledge the help of Dr Jennifer L Matthews during the preparation of the manuscript. We thank Joachim Glaus and Fortunat Luck for assistance with some experiments, Dr J Linda v d Bussche-Hünnefeld for preparing compound **14** and Judith Maag for determining X-ray crystal structures during the crystallographic laboratory course at ETH. The work done in the Laboratorium für Organische Chemie at ETH was supported as part of the CHiral program of the Schweizerischer Nationalfonds zur Förderung der Wissenschaften and by the Sandoz Pharma Division (Basel).

Supplementary material available

Supplementary crystallographic material has been deposited with the British Library, Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK, as supplementary publication N° = SUP 90455 and is available on request from the Document Supply Centre.

References

1 Seebach D, Weidmann B, Widler L, In: *Modern Synthetic Methods*, (Scheffold R, ed), Sauerländer, Aarau, 1983, Vol 3, p 217
2 Seebach D, Beck AK, Schiess M, Widler L, Wonnacott A, *Pure Appl Chem* (1983) 55, 1807
3 Dahinden R, Beck AK, Seebach D, In: *Encyclopedia of Reagents for Organic Synthesis*, (Paquette LA, ed), Wiley, Chichester, 1995, p 2167
4 Pearson RG, *J Chem Educ* (1968) 45, 581
5 Seebach D, Plattner DA, Beck AK, Wang YM, Hunziker D, *Helv Chim Acta* (1992) 75, 2171
6 Seebach D, Beck AK, Schmidt B, Wang YM, *Tetrahedron* (1994) 50, 4363
7 Ito YN, Ariza X, Beck AK, Bohác A, Ganter C, Gawley RE, Kühnle FNM, Tuleja J, Wang YM, Seebach D, *Helv Chim Acta* (1994) 77, 2071
8 Weber B, Seebach D, *Tetrahedron* (1994) 50, 7473
9 Schäfer H, Seebach D, *Tetrahedron* (1995) 51, 2305
10 Minamikawa H, Hayakawa S, Yamada T, Iwasawa N, Narasaka K, *Bull Chem Soc Jpn* (1988) 61, 4379
11 Weber B, Seebach D, *Tetrahedron* (1994) 50, 6117
12 Narasaka K, Iwasawa N, Inoue M, Yamada T, Nakashima M, Sugimori J, *J Am Chem Soc* (1989) 111, 5340
13 Narasaka K, *Synthesis* (1991) 1
14 Seebach D, Dahinden R, Marti RE, Beck AK, Plattner DA, Kühnle FNM, *J Org Chem* (1995) 60, 1788
15 Hayashi Y, Narasaka K, *Chem Lett* (1990) 1295
16 Engler TA, Letavic MA, Reddy JP, *J Am Chem Soc* (1991) 113, 5068
17 Gothelf KV, Jørgensen KA, *J Org Chem* (1994) 59, 5687
18 Gothelf KV, Thomsen I, Jørgensen KA, *J Am Chem Soc* (1996) 118, 59
19 Narasaka K, Hayashi Y, Shimada S, *Chem Lett* (1988) 1609
20 Duthaler RO, Hafner A, *Chem Rev* (1992) 92, 807
21 Seebach D, Beck AK, Dahinden R, Hoffmann M, Kühnle FNM, *Croat Chem Acta* (1996) 69, 459
22 Inoue T, Kitagawa O, Ochiai O, Shiro M, Taguchi T, *Tetrahedron Lett* (1995) 36, 9333
23 Narasaka K, Kanai F, Okudo M, Miyoshi N, *Chem Lett* (1989) 1187
24 Seebach D, Jaeschke G, Wang YM, *Angew Chem Int Ed Eng* (1995) 34, 2395
25 Ramón DJ, Guillena G, Seebach D, *Helv Chim Acta* (1996) 79, 875
26 Beck AK, Bastani B, Plattner DA, Petter W, Seebach D, Braunschweiger H, Gysi P, La Vecchia L, *Chimia* (1991) 45, 238
27 Duthaler RO, Hafner A, Alsters PL, Bold G, Rihs G, Rothe-Streit P, Wyss B, *Inorg Chim Acta* (1994) 222, 95
28 Gothelf KV, Hazell RG, Jørgenson KA, *J Am Chem Soc* (1995) 117, 4435
29 Braun M, *Angew Chem Int Ed Eng* (1996) 35, 519
30 Knowles WS, *Acc Chem Res* (1983) 16, 106
31 Seebach D, Devaquet E, Ernst A, Hayakawa M, Kühnle FNM, Schweizer WB, Weber B, *Helv Chim Acta* (1995) 78, 1636
32 Seebach D, *Angew Chem Int Ed Eng* (1990) 29, 1320
33 Seebach D, Hayakawa M, Sakaki J, Schweizer WB, *Tetrahedron* (1993) 49, 1711
34 Juaristi E, Beck AK, Hansen J, Matt T, Mukhopadhyay T, Simson M, Seebach D, *Synthesis* (1993) 1271
35 Sakaki J, Schweizer WB, Seebach D, *Helv Chim Acta* (1993) 76, 2654
36 Dörpinghaus N, Ph D, Rheinische Friedrich-Wilhelm-Universität Bonn, 1989
37 von dem Bussche-Hünnefeld JL, Ph D, ETH Zürich, 1992
38 Lucchi OD, Maglioli P, Delogu G, Valle G, *Synlett* (1991) 841
39 Helmchen G, Sprinz J, *Tetrahedron Lett* (1993) 34, 1769
40 Allen JV, Dawson GJ, Frost CG, Williams JMJ, Coote SJ, *Tetrahedron* (1994) 50, 799
41 Rieck H, Helmchen G, *Angew Chem Int Ed Eng* (1995) 35, 2687
42 Sprinz J, Kiefer M, Helmchen G, Reggelin M, Huttner G, Walter O, Zsolnai L, *Tetrahedron Lett* (1994) 35, 1523
43 Hayashi T, Iwamura H, Uozumi Y, Matsumoto Y, Ozawa F, *Synthesis* (1994) 526
44 van Klaveren M, Lambert F, Eijkelkamp DJFM, Grove DM, van Koten G, *Tetrahedron Lett* (1994) 35, 6135
45 Nitta H, Yu D, Kudo M, Mori A, Inoue S, *J Am Chem Soc* (1992) 114, 7969
46 Hayashi M, Miyamoto Y, Inoue T, Oguni N, *J Org Chem* (1993) 58, 1515
47 Carreira EM, Singer RA, Lee W, *J Am Chem Soc* (1994) 116, 8837

48 Carreira EM, Lee W, Singer RA, *J Am Chem Soc* (1995) 117, 3649

49 Rijnberg E, Jastrzebski JTBH, Janssen MD, Boersma J, van Koten G, *Tetrahedron Lett* (1994) 35, 6521

50 Spescha M, *Helv Chim Acta* (1993) 76, 1832

51 Kang J, Lee JW, Kim JI, Pyun C, *Tetrahedron Lett* (1995) 36, 4265

52 Zhou Q-L, Pfaltz A, *Tetrahedron* (1994) 50, 4467

53 Albinati A, Pregosin PS, Wick K, *Organometallics* (1996) 15, 2419

54 Seebach D, Rheiner PB, Beck AK, Kühnle FNM, Jaun B, *Pol J Chem* (1994) 68, 2397

55 Burns A, Whitesides GM, *J Am Chem Soc* (1990) 112, 6296

56 Takata T, Endo T, In: *The Chemistry of Sulfinic Acids, Esters, and their Derivatives*, (Patai S, ed), Wiley, Chichester, 1990, p 550

57 Koch P, Ciuffarin E, Fava A, *J Am Chem Soc* (1970) 92, 5971

58 Block E, O'Connor J, *J Am Chem Soc* (1974) 96, 3921

59 Steudel R, *Phosphorus and Sulfur* (1985) 23, 33

60 Steudel R, Latte J, *Chem Ber* (1977) 110, 423

61 Deslongchamps P, In: *Stereoelectronic Effects in Organic Chemistry*, (Balwin JE, ed), Pergamon Press, Oxford, 1983

62 Juaristi E, Guzmán J, Kane VV, Glass RS, *Tetrahedron* (1984) 40, 1477

63 Juaristi E, Cruz-Sánchez JS, *J Org Chem* (1988) 53, 3334

64 Urove GA, Welker ME, Eaton BE, *J Organomet Chem* (1990) 384, 105

65 Weigand W, Bosl G, Robl C, Amrein W, *Chem Ber* (1992) 125, 1047

66 Weigand W, Bosl G, von Dielingen B, Gollnick K, *Z Naturforsch, Teil B* (1994) 49, 513

67 Bosl G, Wünsch R, Robl C, Weigand W, In: *Stereoselective Reactions of Metal-Activated Molecules*, (Werner H, Sundermayer J, eds), Vieweg-Verlag, Braunschweig/Wiesbaden, 1995

68 Weigand W, Wünsch R, *Chem Ber* (1996) 129, 1409

69 Brown JM, Cook SJ, Kimber SJ, *J Organomet Chem* (1984) 269, C 58

70 Bernstein J, Etter MC, Leiserowitz L, In: *Structure Correlation*, (Bürgi H-B, Dunitz JD, eds), VCH, Weinheim, 1994, Vol 2

71 Saenger W, In: *Principles of Nucleic Acid Structure*, (Cantor CR, ed), Springer-Verlag, New York, 1988, p 116

72 Irrure J, Alonso-Alija C, Piniella JF, Alvarez-Larena A, *Tetrahedron: Asymmetry* (1992) 3, 1591

73 Tyblewski M, Ha T-K, Bauder A, *J Mol Spectrosc* (1986) 115, 353