# Stereoisomeric Dichloro[1-(hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II) Complexes, Part I: Synthesis

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Various *erythro*- and *threo*-configurated dichloro[1-(hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II) complexes were synthesized with the hydroxy group located in either the 2-, 3-, or 4-position of the phenyl ring (**38**–**40**). The diastereoisomeric 1-(3-hydroxyphenyl)-2-phenyl-1,2-ethanediamines (**31**, **32**) and *threo*-1-(2-hydroxyphenyl)-2-phenyl-1,2-ethanediamine (**30**) were obtained by reduction of the 1,2-diazidoethanes and subsequent ether cleavage. The configuration of the *threo*-1,2-diazido-1-(2-methoxyphenyl)-2-phenylethane (**5**) was elucidated by X-ray analysis. The reduction of the *erythro*-1,2-diaryl-1,2-diazidoethanes, substituted with a methoxy group in *ortho or para* position, results in elimination reactions with formation of side products. The desired 1,2-diaryl-1,2-ethanediamines were finally synthesized via either an aziridine derivative **21** or by reduction of the respective dioximes **27**, **28**. The diamine ligands were converted into the corresponding dichloroplatinum(II) complexes **38**–**40**.

The antitumor activity[1] of cisplatin [*cis*-diamminedichloroplatinum(II)] is well established for the treatment of a variety of tumors such as cancers of the ovaries and testes as well as solid tumors of the head and neck[2]. In spite of the high response rate of 63% of the ovarian carcinoma the overall survival times remain short[3]. In many cases a relapse occurs within two years. The regrowing tumor usually responds poorly to another therapy with cisplatin[4]. A variety of mechanisms is discussed to explain the incidence of resistance. A P-glycoprotein which accelerates the drug efflux from the cell is responsible for the multidrug resistance against many lipophilic anticancer compounds[5]. Drugs forming adducts with the DNA like alkylating agents or platinum complexes are not affected by this multidrug resistance[6]. The current literature contains discussions of several characteristic properties of tumor cells resistant to cisplatin. For example, increased intracellular levels of peptides and proteins containing thiol or thioether groups can deactivate platinum compounds. Furthermore, an increased DNA-repair activity or a lowered uptake of the drug into the cell may be responsible for the resistance (for references see Canon et al.[7]). Much effort has been made in developing platinum compounds with a specific action in cisplatin-resistant tumor models. The results indicate that a chelating diamine ligand is essential for the antitumor action [e.g. 1,2-diaminocyclohexane, 1,1-bis(aminomethyl)cyclohexane][8]. In earlier publications we described the synthesis and testing of a series of (1,2-diaryl-1,2-ethanediamine)platinum(II) complexes in various cisplatin-resistant tumor models[9–11]. (±)-Dichloro(1,2-diphenyl-1,2-ethanediamine)platinum(II) as well as compounds which were hydroxy-substituted in both phenyl rings showed antitumor action in these models. (±)-[1,2-Bis(2-hydroxyphenyl)-1,2-ethanediamine]dichloroplatinum(II) produced marked inhibitory effects on the cisplatin-resistant Ehrlich ascites tumor (70% of the tumor-bearing mice were cured) as well as on the NIH:OVCAR 3 ovarian cancer cell line[11] and is a promising candidate for the therapy of the ovarian cancer. In order to further investigate the structure-activity relationships of this class of platinum(II) complexes the unsymmetrically substituted compounds, where only one benzene ring is subsituted with a hydroxy group, were of interest. The synthesis of these compounds is described in this publication.

## Results and Discussion

### Synthesis of the 1,2-Diaryl-1,2-ethanediamines

The synthesis of 1,2-diaryl-1,2-ethanediamines with two differently substituted phenyl rings should be achieved following the general synthetic route: After the addition of two azido groups to the 1,2-diarylethene the resulting 1,2-diaryl-1,2-diazidoethanes are reduced to the respective diamines.

The 1,2-diaryl-1,2-diazidoethanes **4**–**8** (Scheme 1) are obtained by modifying the method of Fowler et al.[12] for the addition of $IN_3$ to double bonds. First in a stereospecific *anti* addition of $IN_3$ an azidoiodoethane species is formed as intermediate. An excess of $IN_3$ effects a nucleophilic displacement of $I^-$ versus $N_3^-$. The released iodide comproportionates with $IN_3$ to form $I_2$ and $N_3^-$. Hence a retro reaction is not possible, and the 1,2-diaryl-1,2-diazidoethanes are obtained in good yields. The diastereomeric 1,2-diazido-1-(2-methoxyphenyl)-2-phenylethanes **4** and **5** are separated

by chromatography. An X-ray analysis of the crystalline isomer **5** revealed a *threo* configuration (Figure 1, Table 1).

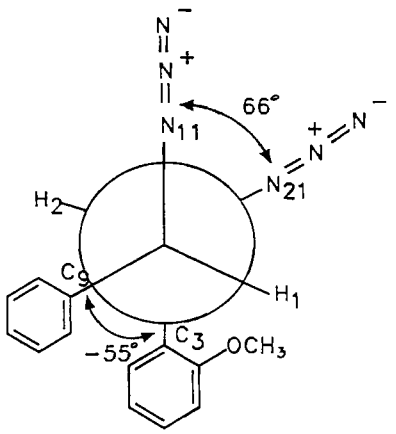



Figure 1. Newman projection of **5** with dihedral angles obtained by an X-ray analysis

Table 1. Dihedral angles of **5** with standard deviations in parentheses

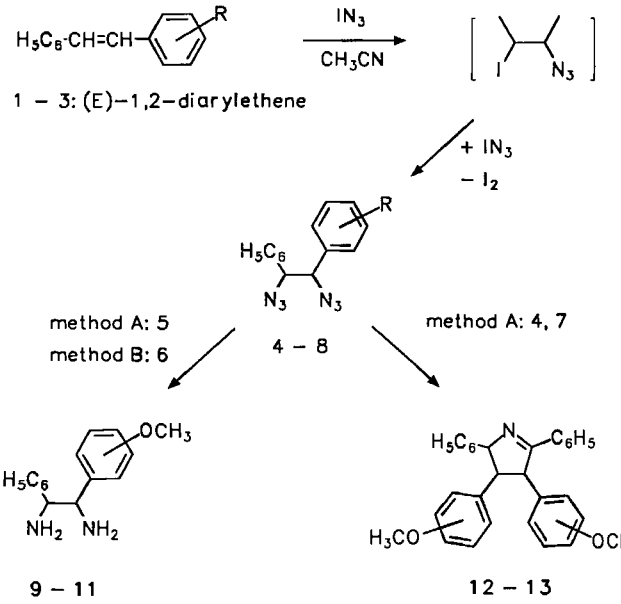
| Atom 1 | Atom 2 | Atom 3 | Atom 4 | Dihedral angle |
|---|---|---|---|---|
| N(11) | C(1) | C(2) | N(21) | 66.4(6) |
| N(11) | C(1) | C(2) | C(3) | −177.4(5) |
| N(11) | C(1) | C(2) | H(2) | −53(3) |
| C(9) | C(1) | C(2) | N(21) | −171.1(5) |
| C(9) | C(1) | C(2) | C(3) | −54.9(7) |
| C(9) | C(1) | C(2) | H(2) | 70(3) |
| H(1) | C(1) | C(2) | N(21) | −51(3) |
| H(1) | C(1) | C(2) | C(3) | 65(3) |
| H(1) | C(1) | C(2) | H(2) | −170(4) |

The $^1$H-NMR spectra of **4** and **5** reveal striking differences between the isomers. The coupling constant of the benzylic protons of the *erythro* isomer shows a higher value (10 Hz) than that of the *threo* isomer (7 Hz). Interestingly the reaction of $IN_3$ with the 4-methoxy-substituted 1,2-diarylethene **3** provided only a single isomer **7**. The high coupling constant of the benzylic protons (9 Hz) and the same reactivity compared with **4** (see the dimerization reaction below) indicate an *erythro* configuration of the 1,2-diazidoethane **7**. The benzylic protons of the *threo/erythro* mixture of 1,2-diazido-1-(3-methoxyphenyl)-2-phenylethane (**6**) appear as singlets in the $^1$H-NMR spectrum. A configurative assignment was not possible.

The ensuing reduction of **6** with $LiAlH_4$ (Scheme 1, method B) gives a mixture of *threo*- and *erythro*-1-(3-methoxyphenyl)-2-phenyl-1,2-ethanediamine (**10**, **11**). The diastereoisomers were separated by fractional crystallization. This drastic reduction method was unsuccessful for the 1,2-diaryl-1,2-diazidoethanes substituted in *ortho* and *para* position. By means of catalytic hydrogenation *threo*-1-(2-methoxyphenyl)-2-phenyl-1,2-ethanediamine (**9**) was obtained free of byproducts and in high yields (Scheme 1, method A).

The same reduction method (method A) carried out with the *erythro*-configurated 1,2-diazidoethane **4** gave no 1,2-

Scheme 1



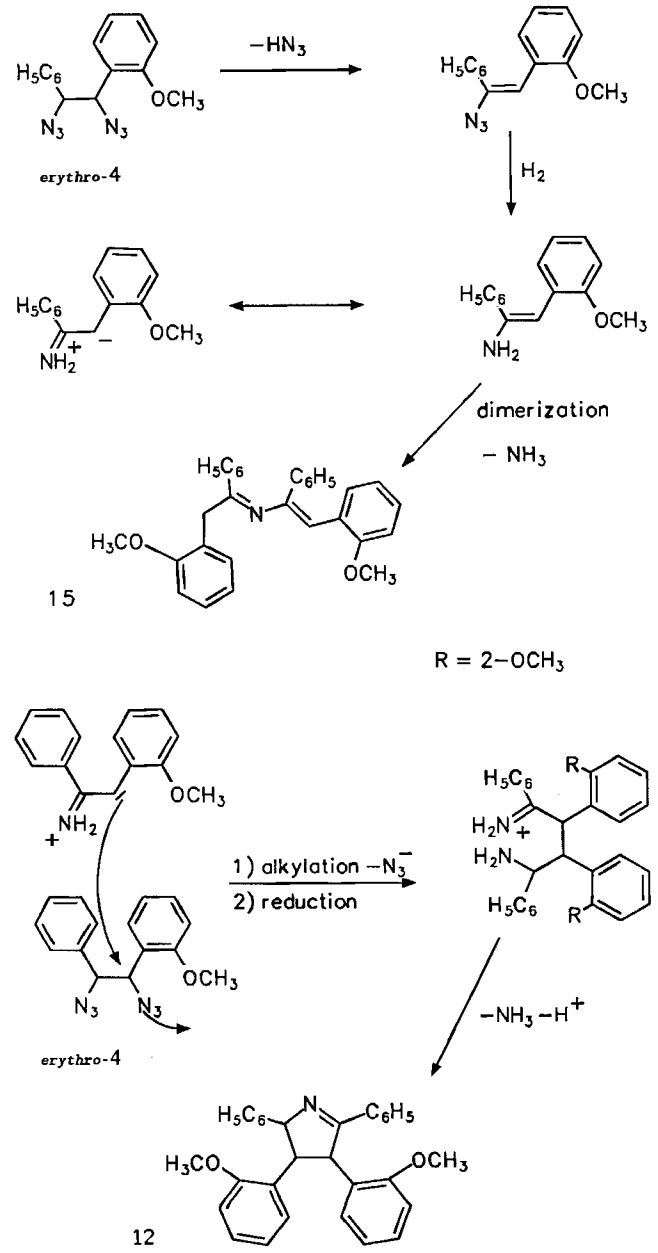

| | R |
|---|---|
| 1, *erythro*-4, *threo*-5, *threo*-9, 12 | 2–$OCH_3$ |
| 2, *erythro/threo*-6, *erythro*-10, *threo*-11 | 3–$OCH_3$ |
| 3, *erythro*-7, 13 | 4–$OCH_3$ |
| 8 | H |

ethanediamine. As reveald by elemental analysis, IR and mass spectrometry a dimerization product with an empirical formula of $C_{30}H_{27}NO_2$ and a C=N bond had been isolated. Taking into account that under the mild conditions of a catalytic hydrogenation both 1,2-diarylethane moieties remain unaffected, only two structures are possible: the pyrroline **12** (Scheme 1) or an open-chain compound *N*-(1,2-diarylethylidene)-1,2-diaryletheneamine **15** (Scheme 2). The dimerization reaction can be explained as follows: The key compound 2-(2-methoxyphenyl)-1-phenyletheneamine is formed by elimination of $HN_3$ from the diazidoethane **4** and subsequent reduction (Scheme 2). A condensation of two enamine molecules gives the open-chain dimer **15**, an addition of the 1,2-diazidoethane **4** to the 1,2-diaryletheneamine initiates the formation of the pyrroline **12** (Scheme 2, compare with the Storck enamine reaction[13]). Both modes of reaction are supported by the observed release of ammonia. In order to determine the nature of the reduction product $C_{30}H_{27}NO_2$ of *erythro*-**4** the open-chain dimer **15** was synthesized starting from 2-(2-methoxyphenyl)-1-phenylethanone (**14**) (Scheme 3). In the $^1$H-NMR spectrum of **15** two singlets for the methoxy groups ($\delta$ = 3.55 and 3.71) and a singlet for the benzylic protons ($\delta$ = 3.78) are observed. The vinylic proton absorbs together with the aromatic protons. This $^1$H-NMR spectrum is quite different from the spectrum of the hydrogenation product of *erythro*-**4**. Here the *ortho*-methoxy groups are isochrone ($\delta$ = 3.45). Furthermore, the benzylic protons of **15** absorbing at $\delta$ = 3.78

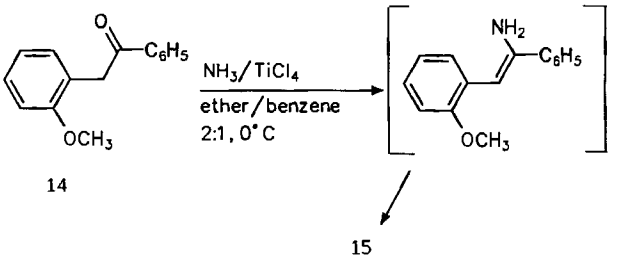
are missing. Their absorption is shifted to the region of the aromatic protons. These observations favor a pyrroline structure **12**. Since many 1,2-diaryl-1,2-ethanediamines are obtained by reduction of the respective 1,2-diazidoethanes without the appearance of elimination products[14], the electron-donating methoxy group in *ortho* position seems to facilitate the cleavage of the azido group at the C-1 atom by stabilizing a positive charge in this position. The *para*-methoxy group of *erythro*-1,2-diazido-1-(4-methoxyphenyl)-2-phenylethane (**7**) also labilizes the azido group at the C-1 position. Reduction with $H_2/PtO_2$ gives an analogous side product **13** (Scheme 1).

An alternative route to obtain the 1,2-ethanediamines from the 1,2-diazidoethanes is shown in Scheme 4; *meso*/(±)-1,2-Diazido-1,2-diphenylethane (**8**) and triphenylphosphine yield 1,2-diphenyl-*N*,*N*′-bis(triphenylphosphoranylidene)-1,2-ethanediamine (**16**). After hydrolysis the desired 1,2-ethanediamine **17** is obtained as a mixture of diastereoisomers. The same reaction performed with *erythro*-1,2-diazido-1-(4-methoxyphenyl)-2-phenylethane (**7**) shows again the sensitivity towards elimination reactions. In the course of the reaction, $HN_3$ and triphenylphosphine imine are released with formation of the corresponding salt **18** by acid-base reactions. Furthermore, 2-(4-methoxyphenyl)-1-phenyl-*N*-(triphenylphosphoranylidene)etheneamine (**19**) is isolated (Scheme 4). No 1,2-ethanediamine could be obtained following this synthetic route. Further attempts to synthesize the 1,2-ethanediamines from either the *ortho*- or the *para*-substituted 1,2-diaryl-1,2-diazidoethanes failed because of elimination reactions.

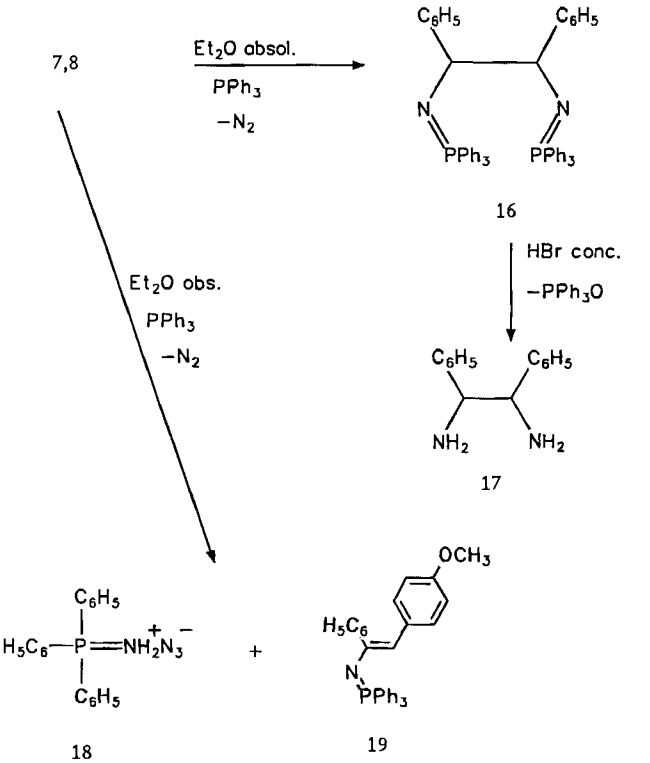
Scheme 2




Scheme 3



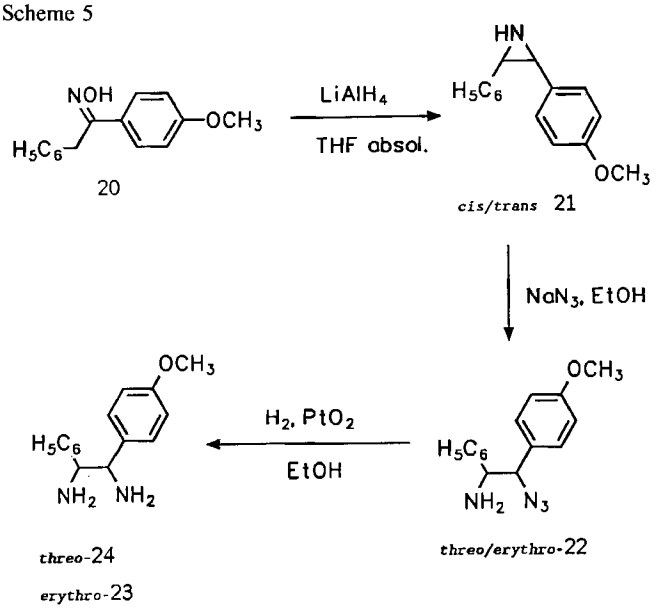

Scheme 4




An alternative way to unsymmetrically phenyl-substituted 1,2-diaryl-1,2-ethanediamines is shown in Scheme 5. The reduction of 1-(4-methoxyphenyl)-2-phenylethanone oxime (**20**) with $LiAlH_4$ in absol. THF yielded the respective 2,3-

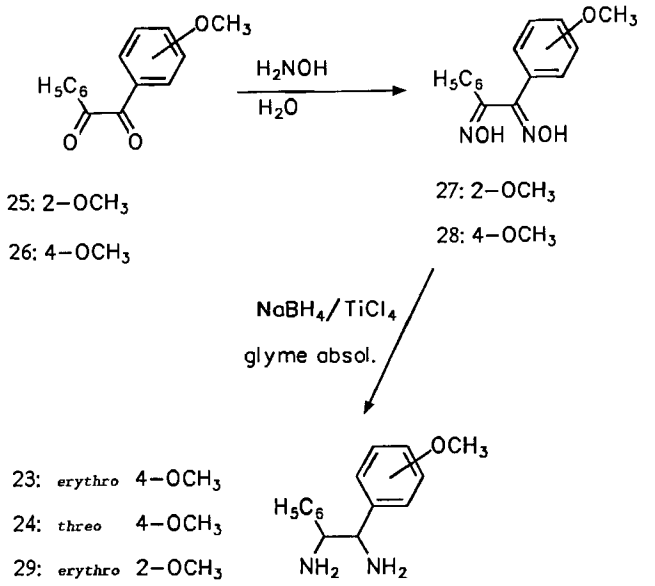
diarylaziridine **21** in a *cis/trans* 4:1 mixture. Because of anisotropic effects the $^1$H-NMR signal of the benzylic protons of the *cis* isomer is shifted about 0.5 ppm to lower field compared with the *trans* isomer. The same phenomenon has already been observed for the isomers of the unsubstituted 2,3-diphenylaziridine, which were obtained from stereospecific elimination reactions of the respective *threo/erythro*-1,2-diaryl-1-azido-2-iodoethanes[15]. The aziridine ring is opened with $N_3^-$. Usually nucleophilic attack occurs at the carbon atom which can best stabilize a positive charge. For this reason, $N_3^-$ adds to the C-2 atom of the aziridine ring. This could be confirmed by MS methods. Because of the stereospecificity of the reaction the 2-azidoethaneamine **22** is obtained as a *threo/erythro* 4:1 mixture. The following catalytic hydrogenation proceeds without elimination, and the resulting diastereomeric 1,2-ethanediamines can be separated by fractional crystallization (*threo*-**24**: 80%, *erythro*-**23**: 20%) (Scheme 5).

Scheme 5

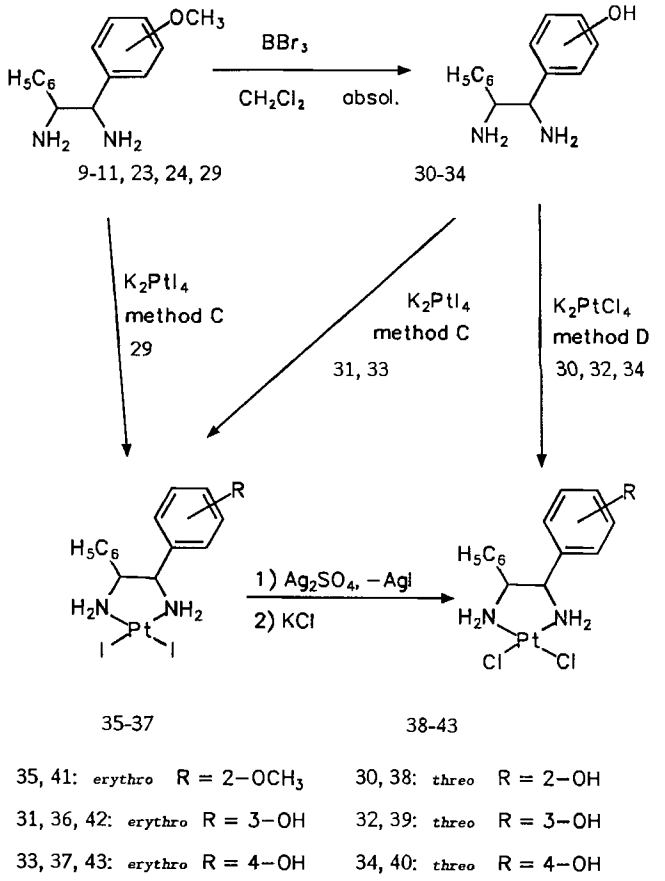



The *erythro*-configurated 1-(2- or 4-methoxyphenyl)-2-phenyl-1,2-ethanediamines were synthesized in the following manner. The ethanediones **25** and **26** were transformed into the corresponding dioximes (**27**, **28**). Reduction with $LiAlH_4$ as described by Dornow et al.[16] gave an impure product, which could not be purified. A reaction with $NaBH_4/TiCl_4$ in absol. glyme provided pure *erythro*-1-(2-methoxyphenyl)-2-phenyl-1,2-ethanediamine (**29**) and a *threo/erythro* 1:3 mixture of 1-(4-methoxyphenyl)-2-phenyl-1,2-ethanediamine (**23**, **24**) (Scheme 6). The ether cleavage was achieved with $BBr_3$ (Scheme 7); *erythro*-**29** could not be cleaved with $BBr_3$ or other commonly used reagents. Therefore the unchanged methoxy derivative was used further.

Scheme 6




Scheme 7




## Synthesis of the Platinum(II) Compounds

The *threo*-configurated 1,2-ethanediamines (**30**, **32**, **34**) reacted with $K_2PtCl_4$ to form the corresponding dichloroplatinum(II) complexes (**38**–**40**) (Scheme 7). The *erythro*-configurated complexes can not be synthesized in this way; the reaction with $K_2PtCl_4$ proceeds too slowly. For this reason, the more rapid reaction with $K_2PtI_4$ to the diiodoplatinum(II) complexes (**35**–**37**) was performed. After the intermediate formation of the diaquaplatinum(II) com-

plexes the *erythro*-configurated dichloro complexes are precipitated with KCl (**41**–**43**) (Scheme 7). After complexation the four amine protons are nonequivalent, and the maximum of four signals is observed in the $^1$H-NMR spectrum (Figure 2).

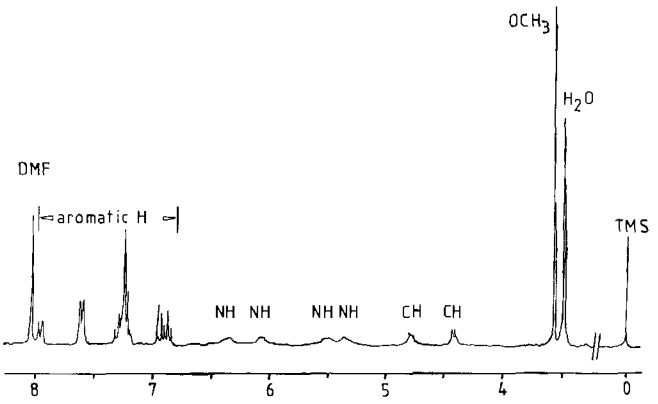



Figure 2. 250-MHz $^1$H-NMR spectrum ([$D_7$]DMF) of **41**

### Configurative Assignment of the Ligands and Platinum(II) Compounds

The configuration of the diastereoisomeric 1-(2-methoxyphenyl)-2-phenyl-1,2-ethanediamines (**9**, **29**) is clearly determinded by an X-ray analysis of the *threo* isomer. The assignment of the configuration of the diastereoisomeric 1-(4-methoxyphenyl)-2-phenyl-1,2-ethanediamines (**23**, **24**) can be achieved by analyzing the *cis/trans* mixture of 2-(4-methoxyphenyl)-3-phenylaziridine (**21**). Each benzylic proton of the *trans* isomer is situated in the shielding zone of two phenyl rings, and therefore these protons absorb at higher field compared with the benzylic protons of the *cis* isomer. In a stereospecific ring-opening reaction with $N_3^-$ the *trans*-aziridine yields the *erythro*-azidoethaneamine and the *cis*-aziridine the *threo*-azidoethaneamine. The following catalytic hydrogenation reaction yielding the 1,2-ethanediamines does not affect the chiral centers. The configuration of the diastereoisomeric 1-(3-methoxyphenyl)-2-phenyl-1,2-ethanediamines could not be established by spectroscopic or crystallographic methods. However, it is known that *meso*- or *erythro*-configurated 1,2-diaryl-1,2-ethanediamines require longer times to react with $K_2PtCl_4$ than the (±)- or *threo*-configurated ligands[14,17]. Therefore the more reactive species is assigned as the *threo* isomer. Furthermore, the signals of the phenolic ring protons of all the dichloroplatinum(II) compounds described in this paper absorb at the same δ values as the ring protons of the already described [1,2-bis(hydroxyphenyl)-1,2-ethanediamine]dichloroplatinum(II) compounds[11,18,19], whose configuration is exactly determined by the stereospecific course of their synthesis.

The evaluation of the biological properties and the activity in cisplatinum-resistant tumor models will be the topic of another publication. Furthermore we will test whether the antitumor activity is elevated by a resolution of the enantiomers.

## Experimental

IR (films or KBr pellets): Acculab 7 (Beckman). – Melting points (uncorrected): Büchi 510. – $^1$H NMR: Varian EM 360 L, 60 MHz; $^1$H-NMR spectra of the platinum complexes: Bruker FT-NMR spectrometer WM 250 at 250 MHz, TMS internal standard. – Elemental analyses: Mikroanalytisches Laboratorium der Universität Regensburg. – MS: Varian MAT 311 A or a MAT 112S.

*1,2-Diarylethenes* **1**–**3** have been reported in the literature[20] and were synthesized by Wittig reaction[21]. The $^1$H-NMR spectra of the obtained *E*/*Z* 1:1 mixtures are in agreement with earlier results[22,23].

*Synthesis of the 1,2-Diaryl-1,2-diazidoethanes* **4**–**8**. – *General Procedure:* In a 100-ml three-neck flask equipped with a reflux condenser 3.2 g (50 mmol) of $NaN_3$ is stirred in 30 ml of $CH_3CN$ at −18°C (ice/NaCl 3:1). After 15 min 4.1 g (25 mmol) of ICl is added dropwise. The orange suspension is stirred for 30 min, and 12.5 mmol of 1,2-diarylethene is added. After stirring overnight the reaction mixture is refluxed for 2.5 h. The violet suspension is allowed to cool and is extracted with ether and water. The combined organic layers are washed with 5% aqueous $Na_2S_2O_3$ solution until discoloring occurs. The ethereal solution is dried with $MgSO_4$ and the solvent evaporated. Further purification of the crude product is achieved by a silica gel chromatography with $CH_2Cl_2$/petroleum ether (1:1). The diastereomers of 1,2-diazido-1-(2-methoxyphenyl)-2-phenylethane can be separated with this method.

*erythro-1,2-Diazido-1-(2-methoxyphenyl)-2-phenylethane* (**4**): Yield 1.36 g (37%), pink oil. – IR (film): $\tilde{\nu}$ = 2100 cm$^{-1}$ s ($N_3$). – $^1$H NMR ($CDCl_3$): δ = 3.88 (s, 3H, $OCH_3$), 4.57, 5.56 (dd, $^3J$ = 10 Hz, 2H, CH), 6.88–7.75 (m, 9H, aromatic H).

$C_{15}H_{14}N_6O$ (294.3) Calcd. C 61.22 H 4.80 N 28.55
Found C 61.10 H 4.87 N 29.17

*threo-1,2-Diazido-1-(2-methoxyphenyl)-2-phenylethane* (**5**): Yield 0.99 g (27%), m.p. 45–46°C (petroleum ether 40–60°C), colorless crystals. – IR (KBr): $\tilde{\nu}$ = 2100 cm$^{-1}$ s ($N_3$). – $^1$H NMR ($CDCl_3$): δ = 3.69 (s, 3H, $OCH_3$), 4.72, 5.16 (dd, $^3J$ = 7 Hz, 2H, CH), 6.59–7.45 (m, 9H, aromatic H).

$C_{15}H_{14}N_6O$ (294.3) Calcd. C 61.22 H 4.80 N 28.55
Found C 61.12 H 4.88 N 28.68

*erythro/threo-1,2-Diazido-1-(3-methoxyphenyl)-2-phenylethane* (**6**): Yield 2.10 g (57%), colorless oil. – IR (film): $\tilde{\nu}$ = 2100 cm$^{-1}$ s ($N_3$). – $^1$H NMR ($CDCl_3$): δ = 3.68 (s, 1.5H, $OCH_3$), 3.77 (s, 1.5H, $OCH_3$), 4.60 (s, 1H, CH), 4.65 (s, 1H, CH), 6.52–7.47 (m, 9H, aromatic H).

*erythro-1,2-Diazido-1-(4-methoxyphenyl)-2-phenylethane* (**7**): Yield 2.50 g (68%), pink oil. – IR (film): $\tilde{\nu}$ = 2100 cm$^{-1}$ s ($N_3$). – $^1$H NMR ($CDCl_3$): δ = 3.68 (s, 3H, $OCH_3$), 4.05, 5.23 (dd, $^3J$ = 9 Hz, 2H, CH), 6.78, 7.17 (dd, $^3J$ = 9 Hz, 4H, $MeOC_6H_4$), 7.24 (s, 5H, Ph).

*meso/(±)-1,2-Diazido-1,2-diphenylethane* (**8**): Yield 1.59 g (48%), pink oil. – The spectroscopic data are in agreement with the literature[24].

*threo-1-(2-Methoxyphenyl)-2-phenyl-1,2-ethanediamine* (**9**)

*Method A:* The product is obtained by a catalytic hydrogenation (28 h) of **5** with catalytic amounts of $PtO_2$ in ethanol (2.9 g, 10 mmol, in 150 ml) at room temp. and atmospheric pressure. After 4, 20, and 24 h the apparatus is purged with fresh $H_2$. At the end of the reaction 1 g of activated charcoal is added and the mixture stirred at 50°C for 15 min. After filtration the solvent is evaporated. Yield 1.74 g (72%), colorless oil. – IR (film): $\tilde{\nu}$ = 3380 cm$^{-1}$ w, 3320 w (NH). – $^1$H NMR ($CDCl_3$): δ = 1.61 (s, 4H, $NH_2$), 3.86 (s,

3H, $OCH_3$), 4.26, 4.44 (dd, $^3J$ = 4.5 Hz, 2H, CH), 6.73–7.51 (m, 9H, aromatic H).

*erythro/threo-1-(3-Methoxyphenyl)-2-phenyl-1,2-ethanediamine* (**10/11**)

*Method B:* To a suspension of 1.51 g (40 mmol) of $LiAlH_4$ in 10 ml of absol. ether 2.94 g (10 mmol) of **6** in 10 ml of absol. ether is added slowly at ice-bath temperature. The mixture is refluxed for 1 h and carefully hydrolyzed with water. The precipitate is filtered off. The organic layer is separated and dried with $MgSO_4$. The solvent is removed. The diastereomeric diamines are separated by fractional crystallization from ether.

*erythro*-**10**: Yield 0.97 g (40%), m.p. 87–88°C (ether), colorless powder. – IR (KBr): $\tilde{\nu}$ = 3340 $cm^{-1}$ m, 3260 m (NH). – $^1H$ NMR ($CDCl_3$): δ = 1.35 (s, 4H, $NH_2$), 3.75 (s, 3H, $OCH_3$), 3.97 (s, 2H, CH), 6.53–7.43 (m, 9H, aromatic H).

*threo*-**11**: Yield 0.97 g (40%), light-brown oil. – IR (film): $\tilde{\nu}$ = 3380 $cm^{-1}$ m, 3300 m (NH). – $^1H$ NMR ($CDCl_3$): δ = 1.57 (s, 4H, $NH_2$), 3.73 (s, 3H, $OCH_3$), 4.07 (s, 2H, CH), 6.57–7.40 (m, 9H, aromatic H).

*3,4-Dihydro-3,4-bis(2-methoxyphenyl)-2,5-diphenyl-2H-pyrrole* (**12**): According to Method A. Yield 1.67 g (77%), m.p. 104–105°C (*n*-hexane), yellow crystals. – IR (KBr): $\tilde{\nu}$ = 1640 $cm^{-1}$ s (C=N). – $^1H$ NMR ($CDCl_3$): δ = 3.45 (s, 6H, $OCH_3$), 6.65–7.43 (m, 21H, CH + aromatic H). – MS: *m/z* (%) = 433 (100) [$M^+$].

$C_{30}H_{27}NO_2$ (433.6) Calcd. C 83.11 H 6.28 N 3.23
Found C 82.89 H 6.30 N 3.16

*3,4-Dihydro-3,4-bis(4-methoxyphenyl)-2,5-diphenyl-2H-pyrrole* (**13**): According to Method A. Yield 1.37 g (63%), orange, glassy mass, decomposes. – IR (film): $\tilde{\nu}$ = 1650 $cm^{-1}$ s (C=N). – $^1H$ NMR ($CDCl_3$): δ = 3.78 (s, 6H, $OCH_3$), 6.46–7.38 (m, 21H, CH + aromatic H).

*2-(2-Methoxyphenyl)-1-phenylethanone*[25] (**14**)

*2-(2-Methoxyphenyl)-N-[2-(2-methoxyphenyl)-1-phenylethylidene]-1-phenylethenamine* (**15**): In a 100-ml three-neck flask 3.0 g (13.3 mmol) of the ethanone **14** is dissolved in 50 ml of absol. ether/absol. benzene (2:1). At ice-bath temp. dry $NH_3$ is passed through the reaction mixture. A solution of 6.0 ml (55 mmol) of $TiCl_4$ in 25 ml of absol. ether/absol. benzene (2:1) is added slowly. After stirring for 3 h the mixture is filtrated and the solvent removed. Yield 0.81 g (28%), m.p. 127–128°C (petroleum ether 40–60°C), yellow crystals. – IR (KBr): $\tilde{\nu}$ = 1630 $cm^{-1}$ s (C=N). – $^1H$ NMR ($CDCl_3$): δ = 3.55 (s, 3H, $OCH_3$), 3.71 (s, 3H, $OCH_3$), 3.78 (s, 2H, $CH_2$), 6.19–8.04 (m, 19H, aromatic + vinylic H). – MS: *m/z* (%) = 433 (100) [$M^+$].

$C_{30}H_{27}NO_2$ (433.6) Calcd. C 83.11 H 6.28 N 3.23
Found C 83.07 H 6.50 N 3.13

*1,2-Diphenyl-N,N'-bis(triphenylphosphoranylidene)-1,2-ethanediamine* (**16**): At ice-bath temp. 4.3 g (16.4 mmol) of triphenylphosphine is dissolved in 25 ml of absol. ether. A solution of 2.2 g (8.3 mmol) of diazide **8** in 20 ml of absol. ether is added dropwise. $N_2$ is released. The mixture is stirred at ice-bath temp. for 30 min at room temp. for 2 h and finally refluxed for 4 h. The precipitate is filtrated and washed with ether. Yield 2.38 g (39%), m.p. 228–236°C [*meso*/(±) mixture], colorless powder. – IR (KBr): $\tilde{\nu}$ = 1115 $cm^{-1}$ s (P=N). – $^1H$ NMR ($CDCl_3$): δ = 4.32, 4.57 (2 × s, 2H, CH), 6.90–7.70 (m, 40H, aromatic H). – MS: *m/z* (%) = 732 (<1) [$M^+$], 366 (100) [$M^+/2$].

*meso/(±)-1,2-Diphenyl-1,2-ethanediamine* (**17**): The phosphoranylidene compound **16** [0.5 g (0.7 mmol)] is refluxed for 12 h with 20 ml of 40% HBr and 1 ml of $H_3PO_2$. After cooling the reaction mixture is extracted with $CH_2Cl_2$. The pH of the aqueous layer is adjusted to 12 with 20% NaOH (ice bath). After another extraction with $CH_2Cl_2$ the organic layer is dried with $MgSO_4$ and the solvent removed under pressure. Yield 0.11 g (77%), colorless oil. The spectroscopic data are in accordance with literature data[26].

*(Triphenylphosphoranylidene)ammonium Azide* (**18**) *and 2-(4-Methoxyphenyl)-1-phenyl-N-(triphenylphosphoranylidene)etheneamine* (**19**): The diazide **7** is treated as described for the synthesis of **16**. The precipitated crude product is dissolved in a small amount of $CHCl_3$. Following the addition of ether, **18** precipitates after standing in the refrigerator. After filtering the ammonium azide (the crude product) the filtrate of the reaction mixture is cooled in the refrigerator, and **19** precipitates.

**18**: Yield 1.06 g (40%), colorless powder. The spectroscopic data and the melting point are in agreement with the literature[27] data.

**19**: Yield 1.21 g (30%), m.p. 169–170°C, yellow powder. – IR (KBr): $\tilde{\nu}$ = 1110 $cm^{-1}$ m (P=N). – $^1H$ NMR ($CDCl_3$): δ = 3.76 (s, 3H, $OCH_3$), 6.60–7.90 (m, 25H, aromatic + vinylic H). – MS: *m/z* (%) = 485 (100) [$M^+$].

*1-(4-Methoxyphenyl)-2-phenylethanone Oxime*[28] (**20**)

*cis/trans-2-(4-Methoxyphenyl)-3-phenylaziridine* (**21**): In a 500-ml three-neck flask 4.2 g (0.11 mmol) of $LiAlH_4$ is suspended in 100 ml of absol. THF. A solution of 13.4 g (56 mmol) of oxime **20** in 150 ml of absol. THF is added dropwise. The mixture is refluxed for 3 h. The excess $LiAlH_4$ is hydrolyzed with water at ice-bath temperature. $Al(OH)_3$ is filtrated off and the filtrate extracted with ether and water. The combined ether layers are dried with $MgSO_4$. After removing the solvent the crude product is chromatographed on silica gel with diethylether/petroleum ether (40–60°C) (1:1) under $N_2$ pressure. A *cis/trans* 4:1 mixture of the desired aziridine **21** is obtained. Yield 4.92 g (39%), yellow oil. – IR (film): $\tilde{\nu}$ = 3320 $cm^{-1}$ m (NH). – $^1H$ NMR ($CDCl_3$): *cis* isomer: δ = 1.64 (s, br, 1H, NH), 3.54 (s, 2H, CH), 3.62 (s, 3H, $OCH_3$), 6.64, 7.05 (dd, $^3J$ = 8 Hz, 4H, $C_6H_4$), 7.13 (s, 5H, Ph); *trans* isomer: δ = 3.07 (s, 2H, CH), 3.82 (s, 3H, $OCH_3$), 7.26 (s, 5H, Ph), the remaining absorptions are obscured by the signals of the *cis* isomer.

*threo/erythro-2-Azido-2-(4-methoxyphenyl)-1-phenylethaneamine* (**22**): To a solution of 3.55 g (13.3 mmol) of aziridine **21** in 70 ml of ethanol a solution of 2.32 g (53.2 mmol) of $NaN_3$ and 1.82 g (53.2 mmol) of $NH_4Cl$ in 20 ml of water is added. The reaction mixture is refluxed for 16 h. After cooling and addition of water the mixture is extracted with $CH_2Cl_2$. The combined organic layers are dried with $MgSO_4$, and the solvent is removed. Yield 3.57 g (100%), orange oil. – IR (film): $\tilde{\nu}$ = 3380 $cm^{-1}$ w, 3320 w (NH), 2100 s ($N_3$). – $^1H$ NMR ($CDCl_3$): *threo* isomer: δ = 1.71 (s, 2H, $NH_2$), 3.70 (s, 3H, $OCH_3$), 4.00, 4.48 (dd, $^3J$ = 8 Hz, 2H, CH), 6.61, 6.91 (dd, $^3J$ = 10 Hz, 4H, $C_6H_4$), 7.03 (s, 5H, Ph); *erythro* isomer: δ = 3.73 (s, 3H, $OCH_3$), 7.17 (s, 5H, Ph), the remaining absorptions are obscured under the signals of the *threo* isomer.

*erythro/threo-1-(4-Methoxyphenyl)-2-phenyl-1,2-ethanediamine* (**23/24**): The product is obtained by a catalytic hydrogenation (24 h) of 3.65 g (13.7 mmol) of azido amine **22** with $PtO_2$ as catalyst in ethanolic solution (200 ml). The reaction is conducted at room temp. and at atmospheric pressure. After 5 h the apparatus is purged with fresh $H_2$. At the end of the reaction the mixture is filtrated and the filtrate evaporated to dryness. The crude product is dissolved in ether, and the dihydrochloride is precipitated with a saturated solution of HCl in ether. The white powder is dissolved in 60 ml of methanol under slight warming. Ether is added until the first turbidity is observed. Within 30 min the *erythro* isomer precipitates. The *threo* isomer remains in solution and is obtained

by removing the solvent. The separated dihydrochlorides are converted into the free bases.

*erythro*-**23**: Yield 0.53 g (16%), m.p. 69°C (*n*-hexane), colorless crystals. – IR (KBr): $\tilde{\nu}$ = 3350 $cm^{-1}$ w, 3270 w (NH). – $^1H$ NMR ($CDCl_3$): δ = 1.49 (s, 4H, $NH_2$), 3.88 (s, 3H, $OCH_3$), 4.05 (s, 2H, CH), 7.00, 7.45 (dd, $^3J$ = 10 Hz, 4H, $C_6H_4$), 7.53 (s, 5H, Ph).

*threo*-**24**: Yield 1.69 g (51%), pale-yellow oil. – IR (KBr): $\tilde{\nu}$ = 3370 $cm^{-1}$ w, 3300 w (NH). – $^1H$ NMR ($CDCl_3$): δ = 1.76 (s, 4H, $NH_2$), 3.84 (s, 3H, $OCH_3$), 4.11 (s, 2H, CH), 6.88, 7.27 (dd, $^3J$ = 8 Hz, 4H, $C_6H_4$), 7.36 (s, 5H, Ph).

*1-(2-Methoxyphenyl)-2-phenylethanedione*[29] (**25**)

*1-(4-Methoxyphenyl)-2-phenylethanedione*[30] (**26**)

*Synthesis of the 1,2-Diarylethanedione Dioximes – General Procedure:* In a 100-ml round flask 7.0 g (0.175 mmol) of NaOH are dissolved in 50 ml of water. A solution of 3.5 g (0.054 mol) of $H_2NOH \cdot HCl$ in 10 ml of water is added. To this solution 5.0 g (20.8 mmol) of 1,2-diarylethanedione is given. After stirring at room temp. for 3 d the dioxime is precipitated with solid $CO_2$ and washed with ethanol.

*1-(2-Methoxyphenyl)-2-phenylethanedione Dioxime* (**27**): Yield 4.89 g (87%), m.p. 223°C, colorless powder. – IR (KBr): $\tilde{\nu}$ = 3270 $cm^{-1}$ m, br (NOH). – $^1H$ NMR ([$D_6$]DMSO): δ = 3.80 (s, 3H, $OCH_3$), 7.00–7.53 (m, 9H, aromatic H).

*1-(4-Methoxyphenyl)-2-phenylethanedione Dioxime* (**28**): Yield 4.61 g (82%), m.p. 190–191°C, colorless powder. – IR (KBr): $\tilde{\nu}$ = 3280 $cm^{-1}$ s, br (NOH). – $^1H$ NMR ([$D_6$]DMSO): δ = 3.78 (s, 3H, $OCH_3$), 7.00, 7.46 (dd, $^3J$ = 9 Hz, 4H, $C_6H_4$), 7.45 (s, 5H, Ph). – The melting point of the product agrees with the value of the *E,E* isomer in the literature[16].

*Reduction of the 1,2-Diarylethanedione Dioximes – General Procedure:* To 5.2 g (0.36 mol) of $NaBH_4$ in absol. glyme in a 250-ml three-neck flask (with a drying tube and a serum cap) through the syringe 13.2 g (70 mmol) of $TiCl_4$ is added. To the turquoise suspension the dioxime (4.89 g, 18.09 mmol) is given. $H_2$ is released. The mixture is stirred at room temp. for 1 d and than hydrolyzed with water at ice-bath temp. The pH is adjusted to 13 and the suspension extracted with $CHCl_3$. The ethereal phase is washed with water and extracted with 0.5 N HCl. The combined aqueous layers are washed with $CHCl_3$. With 20% NaOH the free base is obtained and extracted with $CHCl_3$. The organic layer is dried with $MgSO_4$ and the solvent evaporated. For an elemental analysis the dihydrochloride is precipitated from ethereal solution with a saturated solution of HCl in ether.

*erythro-1-(2-Methoxyphenyl)-2-phenyl-1,2-ethanediamine* (**29**): Yield 2.19 g (50%), pale-yellow oil. – IR (film): $\tilde{\nu}$ = 3370 $cm^{-1}$ w, 3290 w (NH). – $^1H$ NMR ($CDCl_3$): δ = 2.11 (s, 4H, $NH_2$), 3.86 (s, 3H, $OCH_3$), 4.10, 4.35 (dd, $^3J$ = 8 Hz, 2H, CH), 6.68–7.52 (m, 4H, $C_6H_4$), 7.31 (s, 5H, Ph).

$C_{15}H_{18}N_2O \cdot 2HCl$ (315.2)
Calcd. C 57.15 H 5.76 N 8.89
Found C 57.50 H 5.64 N 8.84

*erythro/threo-1-(4-Methoxyphenyl)-2-phenyl-1,2-ethanediamine* (**23/24**): Yield 42%. The 1,2-ethanediamines are obtained as an *erythro* (31%)/*threo* (11%) mixture and are separated as described above.

*Ether Cleavage – General Procedure:* A solution of 0.5 g (2.1 mmol) of a 1-(methoxyphenyl)-2-phenyl-1,2-ethanediamine in 20 ml of absol. $CH_2Cl_2$ is cooled to –60°C (acetone/$CO_2$ solid). At this temp. 0.78 ml (8.4 mmol) of $BBr_3$ is added with a syringe and the mixture stirred for 30 min. Than it is allowed to warm to room temp. and is stirred for further 24 h. Subsequently methanol is added at ice-bath temp. and the solvent evaporated. The crude product is dissolved in 30 ml of water under warming (≈40°C). After filtration the pH is adjusted to 10.5 with 2 N NaOH and the filtrate extracted with ethyl acetate. The organic layer is dried with $MgSO_4$ and the solvent removed. The *threo*-configurated ligands were obtained as oils. In order to correctly determine the elemental compositions the dihydrochlorides were precipitated from ethereal solutions with a saturated solution of HCl in ether.

*threo-1-(2-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine* (**30**): Yield 0.41 g (85%), orange oil. – IR (film): $\tilde{\nu}$ = 3600–2400 $cm^{-1}$ m, br (OH), 3360 m, 3300 m (NH). – $^1H$ NMR ($CDCl_3$): δ = 3.54–4.32 (s, br, 5H, OH + $NH_2$), 4.00, 4.16 (dd, $^3J$ = 7 Hz, 2H, CH), 6.28–7.43 (m, 4H, $C_6H_4$), 7.14 (s, 5H, Ph).

$C_{14}H_{16}N_2O \cdot 2HCl$ (301.2)
Calcd. C 55.83 H 6.02 N 9.30
Found C 55.92 H 5.98 N 9.21

*erythro-1-(3-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine* (**31**): Yield 0.27 g (55%), m.p. 65–67°C, slightly brown powder. – IR (KBr): $\tilde{\nu}$ = 3600–2400 $cm^{-1}$ m, br (OH), 3340 m, 3270 m (NH). – $^1H$ NMR ($CD_3OD$): δ = 3.92 (s, 2H, CH), 6.52–7.40 (m, 9H, aromatic H).

$C_{14}H_{16}N_2O \cdot 0.5H_2O$ (237.3)
Calcd. C 70.89 H 7.17 N 11.81
Found C 70.70 H 6.90 N 11.17

*threo-1-(3-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine* (**32**): Yield 0.36 g (75%), slightly brown oil. – IR (film): $\tilde{\nu}$ = 3600–2400 $cm^{-1}$ m, br (OH), 3380 m, 3300 m (NH). – $^1H$ NMR ($CD_3OD$): δ = 3.73 (s, 2H, CH), 6.40–7.38 (m, 9H, aromatic H).

$C_{14}H_{16}N_2O \cdot 2HCl$ (301.2)
Calcd. C 55.83 H 6.02 N 9.30
Found C 55.57 H 6.23 N 8.94

*erythro-1-(4-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine* (**33**): Yield 0.24 g (51%), m.p. 147–148°C (*n*-hexane), colorless crystalls. – IR (KBr): $\tilde{\nu}$ = 3600–2400 $cm^{-1}$ s, br (OH), 3340 m, 3280 m (NH). – $^1H$ NMR ($CD_3OD$): δ = 4.09 (s, 2H, CH), 6.87, 7.27 (dd, $^3J$ = 9 Hz, 4H, $C_6H_4$), 7.48 (s, 5H, Ph).

$C_{14}H_{16}N_2O$ (228.3)
Calcd. C 73.66 H 7.06 N 12.27
Found C 73.32 H 7.04 N 12.21

*threo-1-(4-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine* (**34**): Yield 0.40 g (84%), orange oil. – IR (film): $\tilde{\nu}$ = 3600–2400 $cm^{-1}$ s, br (OH), 3370 m, 3290 m (NH). – $^1H$ NMR ($CDCl_3$): δ = 3.16 (s, 5H, OH + $NH_2$), 4.11 (s, 2H, CH), 6.71, 7.15 (dd, $^3J$ = 9 Hz, 4H, $C_6H_4$), 7.36 (s, 5H, Ph).

$C_{14}H_{16}N_2O \cdot 2HCl$ (301.2)
Calcd. C 55.83 H 6.02 N 9.30
Found C 55.98 H 5.93 N 9.02

*erythro-(1,2-Diaryl-1,2-ethanediamine)diiodoplatinum(II) Compounds – General Procedure* (Method C): An aqueous solution of 415 mg (1 mmol) of $K_2PtCl_4$ and 3.32 g (20 mmol) of KI in 20 ml of water is stirred at 50°C for 30 min. This solution is added dropwise to 30 ml of an aqueous, acidic solution (pH 3, HCl) of 1 mmol of the respective ethanediamine ligand. The reaction mixture is stirred for 24 h, and the pH is adjusted to 5.5–6.5 several times. The precipitate is collected, washed with 1 N HCl and water, and dried with $CaCl_2$/silica gel at 80°C and 0.1 Torr.

*erythro-Diiodo[1-(2-methoxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**35**): Yield 0.49 g (71%), yellow-brown powder. – IR (KBr): = 3280 $cm^{-1}$ m, 3210 m, 3170 m (NH). – $^1H$ NMR

([D$_7$]DMF): δ = 3.57 (s, 3H, $OCH_3$), 4.27–4.31 (m, 1H, CH), 4.74–4.78 (m, 1H, CH), 5.18–5.38 (m, 2H, $NH_2$), 5.94 (m, 1H, NH), 6.27 (m, 1H, NH), 6.81–7.88 (m, 9H, aromatic H).

*erythro-[1-(3-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine]diiodoplatinum(II)* (**36**): Yield 0.46 g (65%), yellow-brown powder. – IR (KBr): $\tilde{\nu}$ = 3490 $cm^{-1}$ s (OH), 3260 s, 3210 m, 3170 s (NH). – $^1$H NMR ([D$_7$]DMF): δ = 4.20–4.51 (m, 2H, CH), 5.42–5.54 (m, 2H, $NH_2$), 5.99–6.02 (m, 2H, $NH_2$), 6.58–7.51 (m, 9H, aromatic H), 9.65 (s, 1H, OH).

$C_{14}H_{16}I_2N_2OPt \cdot 2H_2O$ (713.2)
Calcd. C 23.57 H 2.80 N 3.93
Found C 23.28 H 2.38 N 3.48

*erythro-[1-(4-Hydroxyphenyl)-2-phenyl-1,2-ethanediamine]diiodoplatinum(II)* (**37**): Yield 0.67 g (99%), yellow-brown powder. – IR (KBr): $\tilde{\nu}$ = 3490 $cm^{-1}$ s (OH), 3260 s, 3210 m, 3170 s (NH). – $^1$H NMR ([D$_7$]DMF): δ = 4.27–4.44 (m, 2H, CH), 5.27–5.38 (m, 2H, $NH_2$), 5.99 (m, 2H, $NH_2$), 6.69, 7.35 (dd, $^3J$ = 7.5 Hz, 4H, $C_6H_4$), 7.25–7.54 (m, 5H, Ph), 9.63 (s, 1H, OH).

*threo-Dichloro(1,2-diaryl-1,2-ethanediamine)platinum(II) Compounds – General Procedure* (Method D): The reaction is carried out as described in method C but without addition of KI. The reaction mixture is stirred for 3 d.

*threo-Dichloro[1-(2-hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**38**): Yield 0.38 g (77%), yellow powder. – IR (KBr): $\tilde{\nu}$ = 3420 $cm^{-1}$ s (OH), 3270 s, 3200 s (NH). – $^1$H NMR ([D$_7$]DMF): δ = 4.83–5.00 (m, 2H, CH), 5.33–5.41 (m, 1H, NH), 5.70–5.78 (m, 1H, NH), 6.29 (m, 2H, $NH_2$), 6.56–7.61 (m, 9H, aromatic H), 10.58 (s, 1H, OH).

$C_{14}H_{16}Cl_2N_2OPt$ (494.3)
Calcd. C 34.03 H 3.26 N 5.67
Found C 33.89 H 3.22 N 5.37

*threo-Dichloro[1-(3-hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**39**): Yield 0.37 g (74%), yellow powder. – IR (KBr): $\tilde{\nu}$ = 3430 $cm^{-1}$ s (OH), 3260 s, 3190 m (NH). – $^1$H NMR ([D$_7$]DMF): δ = 4.66 (m, 2H, CH), 5.62 (m, 2H, $NH_2$), 6.31–6.34 (m, 2H, $NH_2$), 6.62–7.64 (m, 9H, aromatic H), 9.53 (s, 1H, OH).

$C_{14}H_{16}Cl_2N_2OPt$ (494.3)
Calcd. C 34.03 H 3.26 N 5.67
Found C 33.85 H 3.36 N 5.49

*threo-Dichloro[1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**40**): Yield 0.32 g (65%), yellow powder. – IR (KBr): $\tilde{\nu}$ = 3420 $cm^{-1}$ m (OH), 3260 s, 3200 m (NH). – $^1$H NMR ([D$_7$]DMF): δ = 5.02 (m, 2H, CH), 5.71–5.79 (m, 2H, $NH_2$), 6.39 (m, 2H, $NH_2$), 6.66, 7.22 (dd, $^3J$ = 8 Hz, 4H, $C_6H_4$), 7.17–7.71 (m, 5H, Ph), 9.57 (s, 1H, OH).

$C_{14}H_{16}Cl_2N_2OPt$ (494.3)
Calcd. C 34.03 H 3.26 N 5.67
Found C 34.18 H 3.44 N 5.57

*erythro-Dichloro(1,2-diaryl-1,2-ethanediamine)platinum(II) Complexes – General Procedure:* A suspension of 1 mmol of the respective *erythro*-(1,2-diaryl-1,2-ethanediamine)diiodoplatinum(II) and 296 mg (0.95 mmol) of $Ag_2SO_4$ in 100 ml of water is stirred at room temp. for 3 d under light exclusion. After filtration 1.17 g (20 mmol) of NaCl are added to the filtrate. After stirring for 1 d the dichloro complex is collected by suction filtration and washed with 1 N HCl and water. The product is dried at 80°C/0.1 Torr over $CaCl_2$/silica gel.

*erythro-Dichloro[1-(2-methoxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**41**): Yield 0.37 g (72%), yellow powder. – IR (KBr): $\tilde{\nu}$ = 3280 $cm^{-1}$ m, 3200 s (NH). – $^1$H NMR ([D$_7$]DMF): δ = 3.55 (s, 3H, $OCH_3$), 4.42–4.44 (m, 1H, CH), 4.74–4.81 (m, 1H, CH), 5.31–5.39 (m, 1H, NH), 5.50–5.52 (m, 1H, NH), 6.07 (m, 1H, NH), 6.35 (m, 1H, NH), 6.83–7.98 (m, 9H, aromatic H).

$C_{15}H_{18}Cl_2N_2OPt$ (508.3)
Calcd. C 35.56 H 3.58 N 5.53
Found C 35.15 H 3.97 N 5.42

*erythro-Dichloro[1-(3-hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**42**): Yield 0.36 g (73%), yellow powder. – IR (KBr): $\tilde{\nu}$ = 3430 $cm^{-1}$ m (OH), 3210 s, 3120 m (NH). – $^1$H NMR ([D$_7$]DMF): δ = 4.31–4.33 (m, 1H, CH), 4.53–4.58 (m, 1H, CH), 5.48–5.61 (m, 2H, $NH_2$), 6.10–6.20 (m, 2H, $NH_2$), 6.64–7.67 (m, 9H, aromatic H), 9.75 (s, 1H, OH).

$C_{14}H_{16}Cl_2N_2OPt$ (493.3)
Calcd. C 34.03 H 3.26 N 5.67
Found C 34.36 H 3.31 N 5.54

*erythro-Dichloro[1-(4-hydroxyphenyl)-2-phenyl-1,2-ethanediamine]platinum(II)* (**43**): Yield 0.37 g (74%), yellow powder. – IR (KBr): $\tilde{\nu}$ = 3430 $cm^{-1}$ s (OH), 3210 s (NH). – $^1$H NMR ([D$_7$]DMF): δ = 4.42–4.51 (m, 2H, CH), 5.45–5.54 (m, 2H, $NH_2$), 6.14–6.16 (m, 2H, $NH_2$), 6.67, 6.70 (dd, $^3J$ = 7.5 Hz, 4H, $C_6H_4$), 6.69–7.40 (m, 5H, Ph), 9.62 (s, 1H, OH).

$C_{14}H_{16}Cl_2N_2OPt$ (494.3)
Calcd. C 34.03 H 3.26 N 5.67
Found C 34.36 H 3.31 N 5.54

*X-ray Data of threo-1,2-Diazido-1-(2-methoxyphenyl)-2-phenylethane* (**5**)[32]: Monoclinic, space group $P2_1/n$, $a$ = 1017.5(6), $b$ = 833.7(6), $c$ = 1448.6(2) pm, β = 98.53°, $V$ = 1.5549 $nm^3$, $Z$ = 4, $d_x$ = 1.26 g $cm^{-3}$, μ = 0.092 $mm^{-1}$, Enraf-Nonius CAD4, Mo radiation with graphite monochromator, 24°C. ω–2Θ scan, (0.9 + 0.35 tgΘ)° width, 2 ≤ Θ ≤ 25°, 5628 reflections measured (–12 ≤ $h$ ≤ 12, – 10 ≤ $k$ ≤ 10, 0 ≤ $l$ ≤ 20) which gave 2730 unique reflections. An experimental correction for absorption was applied (Ψ scan). The structure was solved with direct methods. The hydrogen atoms were found from a difference Fourier map. Isotropic

Table 2. Fractional atomic coordinates and equivalent thermal parameters [Å$^2$] of **5** with estimated standard deviations in parentheses

| Atom | X | Y | Z | U |
|---|---|---|---|---|
| O | 0.4954 (4) | 0.1689 (6) | 0.3180 (2) | 0.057 (1) |
| N (11) | 0.4708 (6) | -0.1285 (9) | 0.1107 (3) | 0.087 (3) |
| N (12) | 0.5201 (6) | -0.2369 (8) | 0.0847 (3) | 0.080 (3) |
| N (13) | 0.5570 (7) | -0.3310 (1) | 0.0514 (4) | 0.109 (3) |
| N (21) | 0.2277 (5) | 0.0013 (8) | 0.1491 (3) | 0.070 (1) |
| N (22) | 0.2361 (6) | 0.0386 (9) | 0.0840 (3) | 0.090 (3) |
| N (23) | 0.2314 (8) | 0.0750 (1) | 0.0203 (4) | 0.133 (3) |
| C (1) | 0.4327 (6) | 0.1448 (8) | 0.1906 (3) | 0.051 (1) |
| C (2) | 0.3553 (6) | 0.0018 (9) | 0.2033 (3) | 0.046 (1) |
| C (3) | 0.3171 (6) | 0.0034 (8) | 0.2827 (3) | 0.044 (1) |
| C (4) | 0.3918 (6) | 0.0898 (8) | 0.3403 (3) | 0.046 (1) |
| C (5) | 0.3623 (6) | 0.0911 (9) | 0.4151 (3) | 0.056 (1) |
| C (6) | 0.2556 (7) | 0.0060 (1) | 0.4320 (4) | 0.070 (3) |
| C (7) | 0.1784 (7) | -0.0760 (9) | 0.3766 (3) | 0.063 (3) |
| C (8) | 0.2090 (6) | -0.0758 (9) | 0.3027 (3) | 0.057 (3) |
| C (9) | 0.5539 (6) | -0.1679 (8) | 0.2513 (3) | 0.047 (1) |
| C (10) | 0.5498 (7) | -0.2718 (9) | 0.3085 (3) | 0.061 (3) |
| C (11) | 0.6600 (7) | -0.2920 (1) | 0.3686 (4) | 0.082 (3) |
| C (12) | 0.7716 (8) | -0.2050 (1) | 0.3662 (4) | 0.098 (3) |
| C (13) | 0.7744 (8) | -0.1030 (1) | 0.3096 (4) | 0.096 (3) |
| C (14) | 0.6682 (7) | -0.0830 (1) | 0.2493 (4) | 0.076 (3) |
| C (15) | 0.5839 (7) | 0.2510 (1) | 0.3757 (4) | 0.079 (3) |

refinement of all atoms resulted in a $R_w = 0.093$ [$w = 4I/(\sigma^2(I) + 0.01^2 I^2)$]. The residual density in a difference Fourier map was $+0.6 - 0.5$ eA$^{-3}$. The results are given in Table 2 and Figure 3.

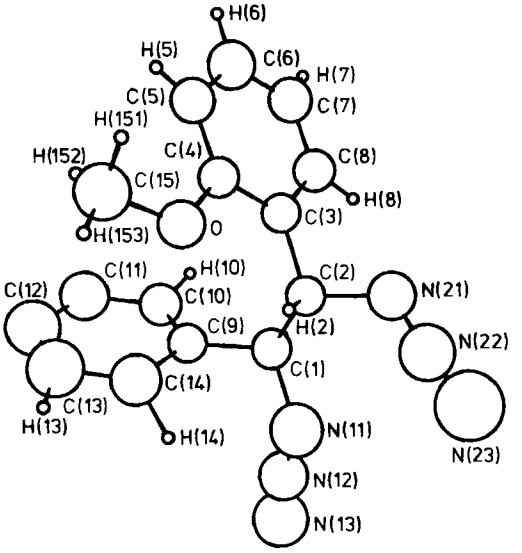



Figure 3. Crystal structure of **5** showing the crystallographic numbering scheme

CAS Registry Numbers

**1**: 52805-92-2 / **2**: 14064-41-6 / **3**: 1694-19-5 / **4**: 135147-65-8 / **5**: 135147-66-9 / **6**: 135147-67-0 / **7**: 135147-68-1 / **8**: 135147-69-2 / **9**: 135147-70-5 / **10**: 135147-71-6 / **11**: 135147-72-7 / **12**: 135147-73-8 / **13**: 135147-74-9 / **14**: 27356-33-8 / **15**: 135147-75-0 / **16**: 135147-76-1 / **17**: 5700-60-7 / **18**: 74255-76-8 / **19**: 135189-76-3 / **20**: 25725-55-7 / *cis*-**21**: 128539-38-8 / *trans*-**21**: 135189-77-4 / *erythro*-**22**: 135147-85-2 / *threo*-**22**: 135147-77-2 / **23**: 93913-22-5 / **24**: 93913-21-4 / **25**: 34082-43-4 / **26**: 22711-21-3 / **27**: 135147-78-3 / **28**: 22719-00-2 / **29**: 135147-79-4 / **30**: 135147-80-7 / **31**: 135147-81-8 / **32**: 135147-82-9 / **33**: 135147-83-0 / **34**: 135147-84-1 / **35**: 135147-86-3 / **36**: 135147-87-4 / **37**: 135147-88-5 / **38**: 135147-89-6 / **39**: 135147-90-9 / **40**: 93856-33-8 / **41**: 135147-91-0 / **42**: 135268-05-2 / **43**: 135268-06-3 / $K_2PtI_4$: 14708-56-6 / $K_2PtCl_4$: 10025-99-7 / $PPh_3$: 603-35-0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[32] Further details of the crystal structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-55396, the names of the authors, and the journal citation.


[14/91]