J. prakt. Chem. 340 (1998) 562 – 566

Journal für praktische Chemie
Chemiker-Zeitung

The Wittig Approach to Ethylene-bridged Catechol/Aminophenol Derivatives: Potential Ligands for Metallosupramolecular Chemistry

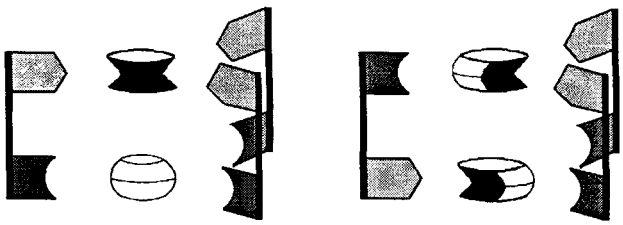
Markus Albrecht, Karen Witt, and Oliver Blau

Karlsruhe, Institut für Organische Chemie der Universität

Received April 15th, 1998

Abstract. The sequential ethylene-bridged catechol/aminophenol derivatives **2-H$_3$** and **3-H$_3$** are potential ligands for metal-directed self-assembly processes. They are prepared *via* Wittig-reaction followed by a high yield reduction step with up to three simultaneous transformations.

Sequential ligands which possess different donor sites are able to bind different metal ions [1–3]. In a metal-directed self-assembly process this can lead to supramolecular oligonuclear coordination compounds in which the ligands are all orientated in one direction (Figure 1, Type 1). As a second possibility the ligands can react with only one kind of metal ions leading in a thermodynamically controlled process to a structure in which the ligands are orientated in opposite directions (Figure 1, Type 2) [1, 3].



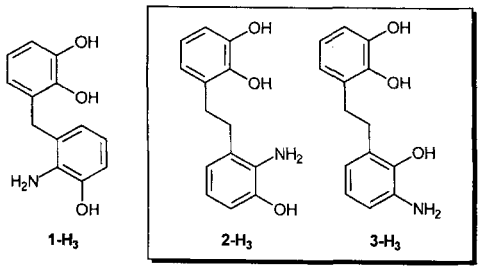


Fig. Schematic representation of dinuclear triple-stranded metal complexes from sequential ligands **1**–**3-H$_3$**.

Just recently we could show that the ligand **1-H$_3$** with gallium(III) **or** titanium(IV) ions forms heterochiral Type 2 complexes. A mixture of gallium(III) **and** titanium(IV) ions leads to the exclusive formation of the corresponding Type 1 structure [3].

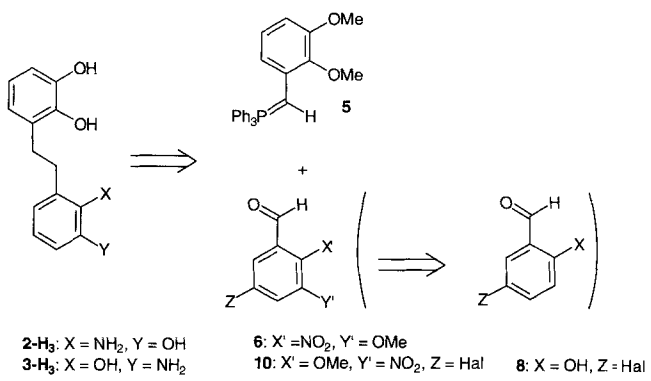
To enable more detailed investigations into this self-assembly process we now synthesized the new sequential catechol/aminophenol ligands **2-H$_3$** and **3-H$_3$**. In contrast to **1-H$_3$** they possess ethylene spacers which upon metal coordination should lead to homochiral triple-stranded helicates [4]. Additionally, **2-H$_3$** and **3-H$_3$** are different regioisomers and the influence of internal hydrogen bonding of the amines to catecholate oxygen atoms during the self-assembly process can be investigated [3].

Results and Discussion

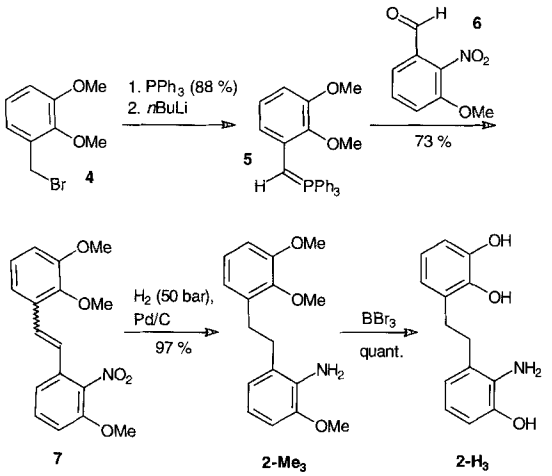
The retrosynthesis of the two derivatives **2-H$_3$** and **3-H$_3$**, which is depicted in Scheme 1, shows that the ethylene spacer should be introduced by Wittig-reaction of the ylide **5**, obtained from 2,3-dimethoxybenzyl triphenylphosphonium bromide with appropriate aromatic aldehydes **6** or **10**.

While **6** is commercially available, the salicyl derivative **10** has to be prepared first by nitration of the salicylaldehyds **8** which bear halogen substituents as protecting groups in 5-position.

1-(2-Amino-3-hydroxyphenyl)-2-(2,3-dihydroxy-



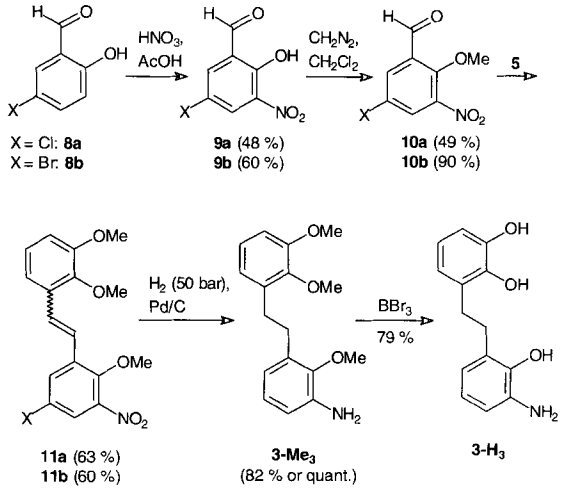
Scheme 1



Scheme 2

phenyl)ethane (**2-H$_3$**) was synthesized as depicted in Scheme 2. First the ylid **5** was prepared *in situ* by deprotonation (*n*BuLi, diethyl ether) of the corresponding phosphonium salt, which was obtained in 88% yield from the bromide **4** [2] and PPh_3. Wittig-reaction of 3-methoxy-2-nitrobenzaldehyde (**6**) with ylid **5** followed by chromatographic work up (silica gel, hexane/ethyl acetate 1:1) leads in 73% yield to the stilbene derivative **7** as a mixture of stereoisomers ($E:Z = 2:5$; by ^{1}H-NMR). In the following reaction step the double bond as well as the nitro group of **7** are simultaneously reduced by catalytic hydrogenation (ethyl acetate/methanol, 50 bar H_2, Pd/C, 15 h) to obtain the ligand precursor **2-Me$_3$** in high yield (97%). Transformation to the ligand **2-H$_3$** is achieved quantitatively by ether cleavage with BBr_3 in dichloromethane. Thus, ligand **2-H$_3$**, which possesses the same substitution pattern as **1-H$_3$** but one more methylene unit in the spacer, is obtained in a 4 step procedure in an overall yield of 62%.

The preparation of the regioisomeric ligand **3-H$_3$** is not so easy to achieve because of the lack of an appro-



Scheme 3

priate precursor (like **10**). Therefore the 3-nitrosalicylaldehyde derivatives **9a,b** had to be prepared first. Unfortunately direct nitration of salicylaldehyde results mainly in the formation of 5-nitrosalicylaldehyde. The desired 3-nitrosalicylaldehyde is only produced in traces [5]. Thus we used halogen substituents (X = Cl, Br) as protecting groups for the 5-position of **8a,b**. Now the nitration with nitric acid/glacial acetic acid (70 °C, 2 h) results in the formation of the 3-nitro substituted derivatives **9a** (48%) [6] or **9b** (60%). Reaction of **9a,b** with methylating agents like MeI/K_2CO_3 or Me_2SO_4/NaOH did not lead to the protected system **10a,b**. The methyl group finally could be introduced by addition of **9a,b** to a freshly prepared solution of CH_2N_2 in dichloromethane [7]. After hydrolytic work up the methoxy derivatives **10a,b** were isolated in 49% (**10a**) or 90% yield (**10b**) respectively. After Wittig-reaction of the aldehydes **10a,b** with the ylid **5** followed by chromatographic workup (silica gel, hexane/ethyl acetate 9:1) the stilbene derivatives **11a,b** are obtained (**a**: 63%, $E:Z = 5:2$; **b**: 60%, $E:Z = 4:1$). Following the protocol for the preparation of **2-H$_3$** the stilbenes **11a,b** are reduced by hydrogen (50 bar) in the presence of Pd/C. In this reaction step three transformations proceed simultaneously. The double bond and the nitro group are reduced and the halogen substituent is removed. In this process the ligand precursor **3-Me$_3$** is obtained in excellent yields (82% from **11a**; quantitative from **11b**). Finally the methyl ethers are cleaved (BBr_3, CH_2Cl_2, 79%). The sequential ligand **3-H$_3$** is obtained in a five step procedure in 10% or 26% overall yield.

Financial support by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

Experimental

Melting points (uncorrected): Büchi 535. IR: Bruker IFS. MS: Finnigan MAT 90. ^{1}H NMR and ^{13}C NMR (BB/DEPT): Bruker DRX 500 or AM 400, T = 296 K; internal standard: chloroform, [D_6]DMSO or [D_4]methanol. All reactions were carried out under argon.

(2,3-Dimethoxybenzyl)triphenylphosphonium bromide

2,3-Dimethoxybenzyl bromide **4** (2.04 g, 9 mmol) and PPh_3 (2.09 g, 8 mmol) are dissolved in acetone (70 ml) and heated to reflux for 45 min. The mixture is then cooled to 0 °C and the precipitating phosphonium bromide is filtered off, washed with diethyl ether and dried *in vacuo* to obtain a white solid (3.45 g, 88% with respect to PPh_3). *m.p.* >250 °C. – IR (KBr): ν/cm^{-1} = 2998, 2840, 2779, 1958, 1807, 1480, 1473, 1437, 1272, 1111, 1062, 993, 802, 737, 729, 695, 685. – ^{1}H NMR ([D_6]DMSO): δ/ppm = 7.87 (m, 3H), 7.71 (m, 6H), 7.65 (m, 6H), 7.00 (d, J = 8.0 Hz, 1H), 6.86 (pseudo t, J = 8.0 Hz, 1H), 6.47 (d, J = 8.0 Hz, 1H), 4.98 (d, J_{PH} = 15.2 Hz, 2H), 3.73 (s, 3H, CH_3), 3.41 (s, 3H, CH_3). – ^{13}C NMR ([D_6]DMSO): δ/ppm = 152.3 (C), 147.4 (C, J_{PC} = 6.0 Hz), 135.0 (CH), 133.9 (CH, J_{PC} = 9.8 Hz), 130.0 (CH, J_{PC} = 12.4 Hz), 123.7 (CH), 122.9 (CH, J_{PC} = 4.6 Hz), 121.0 (C, J_{PC} = 8.6 Hz), 118.0 (C, J_{PC} = 85.7 Hz), 113.7 (CH), 59.9 (CH_3), 55.9 (CH_3), 23.6 (CH_2, J_{PC} = 48.8 Hz).

$C_{27}H_{26}O_2PBr$	Calcd.:	C 65.73	H 5.31
(493.4)	Found:	C 65.50	H 5.52.

(E/Z)-1-(3-Methoxy-2-nitrophenyl)-2-(2,3-dimethoxyphenyl)ethene (**7**)

To (2,3-dimethoxybenzyl)triphenylphosphonium bromide (1.50 g, 3.04 mmol) in dry diethyl ether (30 ml) under argon 1.6 molar *n*BuLi in hexane (1.9 ml, 3.04 mmol) is added. The mixture turns red and a yellow solid (**5**) precipitates. After 1.5 h 1-nitro-2-methoxybenzaldehyde (**6**) (551 mg, 3.04 mmol) in dry ethanol (30 ml) is added. The color of the reaction mixture turns yellow and Ph_3PO precipitates. After 3 h the mixture is filtered and the solvent of the filtrate is evaporated *in vacuo*. After column chromatography (silica gel, hexane : ethyl acetate 1:1) compound **7** is obtained as a yellow solid (700 mg, 73%). – *m.p.* 104 °C. – IR (KBr): ν/cm^{-1} = 2954, 2836, 2568, 1995, 1959, 1920, 1839, 1730, 1604, 1579, 1525, 1473, 1432, 1362, 1278, 1226, 1068, 985, 852, 784, 748. – ^{1}H NMR ($CDCl_3$, *E*:*Z* = 2:5): δ/ppm = 7.51 (d, J = 16.3 Hz), 7.39 (m), 7.15 (t, J = 8.1 Hz), 7.04 (t, J = 8.1 Hz), 6.98–6.91 (m), 6.87 (m), 6.79 (m), 6.74 (d, J = 7.8 Hz), 6.60 (m), 6.52 (d, J = 12.1 Hz), 3.88 (s), 3.87 (s), 3.84 (2 s), 3.83 (s). – ^{13}C NMR ($CDCl_3$, *E*:*Z* = 2:5): δ/ppm = 153.0 (C), 152.7 (C), 150.8 (2 C), 147.3 (C), 140.9 (C), 140.6 (C), 131.0 (C), 130.7 (CH), 130.3 (CH), 130.2 (CH), 128.6 (CH), 124.3 (CH), 123.6 (CH), 123.3 (CH), 121.4 (CH), 118.3 (CH), 117.8 (CH), 112.5 (CH), 112.0 (CH), 111.1 (CH), 61.2 (CH_3), 60.8 (CH_3), 56.4 (CH_3), 56.3 (CH_3), 55.8 (CH_3), 55.7 (CH_3). – MS (EI, 70 eV): *m/z* = 315 (78%) M$^+$, 225 (52%), 149 (100%).

$C_{17}H_{17}NO_5$	Calcd.:	C 64.75	H 5.43	N 4.44
(315.3)	Found:	C 64.35	H 5.56	N 4.48.

1-(2-Amino-3-methoxyphenyl)-2-(2,3-dimethoxyphenyl) ethane (**2-Me$_3$**)

Stilbene derivative **7** (302 mg, 0.96 mmol) is dissolved in ethylacetate/methanol (2:1, 15 ml) and 117 mg of Pd/C is added. The mixture is stirred under hydrogen atmosphere (50 bar) for 16 h. The catalyst is filtered off and the solvent is removed *in vacuo* to obtain **2-Me$_3$** as a white solid (267 mg, 97 %). – *m.p.* 69 °C. – IR (KBr): ν/cm^{-1} = 3480, 3379, 2936, 2835, 1988, 1905, 1821, 1687, 1620, 1600, 1580, 1486, 1281, 1263, 1226, 1073, 1001, 992, 781. – MS (EI, 70 eV): *m/z* = 287 (48%) M$^+$, 136 (100%). – ^{1}H NMR ($CDCl_3$): δ/ppm = 7.3 (m, 1H), 6.88 (t, J = 8.0 Hz, 2H), 6.78 (d, J = 7.1 Hz, 1H), 6.74–6.69 (m, 2H), 4.13 (br, 2H, NH_2), 3.90 (s, 3H), 3.89 (2 s, 6H), 2.90 (m, 2H), 2.78 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 152.7 (C), 147.1 (2 C), 135.9 (C), 134.3 (C), 126.3 (C), 124.0 (CH), 122.0 (CH), 121.7 (CH), 117.3 (CH), 110.5 (CH), 108.3 (CH), 60.8 (CH_3), 55.7 (CH_3), 55.6 (CH_3), 33.5 (CH_2), 30.3 (CH_2).

$C_{17}H_{21}NO_3$	Calcd.:	C 71.06	H 7.37	N 4.87
(287.4)	Found:	C 70.60	H 7.24	N 5.03

High resolution MS: Calcd.: 287.1521 Found: 287.1512.

1-(2-Amino-3-hydroxyphenyl)-2-(2,3-dihydroxyphenyl) ethane (**2-H$_3$**)

The derivative **2-Me$_3$** (403 mg, 1.40 mmol) is dissolved in degassed dichloromethane (30 ml) under argon. At 0 °C a 1M solution of BBr_3 in dichloromethane (7.5 ml, 7.5 mmol) is added and the solution is stirred at room temperature for 15 h. Methanol (5 ml) is added and the solvent is removed *in vacuo*. The residue is dissolved in diethyl ether, washed with sat. aqueous $NaHCO_3$ and dried ($MgSO_4$). Removal of the ether affords **2-H$_3$** as a slightly brown solid (339 mg, 99%). – *m.p.* 170 °C. – IR (KBr): ν/cm^{-1} = 3465, 3388, 3317, 2939, 2868, 2600, 1909, 1831, 1753, 1618, 1595, 1478, 1341, 1287, 1248, 1155, 781. – UV/Vis (methanol) λ/nm = 204 (ε = 67000), 280 (shoulder), 462 (ε = 20). – ^{1}H NMR ([D_4]-methanol): δ/ppm = 6.66 (m, 1H), 6.6–6.5 (m, 5H), 2.8–2.7 (m, 4H). – ^{13}C NMR ([D_4]-methanol): δ/ppm = 146.4 (C), 145.9 (C), 144.4 (C), 133.5 (C), 130.2 (C), 129.6 (C), 122.0 (CH), 121.8 (CH), 120.3 (CH), 119.7 (CH), 114.1 (CH), 113.3 (CH), 33.4 (CH_2), 32.1 (CH_2). – MS (EI, 70 eV): *m/z* = 245 (42%) M$^+$, 122 (100%).

$C_{14}H_{15}NO_3$	Calcd.:	C 68.56	H 6.16	N 5.71
(245.3)	Found:	C 68.39	H 6.32	N 5.42

High resolution MS: Calcd.: 245.1052 Found: 245.1065.

5-Chloro-2-hydroxy-3-nitrobenzaldehyde (**9a**)

Following the procedure of Lovett and Roberts [6] **9a** is obtained from **8a** in 48% yield. – ^{1}H NMR ($CDCl_3$): δ/ppm = 11.25 (s, 1H), 10.40 (s, 1H), 8.35 (d, J = 2.0 Hz, 1 H), 8.07 (d, J = 2.0 Hz, 1H).

5-Bromo-2-hydroxy-3-nitrobenzaldehyde (**9b**)

5-Bromo-2-hydroxybenzaldehyde **8b** (5.00 g, 25.00 mmol) in glacial acetic acid is heated to 70 °C and conc. nitric acid (4.0 ml, 87.5 mmol) is added. After 1.5 h the mixture is poured on ice and the precipitating yellow needles are collected and dried to obtain **9b** (3.73 g, 60%). – *m.p.* 121 °C. – ^{1}H NMR

($CDCl_3$): δ/ppm = 11.27 (s, 1H), 10.38 (s, 1H), 8.48 (d, J = 2.5 Hz, 1H), 8.21 (d, J = 2.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 187.5 (CH), 155.4 (C), 139.5 (CH), 135.7 (C), 133.4 (CH), 126.8 (C), 111.8 (C). – MS (EI, 70 eV): m/z = 247/245 (63%) M^+, 229 (100%).

High resolution MS:	Calcd.: 244.9324
($C_7H_4NO_4Br$)	Found: 244.9336.

5-Chloro-2-methoxy-3-nitrobenzaldehyde (**10a**)

To 5-chloro-2-hydroxy-3-nitrobenzaldehyde **9a** (1.50 g, 7.5 mmol) in dichloromethane (50 ml) a 1M solution of CH_2N_2 in dichloromethane (7.5 ml, 7.5 mmol) [7] is added. After one hour additional 7.5 ml (7.5 mmol) and after further 2 hrs 3.5 ml (3.5 mmol) of the CH_2N_2 solution is added. Excess of methylating reagent is destroyed by addition of acetic acid. The organic phase is washed with sat. aqueous $NaHCO_3$, dried ($MgSO_4$) and the solvent is removed *in vacuo*. After column chromatography (silica gel, hexane/dichloromethane 2:1) **10a** is obtained as a yellow solid (795 mg, 49%). – *m.p.* 89 °C. – IR (KBr): ν/cm^{-1} = 3355, 3080, 2959, 2903, 1821, 1698, 1601, 1530, 1473, 1407, 1363, 1225, 982, 935, 903, 777. – ^1H NMR ($CDCl_3$): δ/ppm = 10.40 (s, 1H), 8.07 (d, J = 2.8 Hz, 1H), 8.04 (d, J = 2.8 Hz, 1H), 4.09 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 186.3 (CH), 154.6 (C), 144.4 (C), 133.0 (CH), 132.3 (C), 130.6 (CH), 130.2 (C), 65.6 (CH_3). – MS (EI, 70 eV): m/z = 217/215 (12/43%) M^+, 139 (100%).

$C_8H_6NO_4Cl$	Calcd.: C 44.57	H 2.81	N 6.50
(215.6)	Found: C 45.12	H 3.21	N 6.38

High resolution MS: Calcd.: 214.9985 Found: 214.9970.

5-Bromo-2-methoxy-3-nitrobenzaldehyde (**10b**)

Yield 7.5 g (90 %) as red solid. – *m.p.* 88 °C. – IR (KBr): ν/cm^{-1} = 3357, 3068, 2957, 2899, 1695, 1595, 1531, 1469, 1424, 1393, 1358, 1252, 1226, 1184, 984, 931, 713 . – ^1H NMR ($CDCl_3$): δ/ppm = 10.33 (s, 1H), 8.19 (d, J = 2.4 Hz, 1H), 8.18 (br, 1H), 4.08 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 186.2 (CH), 155.1 (C), 144.6 (C), 136.1 (CH), 133.4 (CH), 132.4 (C), 117.0 (C), 65.5 (CH_3). – MS (EI, 70 eV): m/z = 261/259 (75%) M^+, 185 (100%).

$C_8H_6NO_4Br$	Calcd.: C 36.95	H 2.33	N 5.39
(260.0)	Found: C 36.85	H 2.76	N 5.42

High resolution MS: Calcd.: 258.9480 Found 258.9470.

(E/Z)-1-(5-Chloro-2-methoxy-3-nitrophenyl)-2-(2,3-dimethoxyphenyl)ethene (**11a**)

The phosphonium bromide **5** (318 mg, 0.645 mmol) is suspended in dry diethyl ether (15 ml) under argon and a 1.6M solution of *n*BuLi in hexane (0.38 ml, 0.608 mmol) is added. A solution of aldehyde **10a** (124 mg, 0.575 mmol) in diethylether (20 ml) is slowly added after 1.5 h. After further 2.5 h the mixture is filtered and the clear filtrate is washed with 2N H_2SO_4, dried ($MgSO_4$) and the solvent evaporated *in vacuo*. The crude product is purified by column chromatography (silica gel, hexane : ethyl acetate 9:1) to obtain **11a** as a yellow solid (127 mg, 63%). – *m.p.* 119 °C. – IR (KBr): ν/cm^{-1} = 3067, 3007, 2929, 2840, 1699, 1576, 1533, 1476, 1356, 1261, 1073, 1007, 988, 894, 812, 786, 771. – ^1H NMR ($CDCl_3$, E:Z = 5:2): δ/ppm = 7.84 (d, J = 2.5 Hz), 7.67 (d, J = 2.5 Hz), 7.61 (d, J = 2.6 Hz), 7.50 (d, J = 16.6 Hz), 7.33 (d, J = 16.6 Hz), 7.25 (t, J = 7.7 Hz), 7.10 (t, J = 8.0 Hz), 6.99 (d, J = 12.2 Hz), 6.90 (m), 6.86 (d, J = 1.2 Hz), 6.84 (d, J = 1.2 Hz), 6.67 (d, J = 12.7 Hz), 6.64 (d, J = 1.0 Hz), 3.97 (s), 3.93 (s), 3.90 (2 s), 3.88 (s), 3.85 (s). – ^{13}C NMR ($CDCl_3$, E:Z = 5:2): δ/ppm = 153.2 (C), 153.1 (C), 150.1 (C), 149.4 (C), 147.5 (C), 147.3 (C), 145.0 (C), 136.0 (C), 135.6 (C), 134.3 (CH), 130.4 (C), 129.8 (C), 129.5 (C), 129.4 (CH), 128.5 (C), 128.0 (CH), 124.3 (CH), 124.0 (CH), 123.6 (CH), 123.4 (CH), 123.1 (CH), 121.1 (CH), 118.3 (CH), 112.6 (CH), 112.4 (CH), 63.3 (CH_3), 62.8 (CH_3), 61.2 (CH_3), 60.9 (CH_3), 55.9 (CH_3), 55.8 (CH_3). – MS (EI, 70 eV): m/z = 351/349 (32%/100%) M^+.

$C_{17}H_{16}NO_5Cl$	Calcd.: C 58.38	H 4.61	N 4.00
(349.8)	Found: C 58.76	H 4.85	N 3.70

High resolution MS: Calcd.: 349.0717 Found: 349.0735.

(E/Z)-1-(5-Bromo-2-methoxy-3-nitrophenyl)-2-(2,3-dimethoxyphenyl)ethene (**11b**)

Yield 60% of **11b** as a yellow solid. – *m.p.* 119 °C. – ^1H NMR ($CDCl_3$, E:Z = 4:1): δ/ppm = 7.98 (d, J = 2.4 Hz), 7.81 (d, J = 2.4 Hz), 7.74 (d, J = 2.4 Hz), 7.50 (d, J = 16.6 Hz), 7.41 (d, J = 2.4 Hz), 7.32 (d, J = 16.6 Hz), 7.24 (m), 7.10 (t, J = 8.0 Hz), 6.99 (d, J = 12.3 Hz), 6.91 (m), 6.85 (dd, J = 8.2, 1.7 Hz), 6.68 (d, J = 12.3 Hz), 6.65 (dd, J = 7.4, 1.7 Hz), 3.97 (s, 3.93 (s), 3.91 (s), 3.90 (s), 3.89 (s), 3.85 (s). – ^{13}C NMR ($CDCl_3$, E:Z = 4:1): δ/ppm = 153.1 (2 C), 150.5 (C), 149.8 (C), 147.4 (C), 147.2 (C), 145.1 (C), 144.9 (C), 137.2 (CH), 136.3 (C), 135.9 (C), 133.4 (C), 130.3 (CH), 129.7 (C), 129.3 (CH), 127.9 (CH), 126.2 (CH), 124.3 (CH), 123.0 (CH), 121.1 (CH), 121.0 (CH), 118.2 (CH), 116.5 (C), 115.5 (C), 112.5 (CH), 112.3 (CH), 63.3 (CH_3), 62.7 (CH_3), 61.2 (CH_3), 60.9 (CH_3), 55.9 (CH_3). – MS (EI, 70 eV): m/z = 395/393 (100%/81%) M^+.

High resolution MS:	Calcd.: 393.0212
($C_{17}H_{16}NO_5Br$)	Found: 393.0229.

1-(3-Amino-2-methoxyphenyl)-2-(2,3-dimethoxyphenyl)ethane (**3-Me$_3$**)

A mixture of the stilbene derivative **11b** (700 mg, 1.78 mmol) and Pd/C (300 mg) in dichloromethane/methanol (1:1) is stirred for 75 h under an hydrogen atmosphere (50 bar). The catalyst is filtered off and solvent is removed *in vacuo*. The residue is dissolved in dichloromethane, washed with sat. aqueous $NaHCO_3$, dried ($MgSO_4$) and the dichloromethane is removed again. **3-Me$_3$** is obtained in quantitative yield as a brown oil. (**3-Me$_3$** analogously is obtained from **11a** in 82% yield). – IR (KBr): ν/cm^{-1} = 3452, 3364, 2935, 2830, 1612, 1585, 1482, 1430, 1291, 1269, 1220, 1081, 1008, 787, 751. – ^1H NMR ($CDCl_3$): δ/ppm = 7.01 (m, 1H), 6.91–6.80 (m, 3H), 6.69–6.64 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.79 (s, 3H), 2.97–2.87 (m, 4H). – ^{13}C NMR ($CDCl_3$): δ/ppm = 152.8 (C), 147.2 (C), 145.6 (C), 139.7 (C), 136.1 (C), 135.4 (C), 124.5 (CH), 123.8 (CH), 122.0 (CH), 119.8 (CH), 114.1 (CH), 110.3 (CH), 60.7 (CH_3), 59.7 (CH_3), 55.7 (CH_3), 31.4 (CH_2), 31.1 (CH_2). – MS (EI, 70 eV): m/z = 287 (100%) M^+.

High resolution MS:	Calcd.: 287.1521
($C_{17}H_{21}NO_3$)	Found: 287.1534.

1-(3-Amino-2-hydroxyphenyl)-2-(2,3-dihydroxyphenyl)ethane (**3-H$_3$**)

The derivative **3-Me$_3$** (164 mg, 0.571 mmol) is dissolved in

degassed dichloromethane (10 ml) under argon. At 0 °C a 1M solution of BBr_3 in dichloromethane (3 ml, 3 mmol) is added and the solution is stirred at room temperature for 15 h. Methanol (3 ml) is added and solvent is removed *in vacuo*. The residue is dissolved in diethyl ether, washed with sat. aquaeous $NaHCO_3$ and dried ($MgSO_4$). Removal of the ether affords **3-H$_3$** as a slightly brown solid (110 mg, 79%). – *m.p.* 190 °C. – IR (KBr): ν/cm^{-1} = 3306, 3052, 2953, 2871, 2645, 1624, 1591, 1485, 1360, 1203, 1018, 925, 826, 739. – UV/Vis (methanol) λ/nm = 204 (ε = 65000), 280 (shoulder), 442 (ε = 320). – ^{1}H NMR ([D$_4$]-methanol): δ/ppm = 6.58–6.64 (m, 6H), 2.81 (s, 4H). – ^{13}C NMR ([D$_4$]-methanol): δ/ppm = 145.0 (C), 144.1 (C), 143.9 (C), 130.4 (C), 130.3 (C), 121.9 (CH), 121.5 (CH), 121.4 (CH), 120.4 (CH), 115.9 (CH), 114.1 (CH), 32.2 (CH_2), 31.9 (CH_2). – MS (EI, 70 eV): m/z = 245 (100%) M$^+$.

High resolution MS:	Calcd.: 245.1052			
($C_{14}H_{15}NO_3$)	Found: 245.1070			
$C_{14}H_{15}NO_3 \cdot$ ¼ H_2O	Calcd.:	C 67.32	H 6.25	N 5.61
(249.8)	Found:	C 67.52	H 6.37	N 5.38.

References

[1] Recent review: C. Piguet, G. Bernardinelli, G. Hopfgartner, Chem. Rev. **1997**, *97*, 2005

[2] a) M. Albrecht, C. Riether, Synlett **1995**, 309; b) M. Albrecht, C. Riether, Synthesis **1997**, 957

[3] M. Albrecht, R. Fröhlich, J. Am. Chem. Soc. **1997**, *119*, 1656

[4] a) M. Albrecht, S. Kotila, Angew. Chem. **1996**, *108*, 1299; Angew. Chem. Int. Ed. Engl. **1996**, *35*, 1208; b) M. Albrecht, H. Röttele, P. Burger, Chem. Eur. J. **1996**, *2*, 1264

[5] W. v. Miller, Ber. Deutsch. Chem. Ges. **1887**, *20*, 1927

[6] M. Lovett, L. Roberts, J. Chem. Soc. **1928**, 1978

[7] a) M. Hudlicky, J. Org. Chem. **1980**, *45*, 5377; b) T. H. Black, Aldrichchimica Acta **1983**, *16*, 3

Address for correspondence:
Priv.-Doz. Dr. Markus Albrecht
Institut für Organische Chemie der Universität Karlsruhe
Richard-Willstätter-Allee
D-76131 Karlsruhe
Fax Int. Code + (721) 698 529
E-mail: albrecht@ochhades.chemie.uni-karlsruhe.de