134. Cyclometalation of Arylazo Compounds. Part 1 Synthesis and Cyclopalladation of Some Substituted 1-Arylazonaphthalenes

1st Communication on Compounds with a Metal-Arene σ-Bond

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(4. V. 81)

Summary

The syntheses of 1-phenylazonaphthalene (**1a**) and its [3′-methyl- (**1b**), 4′-methoxy- (**1c**), 3′-methoxy- (**1d**)] derivatives are described. Cyclopalladation of these azo ligands with Pd(II) acetate or Na_2PdCl_4 leads to complexes with Pd(II) coordinated on the azo N_β-atom and a Pd-C σ-bond at C(2) in the naphthalene moiety. The preference of Pd(II) for this type of metalation at C(2) over the palladation at the *ortho* positions of the phenyl ring or at the *peri* position of the naphthyl ring is believed to be largely due to steric effects and the different reactivities of the two arene moieties. Substitution of the acetato-bridge with bromide or iodide allows the syntheses of the corresponding bromo- and iodo-bridged complexes, and a chloro-bridged dimer complex can be converted to a monomeric ethylenediamino-Pd(II)-azo species with ethylenediamine. Cyclopalladation of sulfonated azo ligands leads to water-soluble Pd(II) complexes with a Pd-C σ-bond at C(2).

Cyclometalation is the reaction of a transition metal complex in which a suitable ligand interacts intramolecularly with the metal ion *via* a coordinative bond and a metal-carbon σ-bond, thus generating a chelate ring [2]. The first examples of a cyclometalation reaction with azobenzenes as ligands were a Ni(II)-azobenzene complex [3] and the Pd(II) and Pt(II) analogues [4]. Since these discoveries, a growing interest in cyclometalated compounds has become apparent in numerous reviews of an increasing flood of papers on this branch of organometallic chemistry [5–9].

Azobenzene and some of its symmetrically or unsymmetrically substituted derivatives have always played an important role as ligands for cyclometalations, but cyclopalladations with the unsymmetrical 1-phenylazonaphthalenes have not yet been described. With these ligands, however, the different reactivities of the phenyl and the naphthyl rings with respect to the palladation reaction can be compared directly. At the same time the pre-coordination of Pd(II) on one of the two azo N-atoms and thus the site of palladation can also be governed by steric influences.

[1]) Results taken from the PhD. thesis of *A. J. Klaus* [1].

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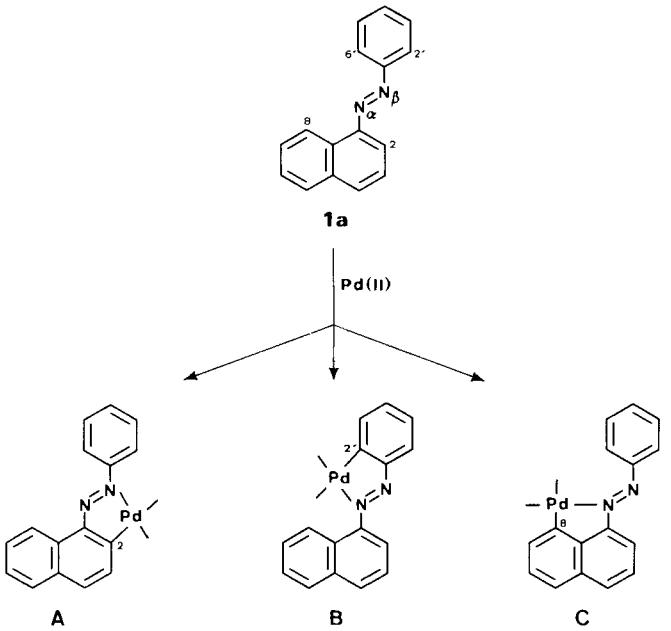
Investigations of *Cope & Friedrich* [10] have shown that the formation of a five-membered chelate ring is a necessary prerequisite for cyclopalladation. Thus, the cyclopalladation of 1-phenylazonaphthalene (**1a**) could theoretically lead to Pd(II)-azo complexes having the general structures A, B, and C *(Scheme 1)*.

Scheme 1



We assume as a simplified mechanism of cyclopalladation that in a first step the Pd(II) species is coordinated at one N-atom of the azo function and that in the second step the Pd-C σ-bond is formed[2]). For the pre-coordination, in addition to the different basicities of the two N-atoms, steric factors will be predominant, whereas the electrophilic metalation step will be determined mainly by electronic influences (inductive and mesomeric effects). Both steric and electronic factors favour the formation of a complex of type A, because the azo N_β-atom seems to be more easily accessible for the pre-coordination and the more electron-rich naphthyl ring seems to be better suited for the electrophilic palladation. In contrast, the formation of complexes of type B and C requires that the Pd(II) species be coordinated at the N_α-atom which is sterically shielded by the *peri*-proton H–C (8).

Our experiments with the azo ligands **1a, 1b, 1c,** and **1d** confirm our assumptions: only cyclopalladated complexes of type A are formed *(Scheme 2)*, even though the phenyl moiety has been substituted by increasingly stronger electron donor substituents (**1a**: R=R′=H, **1b**: R=H, R′=CH_3 at C(3′), **1c**: R=H, R′=OCH_3 at C(4′), **1d**: R=H, R′=OCH_3 at C(3′)).

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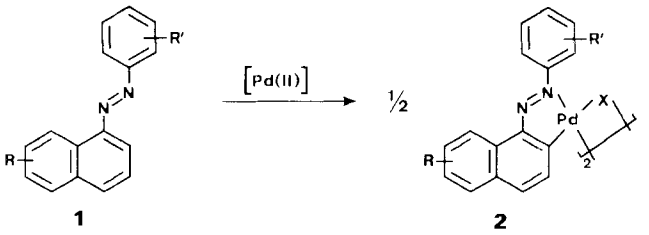
[2]) *Parshall* [11] has proposed a more detailed mechanism for the cyclopalladation of azobenzene with Na_2PdCl_4.

Scheme 2

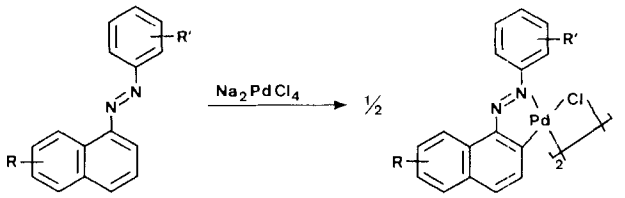


1 **2**

1a	R=R'=H	**2a**	R=R'=H, X=OAc
1b	R=H, R'=CH_3 at C(3')	**2b**	R=H, R'=CH_3 at C(3'), X=OAc
1c[3])	R=H, R'=OCH_3 at C(4')	**2c**[3])	R=H, R'=OCH_3 at C(4'), X=OAc
1d	R=H, R'=OCH_3 at C(3')	**2d**	R=H, R'=OCH_3 at C(3'), X=OAc
		2e	R=R'=H, X=Cl
		2f	R=H, R'=CH_3 at C(3'), X=Cl
		2g[3])	R=H, R'=OCH_3 at C(4'), X=Cl
		2h	R=H, R'=OCH_3 at C(3'), X=Cl
		2i	R=R'=H, X=Br
		2k	R=H, R'=OCH_3 at C(4'), X=Br
		2l	R=R'=H, X=I
		2m	R=H, R'=OCH_3 at C(4'), X=I

The acetato-bridged complexes **2a–d** are soluble in most organic solvents except alcohols, whereas the chloro-bridged complexes **2e–h** are dissolved only by *N,N*-dimethylformamide (DMF). Water-soluble complexes were obtained by cyclopalladation of the sulfonated ligands **3a–c** *(Scheme 3)*.

Scheme 3



3 **4**

3a and **4a**	R=H, R'=SO_3^- at C(4')
3b and **4b**	R=SO_3^- at C(7), R'=H
3c[4]) and **4c**[4])	R=SO_3^- at C(6), R'=SO_3^- at C(4')

An osmometric molecular weight determination of the acetato-bridged complex **2a** in methylene chloride shows a binuclear structure. The complexes with chlorine ligands exist as dimers in the solid state, as an X-ray analysis of the chloro-bridged Pt(II)-azobenzene complex has shown [12]. For the dissolved complexes of this kind, however, it still has to be shown, whether they are binuclear or a monomeric species is formed by a solvent molecule *S* cleaving the chloro-bridge:

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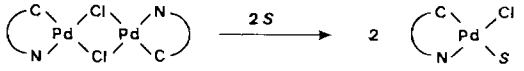
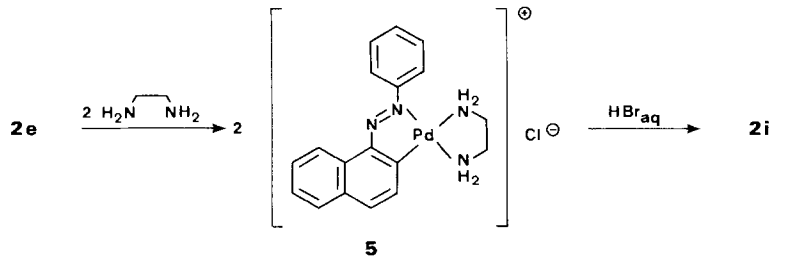
[3]) Syntheses of **1c**, **2c** and **2g** formed part of the diploma work of *M. Hugentobler*, ETHZ (1979).

[4]) Syntheses of **3c** and **4c** formed part of the diploma work of *H. Diener*, ETHZ (1979).



The exchange of the chlorine ligands of complex **2e** by ethylenediamine led to the ionic, monomeric complex **5**[5]). By treating this complex with hydrogen bromide the bromo-bridged complex **2i** could be obtained *(Scheme 4)*.

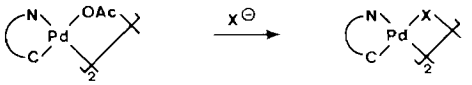
Scheme 4



5

Generally, halogeno-bridged complexes are also accessible by the reaction of acetato-bridged complexes with halogenides X^- [13] *(Scheme 5)*. Using this method we synthesized the bromo-bridged complex **2k**[6]) and the iodo-bridged complexes **2l** and **2m**[6]).

Scheme 5



The IR. spectra of the chloro-bridged complexes **2e–h** show a medium to strong Pd, Cl-stretching vibration band around 280 cm^{-1}. This absorption is assigned to the vibration of the Pd,Cl-bond *trans* to the Pd,C-bond. The other Pd,Cl-bond *trans* to Pd,N gives rise to an absorption band around 330 cm^{-1}. These assignments are in agreement with those for the chloro-bridged Pd(II)-azobenzene complex [14] and take into consideration the stronger *trans-influence* [15] of the aromatic C-atom compared to the azo N-atom as donor. Increasing *trans-influence* of a ligand results in lengthening and weakening of the Pd,Cl-bond *trans* to it, *i.e.* in a shift of the corresponding stretching frequency towards lower energies. On the other hand, the decrease of the *trans-influence* and with it the decrease of the σ-donor quality of the C-atom ligand *trans* to the Pd,Cl-bond can be correlated with an increase of the stretching frequency of the Pd,Cl-bond *(Table 1)*.

In contrast to the practically insoluble chloro-bridged complexes **2e–h**, the aceto-bridged Pd(II)-azo complexes **2a–d** are suitable for ^{13}C-NMR. investigations. The ^{13}C-resonance of the palladated C(2)-atom typically appears around 161 ppm. This corresponds to a low-field shift of about 40 ppm compared to the chemical shift of this C-atom in the non-coordinated ligand *(Table 2)*.

5) For **5** also *non-ionic* structures could be assumed such as, for example, either a four-coordinated complex with Cl^- instead of one of the azo N-atoms as ligand, or a five-coordinated species with Cl^- as an additional ligand. This structural problem is under investigation.

6) Syntheses of **2k** and **2m** formed part of the diploma work of *M. Hugentobler*, ETHZ (1979).

Table 1. *Far-IR. data for some chloro-bridged Pd(II) complexes (CsBr disks). Influence of the C-atoms as donor system on the Pd, Cl-stretching vibration ν (Pd, Cl)* trans *to the Pd, C-bond.*

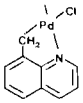
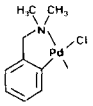
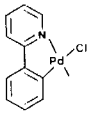
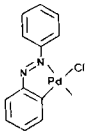
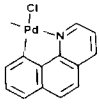
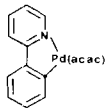
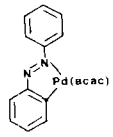
Complex	Type of the palladated C-atom	Wavenumber of the Pd, Cl-stretching vibration	Ref.
	C(aliphatic)	227	[16]
	C(phenyl)	247	[14]
	C(phenyl)	248/251	[17]
	C(phenyl)	262 264	[14] [16]
	C(naphthyl)	287	[16]
2e **2f** **2g** **2h**	C(naphthyl)	280 282 278 281	this work

Table 2. *^{13}C-NMR. data for some palladated ^{13}C-centres ($CDCl_3$, TMS as internal reference). Comparison with the chemical shifts δ of the same centre in the non-coordinated ligand.*

	δ (C(2)) / (ppm)		Ref.
	Complex	Ligand	
	165.6	126.3	[17]
	163.8	122.5	[18]
2a	161.1	123.5	this work
2b	161.2	123.5	
2c	161.4	123.6	

In the ^{1}H-NMR. spectrum the cyclopalladation at C(2) generates an *AB*-coupling system for the protons H-C(3) and H-C(4). The chemical shift of the sharp doublet for H-C(3) depends strongly upon the additional ligands at the Pd(II) centre: it is shifted towards lower field in the series OAc < en < Cl < Br < I *(Table 3)*.

Table 3. *^{1}H-NMR. data of complexes of the general structure*  *with different ligands X* (chemical shifts [ppm] of proton H-C(3), *ortho* to the Pd,C-bond)
en = X–X = ethylenediamine (*N,N*-coordinated); OAc = acetate (*O,O*-coordinated)

Ligand ()	Complex				
	X = OAc	X–X = en	X = Cl	X = Br	X = I
1a	6.77	7.38	8.24	8.52	8.97
1c	6.78		8.22	8.50	8.95
Solv.	$CDCl_3$	CD_3OD	*N,N*-dimethylformamide-d_7		

Cyclopalladation with Pd(II) acetate (acetato-bridged complexes **2a–d**) results in a high-field shift of the H-C(3) resonance, whereas in the halogeno-bridged complexes **2e–m** and **4a–c** the H-C(3) signal is shifted significantly towards lower field compared to that in the non-coordinated ligand *(Table 4)*.

Table 4. *Chemical shifts of H-C(3)* ortho *to the Pd, C-bond* vs. *bridging group* (all δ-values in ppm; numbers of the complexes in parentheses)

Ligand	δ(H-C(3)$_{lig}$)	δ(H-C(3)$_{complex}$) *vs.* bridging group			
		OAc	Cl	Br	I
1a	7.56	6.77 (**2a**)	8.24 (**2e**)	8.52 (**2i**)	8.97 (**2l**)
1b	7.57	6.78 (**2b**)[7])	8.24 (**2f**)		
1c	ca. 7.58	6.78 (**2c**)	8.22 (**2g**)	8.50 (**2k**)	8.95 (**2m**)
1d	7.56	6.78 (**2d**)	8.25 (**2h**)		
3a	ca. 7.67		8.24 (**4a**)		
3b	ca. 7.54		8.24 (**4b**)		
3c	ca. 7.70		8.24 (**4c**)		
Solv.	$CDCl_3$[8])	$CDCl_3$	*N,N*-dimethylformamide-d_7		

Conclusion. – The formation of complexes of type A *(Scheme 1)* when ligands **1a–d** and **3a–c** were cyclopalladated could be predicted. It is not yet clear, however, which factor is responsible for the cyclopalladation at the naphthyl C(2)-atom, whether this is due to the less hindered access of the Pd(II) species to the azo N_β-atom or to the electronically favoured metalation at the more electron-rich naphthyl moiety in the intrinsic substitution step. The first factor can be influenced by steric action of *ortho*-substituents in the phenyl ring making the pre-coordination of the

[7]) The H-C(3) signal in DMF-d_7 appears at 6.81 ppm.

[8]) With the sulfonated ligands **3a–c** a few drops of CD_3OD or DMSO-d_6 were added to improve their solubility in $CDCl_3$.

Pd(II) species at N_β more difficult or even impossible. The second factor, *i. e.* the nucleophilicity of the naphthyl moiety, can be changed by introducing deactivating substituents such as, for example, nitro groups into the ring. A variation of substituents (electron-withdrawing/electron-releasing and substituents with steric influence) in the phenyl and naphthyl rings could allow the site of cyclopalladation to be altered at will.

Partial financial support of this work by *Ciba-Geigy AG., Basel* is gratefully acknowledged. We also thank Mr. *Felix Bangerter* for his important contributions to our NMR. investigations.

Experimental Part

General remarks. For the syntheses, solvents of the highest available purity (*Fluka AG, Buchs SG,* Switzerland or *Merck AG, Darmstadt,* Germany) were used. 1-Naphthylamine was a *Merck* product of *puriss.* quality. Pd(II) salts were bought from *Johnson, Matthey & Brandenberger AG, Zürich* ($PdCl_2$, Na_2PdCl_4 and Palladium(II) acetate = $Pd(OAc)_2$) or from *Fluka AG, Buchs SG,* Switzerland (Na_2PdCl_4 and $Pd(OAc)_2$). Yields are not optimized. Abbreviations: i.V. = in vacuum; RT. = room temperature.

For thin layer chromatography (TLC.), 0.25 mm precoated silica gel plates (Kieselgel 60 F_{254}, *Merck AG*) and for preparative thick layer chromatography 2 mm precoated silica gel plates (PSC-Fertigplatten Kieselgel F_{254}, *Merck AG*) were used. Column chromatography was performed on silica gel (Kieselgel 60, 70–230 mesh, *Merck AG*) or alumina (*Woelm* B, neutral).

Melting points (m.p.) were determined on a *Büchi*-SMP-20 or on a *Mettler*-FP-61 apparatus and are uncorrected.

Microanalyses and the molecular weight determination were carried out by *D. Manser* (Dept. of Organic Chemistry, ETHZ). The palladium content was analyzed by atomic absorption spectroscopy in the Dept. of Inorganic Chemistry, ETHZ (PD Dr. *B. Magyar*).

Electronic spectra (UV./VIS.) were recorded on a *Beckman* Acta II or *Beckman* Acta III spectrometer (absorption maxima λ_{max} in nm, absorption coefficient ε in M^{-1} cm^{-1} in parenthesis, *S* denotes a shoulder). The absorption coefficients for the Pd(II) complexes are calculated assuming dimeric complexes. IR. spectra (CsBr disks) were run on the *Beckman* IR.-4250 spectrophotometer of the Dept. of Inorganic Chemistry, ETHZ. Absorptions are given in cm^{-1} (intensities: *vs* = very strong, *s* = strong, *m* = medium, *w* = weak, *vw* = very weak, *S* = shoulder, br. = broad absorption band). ^{1}H-NMR. spectra (90 MHz) were measured by Mr. *F. Bangerter* on a *Bruker* HX-90 or on a *Bruker* WH-90 spectrometer which was also used to record the ^{13}C-NMR. spectra at 22.63 MHz. ^{1}H-NMR. spectra (360 MHz) were run by Mr. *A. Eugster* on a *Bruker* HX-360 spectrometer in the Dept. of Molecular Biology & Biophysics, ETH Hönggerberg (Prof. Dr. *K. Wüthrich*). The chemical shifts are reported in δ (ppm) relative to TMS as internal reference (TSP as reference when D_2O was used as solvent). For each signal the multiplicity (with the abbreviations: *s* = singlet, *d* = doublet, *d* × *d* = doublet which is split by a second spin coupling, *t* = triplet, *qa* = quadruplet, *m* = multiplet, br. = broad), the coupling constant *J* in Hz, and – where possible – the relative intensity and the assignment are given in parenthesis. For some multiplets in the 360-MHz spectra a medium chemical shift instead of the range is reported. Signals were assigned to the corresponding protons on the basis of couplings and signal patterns. In some cases assignments were confirmed by decoupling experiments.

Mass spectra (MS.) were registered on a *Hitachi-Perkin Elmer* RMU-6M mass spectrometer (double-focusing, 70 eV) by Mrs. *L. Golgowski* in the Dept. of Organic Chemistry, ETHZ (Prof. Dr. *J. Seibl*). Ions are reported in *m/z*-values and relative intensities in % relative to the base peak in parenthesis. A metastable transition is denoted as *m**.

The nomenclature system for the azo compounds and their cyclometalated complexes is described in detail in [1].

Syntheses of the ligands. – *Synthesis of 1-phenylazonaphthalene* (**1a**). Ligand **1a** was obtained by the method of *Martynoff* [19] from 1-naphthylamine and nitrobenzene with addition of powdered NaOH at about 180° in 13% yield.

Synthesis of **1a** *from N-sulfinyl-1-naphthylamine and N-phenylhydroxylamine* [20]. To a solution of 5 g (35 mmol) 1-naphthylamine in 50 ml dry benzene were added 2.5 ml (35 mmol) $SOCl_2$. The resulting yellow precipitate dissolved almost completely after the suspension had been refluxed for 3 h. The remaining small amount of black precipitate was filtered off, and the clear, yellowish brown filtrate was dropped into 150 ml of a benzene solution containing about 70 mmol *N*-phenylhydroxylamine (synthesized according to [21]). The reddish-brown reaction mixture was stirred for 16 h at 50°, the black precipitate separated, and the clear dark red filtrate dried (Na_2SO_4) and passed through a column filled with alumina. The crude product was purified by column chromatography (silica gel, toluene, toluene/CH_2Cl_2, CH_2Cl_2). Recrystallization from ethanol/water or ether/methanol yielded 1.49 g (18%) **1a** as dark red crystals, m.p. 69–70° ([19]: 70°). – UV./VIS. (EtOH): 273 (11000), 371 (13200); (DMF): 375 (10400). – IR.: 3065*m*, 3050*m*, 1588*m*, 1572*m*, 1509*s*, 1481*m*, 1470*w*, 1457*m*, 1432*w* br., 1390*s*, 1348*m*, 1309*w*, 1302*w*, 1261*w*, 1216*s*, 1185*w*, 1158*m*, 1141*m*, 1081*w*, 1070*m*, 1032*w*, 1021*m*, 1013*m*, 998*w*, 989*w*, 974*w S*, 968*w*, 960*w S*, 923*s*, 870*m*, 840*w*, 805*vs*, 781*s*, 762*vs*, 736*s S*, 689*vs*, 658*m*, 568*s*, 550*m*, 501*s*, 484*m*, 421*m*, 399*m*, 250*w*. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.50 (*m*, 1H, H–C(4′)); 7.56 (*m*, 1H, H–C(3)); 7.57–7.64 (*m*, 4H, H–C(3′, 5′, 6 and 7)); 7.82 (*d* × *d*, *J*=7.5 and 1.1, 1H, H–C(2)); 7.92 (br. *d*, *J*=8.2, 1H, H–C(5)); 7.98 (*d*, *J*=8.2, 1H, H–C(4)); 8.05 (*m*, 2H, H–C(2′ and 6′)); 8.93 (br. *d*, *J*=8.6, 1H, H–C(8)). – ^{13}C-NMR. ($CDCl_3$): 111.9 (*d*), 123.2 (*d*, 2C), 123.5 (*d*, C(2)), 125.7 *(d)*, 126.5 *(d)*, 126.9 *(d)*, 128.0 *(d)*, 129.2 (*d*, 2C), 131.1 *(d)*, 131.27 *(s)*, 131.31 *(d)*, 134.4 *(s)*, 147.9 *(s)*, 153.3 *(s)*. – MS.: 233 (16), 232 (M^+,84), 203 (12), 202 (15), 155 (6), 128 (18), 127 (100), 126 (14), 105 (7), 101 (8), 77 (57), 63 (4), 51 (15), 39 (2).

$C_{16}H_{12}N_2$ (232.3) Calc. C 82.73 H 5.21 C 12.06% Found C 82.55 H 5.28 N 12.19%

Synthesis of 1-(3′-methylphenylazo)naphthalene **1b** [19]: The solution of 70.30 g (491 mmol) 1-naphthylamine in 56.11 g (409 mmol) 3-nitrotoluene was heated to 160–170°. Then 62 g (1.55 mol) powdered NaOH(s) were added slowly in small portions. The temperature was raised to 180°. After 1 h the reaction mixture was cooled to RT. and extracted alternately with water and ether. After several extractions the tarry residue was separated and the aqueous layer neutralized with 160 ml conc. HCl-solution and once more extracted with ether. The ether solutions were dried (Na_2SO_4), evaporated and the dark brown residue distilled three times i. V.. Crystallization of the red oil from cold ether/methanol yielded 12.43 g (12%) bright red crystals of **1b**, m.p. 44.5°. – UV./VIS. ($CHCl_3$): 374 (10700), 460 *S*; (DMF): 299 (8000), 375 (11300), 460 *S*. – IR.: 3060*s* br., 3035*m* sh, 2955*w*, 2925*m*, 2865*w*, 1609*m*, 1604*m*, 1590*m*, 1575*w*, 1512*s*, 1485*m*, 1436*w*, 1390*s*, 1380*m*, 1348*s*, 1309*w*, 1290*w*, 1264*w*, 1250*m*, 1242*m*, 1224*m*, 1204*m*, 1158*w*, 1145*w*, 1129*w*, 1088*m* br., 1036*w* br., 1018*m*, 1001*w*, 972*w*, 955*w*, 915*m*, 881*m*, 868*w*, 807*vs*, 775*vs* br., 739*w*, 695*vs*, 662*w*, 579*s* br., 560*m*, 538*m*, 501*m*, 490*m*, 470*w*, 448*s*, 418*m* br., 332*m* br., 255*w* br., 220*w* br. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 7.33 (br. *d*, *J*=7.6, 1H, H–C(4′)); 7.45 (*m*, 1H, H–C(5′)); 7.57 (*t*, *J*=7.6, H–C(3)); ~7.58 (*m*, H–C(6)); 7.65 (*m*, H–C(7)); 7.80 (*d* × *d*, *J*=7.6 and 1.0, 1H, H–C(2)); ~7.85 (*m*, 2H, H–C(2′ and 6′)); 7.93 (br. *d*, *J*=8.0, 1H, H–C(5)); 7.98 (*d*, *J*=8.3, 1H, H–C(4)); 8.93 (*d*, *J*=8.5, 1H, H–C(8)). – ^{13}C-NMR. ($CDCl_3$): 21.4 (*qa*, CH_3), 111.9*(d)*, 120.6*(d)*, 123.5*(d*, 2C), 125.6*(d)*, 126.4 *(d)*, 126.8 *(d)*, 127.9 *(d)*, 128.9 *(d)*, 131.2 *(d)*, 131.3 *(s)*, 131.8 *(d)*, 134.3 *(s)*, 139.0 *(s)*, 147.9 *(s)*, 153.3 *(s)*. – MS.: 247 (11), 246 (M^+, 55), 245 (5), 231 (1), 217 (3), 215 (4), 210 (6), 203 (8), 202 (15), 155 (4), 128 (14), 127 (100), 126 (12), 119 (6), 101 (7), 92 (6), 91 (74), 89 (5), 77 (14), 76 (3), 75 (6), 74 (2), 65 (24), 64 (2), 63 (7), 62 (2), 52 (2), 51 (8), 50 (3), 41 (5), 39 (12), 28 (3).

$C_{17}H_{14}N_2$ (246.3) Calc. C 82.90 H 5.73 N 11.37% Found C 82.70 H 5.78 N 11.47%

Synthesis of 1-(4′-methoxyphenylazo)naphthalene (**1c**). – *a) Synthesis of 1-(4′-hydroxyphenylazo)naphthalene* (**6**). A suspension of 12.11 g (50 mmol) 1-naphthyldiazoniumtetrafluoroborate (see [22]) in 100 ml 0.5M HCl was mixed with a concentrated aqueous solution of 5.0 g (53 mmol) phenol. The mixture was cooled to 0° and a solution of 25 g Na_2CO_3 in 100 ml water was added. After 1 h the temperature was raised to 70° for some minutes, the mixture acidified with phosphoric acid up to pH=2 and the brown precipitate collected. The crude product was dissolved almost quantitatively in CH_2Cl_2, the black insoluble material separated, and the organic solution extracted with 2M NaOH. The aqueous alkaline solution was acidified to pH=1 and extracted with ether. This ether solution was dried (Na_2SO_4) and evaporated, and an oily residue was obtained. Recrystallization from CH_2Cl_2/cyclohexane yielded 5.60 g (45%) orange needles of **6**. M.p. 136° ([23]: 136°). – UV./VIS. (EtOH): 250 *S*, 380 (21600). – IR.: 3600–2360*s* br., 1605*s*, 1600*s S*, 1568*w*, 1509*s*, 1468*m*, 1455*m*, 1438*m*, 1430*m S*, 1424*s*, 1390*m*, 1371*m*, 1348*w*, 1300*w S*, *1280s*, 1231*s*, 1204*w S*, 1160*s*, 1146*s*, 1105*w*, 1089*w*, 1013*w*, 975*w*, 953*w*, 942*w*, 931*w*, 874*w*, 865*w*, 839*s*, 822*m*, 803*s*, 791*w*, 780*s*, 777*s*, 738*m*, 714*w*, 640*w*, 572*w*, 538*m*, 518*s*, 480*m*, 432*w*, 391*w*, 378*w*, 364*w*, 340*w*, 318*w*, 233*w*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 5.12 (*s*, 1H, OH); 6.98 (*d* of the *AA′*-type, 2H, H–C(3′ and 5′)); 7.79 (*d* × *d*, *J*=7.5 and 2.1, 1H, H–C(2)); 7.45–8.00 (*m*, 5H); 8.01 (*d* of the *XX′*-type, 2H, H–C(2′ and 6′)); 8.81–9.00 (*m*, 1H, H–C(8)). –

MS.: 248 (M^+, 100), 219 (10), 155 (5), 149 (11), 128 (15), 127 (99), 126 (11), 121 (29), 93 (69), 77 (10), 65 (18), 57 (7), 51 (5), 43 (4), 41 (4), 39 (10).

$C_{16}H_{12}N_2O$ (248.3) Calc. C 77.40 H 4.87 N 11.28% Found C 76.88 H 4.96 N 11.09%

b) Synthesis of ligand **1c.** To a solution of 5.40 g (21.8 mmol) **6** in 14 ml 10% NaOH-solution were added 2.1 ml (22 mmol) dimethyl sulfate. This solution was stirred for 1 h at RT. and then refluxed for ½ h. Afterwards it was extracted with ether, the organic layer washed with diluted NaOH-solution, dried (Na_2SO_4), and evaporated. The oily residue was recrystallized from ether/methanol affording 2.93 g (51%) reddish-brown crystals of **1c**, m.p. 79.5° ([24]: 73–74.5°). – UV./VIS. ($CHCl_3$): 381 (15500), 470 *S*; (DMF): 384 (17200), 460 *S*; (EtOH): 378 (13500), 465 *S*. – IR.: 3058*m*, 3004*w*, 2970*m*, 2948*w*, 2930*w*, 2840*m*, 1596*s*, 1571*m*, 1501*s*, 1461*m*, 1455*m*, 1446*m*, 1417*w*, 1386*m*, 1312*s*, 1296*w*, 1264*s* sh, 1256*s*, 1220*w*, 1190*w* sh, 1182*m*, 1165*w*, 1156*m*, 1138*s*, 1105*m*, 1081*w*, 1035*s*, 1013*w*, 975*w*, 960*w*, 948*w*, 868*w*, 838*s*, 810*m*, 805*m*, 795*w*, 778*s*, 725*w*, 642*w*, 564*w*, 541*m*, 518*m*, 482*w*, 448*w*, 435*w*, 388*w*. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 3.91 (*s*, 3H, OCH_3); 7.04 (*d*, *J*=9, 2H, H–C(3′ and 5′)); 7.52–7.64 (*m*, 3H, H–C(3, 6 and 7)); 7.78 (*d*, *J*=8.5, 1H, H–C(2)); 7.90 and 7.93 (two *d*, 2H, H–C(4 and 5)); 8.04 (*d*, *J*=9, 2H, H–C(2′ and 6′)); 8.91 (*d*, *J*=9, 1H, H–C(8)). – ^{13}C-NMR. ($CDCl_3$): 55.4 (*qa*, OCH_3), 111.7 *(d)*, 114.3 (*d*, 2C, C(3′) and C(5′)), 123.6 *(d*, C(2)), 125.1 (*d*, 2C, C(2′) and C(6′)), 125.7 *(d)*, 126.4 *(d)*, 126.6 *(d)*, 127.9 *(d)*, 130.6 *(d)*, 131.4 *(s)*, 134.4 *(s)*, 147.8 *(s)*, 148.0 *(s)*, 162.2 *(s*, C(4′)). – MS.: 264 (2), 263 (19), 262 (M^+, 100), 261 (4), 247 (5), 219 (4), 218 (2), 202 (2), 191 (4), 190 (5), 189 (6), 155 (2), 149 (5), 136 (3), 135 (29), 131 (4), 128 (8), 127 (73), 126 (7), 108 (6), 107 (57), 101 (4), 97 (2), 92 (11), 83 (3), 79 (2), 78 (3), 77 (23), 76 (2), 75 (3), 71 (3), 69 (3), 64 (6), 63 (3), 57 (4), 55 (3), 51 (3), 43 (4), 41 (3); *m** 84.5 (*m/z* 135→ *m/z* 107), *m** 194 (*m/z* 247→ *m/z* 219), *m** 233 (*m/z* 262→ *m/z* 247).

$C_{17}H_{14}N_2O$ (262.3) Calc. C 77.84 H 5.38 N 10.68% Found C 77.80 H 5.40 N 10.68%

Synthesis of 1-(3′-methoxyphenylazo)naphthalene (**1d**) [24]. To the solution of the *Grignard* reagent synthesized from 9.37 g (50 mmol) 3-bromoanisole *(Fluka, purum)* in 20 ml dry ether and 1.22 g (50 mmol) magnesium turnings in 10 ml ether a suspension of 12.10 g (50 mmol) 1-naphthyldiazoniumtetrafluoroborate (see [21]) in 150 ml dry ether was added slowly. Vigorous stirring kept the reaction mixture boiling for ½ h. This mixture was left at RT. for 12 h and the precipitate filtered off. The dark red filtrate was washed with 1 *M* HCl and water and dried ($MgSO_4$). The solution was concentrated i.V. and the residue chromatographed (140 g silica gel, toluene). Naphthalene and 1,1′-azonaphthalene were among the side products eluted from the column. Ligand **1d** was obtained as a dark red oil that crystallized from the melt. Two recrystallizations from ether/methanol yielded 0.188 g (1.4%) **1d** ([24]: 11%[9]), m.p. 50° ([24]: 55–56°). – UV./VIS. ($CHCl_3$): 295 (7100), 377 (13500), 460 *S*; (DMF): 297 (7200), 380 (13900), 465 *S*. – IR.: 3065*w*, 3020*m*, 2975*w*, 2945*w*, 2840*w*. 1610*s*, 1584*s*, 1575*m S*, 1512*m*, 1496*s*, 1470*w*, 1458*m*, 1432*s*, 1390*w*, 1378*w*, 1162*w*, 1131*m*, 1085*m*, 1050*s*, 1037*m*, 1016*w*. 997*w*, 980*w*, 969*w*, 940*w*, 917*w*, 891*m*, 874*s*, 830*w*, 810*s*, 789*m S*, 778*vs*, 730*w*, 693*s*, 665*w*, 571*m* br., 510*m*, 500*w*, 478*w*, 460*w*, 430*w*, 376*w*, 270*w*. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 3.92 (*s*, 3H, OCH_3); 7.07 (*d* × *d*, *J*=7.8 and 1.9, H–C(4′)); 7.46 (*t*, *J*=7.8, H–C(5′)); 7.47–7.71 (*m*), including 7.63 (*t*, H–C(7)); 7.80 (*d* × *d*, *J*=7.8 and < 1, H–C(2)); 7.91 and 7.97 (2*d*, *J*=7.8 and 8.7 resp., H–C(4 and 5)); 8.91 (*d*, *J*=8.4, H–C(8)). – MS.: 264 (2), 263 (17), 262 (M^+, 85), 261 (4), 247 (2), 234 (2), 233 (1), 219 (3), 218 (4), 204 (3), 203 (4), 202 (2), 191 (4), 190 (4), 189 (7), 155 (7), 135 (2), 128 (15), 127 (100), 126 (8), 108 (3), 107 (26), 101 (4), 92 (10), 77 (16), 76 (2), 75 (3), 64 (5), 63 (4), 51 (4), 39 (2); *m** 104 (*m/z* 155→ *m/z* 127), *m** 233 (*m/z* 262→ *m/z* 247).

$C_{17}H_{14}N_2O$ (262.3) Calc. C 77.84 H 5.38 N 10.68% Found C 77.37 H 5.41 N 11.07%

Synthesis of 1-(4′-sulfophenylazo)naphthalene (**3a**). – a) *Synthesis of 4-amino-1-(4′-sulfophenylazo)naphthalene* (**7**). The suspension of the diazonium salt obtained from 17.32 g (100 mmol) sulfanilic acid *(Fluka, puriss.)* by diazotation was added at 0° to 14.32 g (100 mmol) 1-naphthylamine in 1 *M* HCl. After 1 h the temperature was raised to 25° and the suspension stirred furthermore for 1 h. The thick reddish-brown paste was separated in a centrifuge and treated with hot 5% Na_2CO_3-solution. The undissolved material was filtered off and identified as the *ortho*-coupling product. Cooling of the hot filtrate yielded an orange precipitate that was collected and recrystallized from hot water to afford the pure aminoazo compound **7**. – ^{1}H-NMR. (90 MHz, DMSO-d_6): 6.78 (*d*, *J*=8.4, H–C(3)); 7.53–7.59 (*m*); 7.78 (*s*) and 7.79 (*s*), H–C(2′ and 6′) and H–C(3′ and 5′) or *vice versa*; 7.90 (*d*, *J*=8.6, 1H, H–C(2)); 8.15–8.25 (*m*, H–C(5)); 8.86–8.95 (*m*, H–C(8)).

$C_{16}H_{12}N_3NaO_3S$ (349.3) Found C : N : S = 16 : 3 : 1.

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[9]) In [24] the zinc-chloride double salt of the diazonium ion was used instead of the tetrafluoroborate.

b) *Synthesis of ligand* **3a** (by reductive deamination according to [25]). The suspension of 35 g (100 mmol) **7** in 100 ml glacial acetic acid and 150 ml ethanol was cooled to 0° and a total of 11.7 g (100 mmol) isoamyl nitrite added dropwise. After 2 h the temperature was raised to 25° and the reaction mixture left at that temperature for 24 h. The mixture was kept at 53° during 48 h and the warm suspension filtered. A yield of 3 g of practically pure **3a** was obtained after the filtrate had been evaporated and the crude product recrystallized twice from water/ethanol. Column chromatography of the purified product (150 g silica gel, acetone/methanol 9 :1 and acetone/methanol/water 18 :2 :1) yielded 1.5 g (4.5%) of **3a**. – UV./VIS. (H_2O): 278 (12000), 290 *S*, 380 (9200). – ^{1}H-NMR. (360 MHz, DMSO-d_6, 61°): 7.65–7.69 (*m*, H–C(3 and 6)); 7.74 (*m*, H–C(7)); 7.82 (*d* × *d*, *J*=7.5 and 1.1, H–C(2)); 7.86 and 8.00 (*d* of the *AA'*-type and *d* of the *BB'*-type resp., phenyl protons); 8.08 (br. *d*, *J*=8.0 H–C(5)); 8.16 (*d*, *J*=8.2, H–C(4)); 8.88 (br. *d*,, *J*=8.4, H–C(8)). – ^{1}H-NMR. (360 MHz, $CDCl_3$[10]), 25°): 7.59 (*t*, *J*=7.8, H–C(3)); 7.61 (*m* with 7 lines, H–C(6)); 7.68 (*m* with 7 lines, H–C(7)); 7.85 (*d* × *d*, *J*=7.5 and 1.1, H–C(2)); 7.97 (br. *d*, *J*=8.0, H–C(5)); *ca.* 8.05 (≈ *d*, H–C(4)); 8.07 (*s*, phenyl protons); 8.92 (*d*, *J*=8.4, H–C(8)).

$C_{16}H_{11}N_2NaO_3S$	Calc.	C 57.48	H 3.32	N 8.38	S 9.59%
(334.3)	Found	„ 57.32	„ 3.34	„ 8.42	„ 9.43%

Synthesis of sodium 1-phenylazonaphthalene-7-sulfonate (**3b**) [26]. The suspension of 5 g (22 mmol) 1-naphthylammonio-7-sulfonate (*Clève* acid-1,7, I. R. *Geigy AG*, 99%) in 25 ml 36% $NaHCO_3$-solution was mixed with 2.4 g (22 mmol) phenylhydrazine and heated to 140–150° for 24 h. On cooling the mixture a precipitate was obtained which was collected on a funnel and suspended in 60 ml 16% NaOH-solution. This suspension was heated under reflux, and air was blown into the mixture by means of a capillary. During this procedure the yellow-orange suspension turned clear. After 7 h the solution was cooled and the resulting precipitate recrystallized from hot water giving 3.2 g (43%) **3b** as orange needles, m.p. >300°. – UV./VIS. (EtOH): 268 (12800), 275 (12600), 368 (12900). – ^{1}H-NMR. (90 MHz, $CD_3OD/CDCl_3$ 1:1): 7.46–7.62 (*m*, *ca.* 2H); 7.69 (*d*, *J*=7.6, 1H); 7.87 (*d* × *d*, *J*=7.6 and 1.5, 1H, H–C(2)); 7.97–8.16 (*m*, 6H); 9.43–9.49 (*m*, 1H, H–C(8)).

$C_{16}H_{11}N_2NaO_3S$ (334.3) Found C : N : S = 16 : 2 : 1.1

Synthesis of sodium 1-(4'-sulfophenylazo)naphthalene-6-sulfonate (**3c**). – a) *Synthesis of 4-ammonio-1-(4'-sulfophenylazo)naphthalene-6-sulfonate* (**8**): Coupling diazotized sulfanilic acid on 1-naphthylammonio-7-sulfonate (I. R. *Geigy AG*, 99%) in 0.5 *M* NaOH at 0° yielded compound **8** almost quantitatively. – ^{1}H-NMR. (90 MHz, D_2O): 6.62 (*d*, *J*=8.8, 1H, H–C(3)); 7.47 (*d*, *J*=8.8, 1H, H–C(2)); 7.53 (*d* of the *AA'*-type, 2H, phenyl protons); 7.82 (*d* of the *BB'*-type, 2H, phenyl protons); 7.84 (*d* × *d*, *J*=9.0 and 1.6, 1H, H–C(7)); 8.19 (*d*, *J*=1.6, 1H, H–C(5)); 8.51 (*d*, *J*=9.0, 1H, H–C(8)).

b) *Synthesis of ligand* **3c** *by reductive deamination of* **8** *with* H_3PO_2 [27]. The solution of 16.93 g (30 mmol) **8** in 60 g (450 mmol) 50% aq. H_3PO_2-solution was cooled to 0° and a solution of 2.25 g (33 mmol) $NaNO_2$ in 15 ml water was added dropwise, whereby nitrogen gas was evolved. The reaction mixture was kept at RT. for 15 h and 57.8 g crude product collected. The main part of that product was sodium hypophosphite. The yield of pure **3c** was 4.6 g (28%). – UV./VIS. (H_2O): 278 (12100), 372 (10900), 460 *S*. – ^{1}H-NMR. (90 MHz, D_2O): 7.31–7.53 (*m*, 2H, H–C(2 and 3)); 7.54–7.94 (*m*, 6H); 8.14 (*d*, *J*=1.8, 1H, H–C(5)); 8.51 (*d*, *J*=9.0, 1H, H–C(8)). – ^{1}H-NMR. (90 MHz, $CD_3OD/CDCl_3$ 1:1): 7.70 (≈ *d*, *J*=7.9, *ca.* 1H); 7.92 (*d* × *d*, *J*=7.6 and 1.5, 1H, H–C(2 or 4); 8.00–8.20 (*m*, *ca.* 6H); 8.50 (*d*, *J*=1.5, 1H, H–C(5)); 8.98 (*d*, *J*=9.0, 1H, H–C(8)).

$C_{16}H_{10}N_2Na_2O_6S_2$ (436.4) Found C : N : S = 16 : 2 : 1.8

Syntheses of the Pd(II)-arylazonaphthalene complexes. – *General procedure for the syntheses of the aceto-bridged complexes* **2a–d**. The mixture of equimolar amounts of Pd(II) acetate and azo ligand in chloroform (passed through basic alumina) or methylene chloride solution is kept at RT. for several hours, then evaporated to dryness and the solid residue recrystallized from methylene chloride/light petroleum ether or from acetone/water.

General procedure for the syntheses of the chloro-bridged complexes **2e–h** and **4a–c**. The mixture of equimolar amounts of Na_2PdCl_4 and azo ligand (or Na_2PdCl_4 in slight excess) in methanolic solution is kept at RT. for several hours; the resulting precipitate of the chloro-bridged complex is then collected on a funnel and washed exhaustingly with methanol, water, methanol, and ether. In some cases the crude complex is recrystallized from DMF/ether.

[10]) One drop of CD_3OD was added in order to dissolve **3a** in $CDCl_3$.

Di-μ-acetato-bis(1-phenylazonaphthyl-C(2),N$_\beta$)dipalladium(II) (**2a**). From 0.858 g (3.7 mmol) **1a** in 10 ml $CHCl_3$ and 0.829 g (3.7 mmol) $Pd(OAc)_2$ in 10 ml $CHCl_3$, 120 h at RT.; yield 1.34 g (91%), m.p. 162–169° (dec.). – Mol.-wt. (CH_2Cl_2): 789 (calc.as dimer: 793). – UV./VIS. ($CHCl_3$): 305 (16900), 350 *S*, 402 (14000), 415 *S*, 510 (11800). – IR.: 3100*w*, 3065*s*, 3020*w S*, 1712*m*, 1618*s*, 1575*vs* br., 1496*vs*, 1482*s S*, 1458*s*, 1415*vs* br., 1366*s*, 1345*s S*, 1322*vs* br., 1265*m*, 1238*w*, 1220*m*, 1210*m*, 1192*vs*, 1170*w*, 1154*m*, 1140*w*, 1130*m*, 1109*w*, 1070*m*, 1047*w*, 1022*m*, 1000*w*, 964*w*, 920*m*, 887*m*, 863*w*, 828*s*, 818*s*, 767*vs*, 740*vs*, 710*w*, 692*vs*, 662*vs*, 650*m*, 630*m*, 578*s*, 545*m*, 522*m*, 501*w*, 434*s*, 401*w*, 378*w*, 338*s* br., 294*w* br., 262*w*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.18 (*s*, 3H, CH_3); 6.77 (*d*, *J*=8.5, 1H, H–C(3)); 6.90–7.85 *(m)*; 8.16–8.32 (*m*, 1H, H–C(8)); additional signals of the *cis*-dimer: 1.83 *(s)* and 2.41 *(s)* (CH_3); 7.90–8.15 *(m)* and 8.35–8.60 *(m*, arom. protons). – ^{13}C-NMR. ($CDCl_3$): 24.6 (*qa*, CH_3), 123.2 *(d)*, 125.3 *(d)*, 126.1 *(d)*, 127.7 *(d)*, 130.0 *(d)*, 130.8 *(d)*, 131.1 *(d)*, 131.5 *(s)*, 131.8 *(s)*, 132.1 *(d)*, 151.2 *(s)*, 156.7 *(s)*, 161.1 (*s*, Pd-C(2)), 180.9 (*s*, C=O). – MS.: 794 (M^+ of the dimer, trace), 735 (trace), 400 (2), 398 (4), 396 (M^+ of the monomer, 4), 395 (3), 394 (2), 358 (4), 357 (10), 350 (5), 348 (10), 346 (12), 345 (9), 344 (5), 339 (4), 337 (5), 336 (4), 308 (11), 307 (28), 291 (10), 290 (3), 289 (21), 288 (4), 287 (26), 286 (20), 285 (9), 257 (6), 233 (12), 232 (55), 220 (4), 204 (4), 203 (18), 202 (23), 183 (3), 182 (19), 155 (5), 154 (4), 153 (23), 152 (22), 151 (6), 128 (14), 127 (98), 126 (10), 115 (3), 108 (4), 106 (4), 105 (14), 101 (6), 78 (8), 77 (89), 76 (4), 75 (6), 45 (38), 44 (5), 43 (100).

$[C_{18}H_{14}N_2O_2Pd]_2$	Calc.	C 54.50	H 3.56	N 7.06	Pd 26.82%
(793.4)	Found	„ 54.50	„ 3.66	„ 7.01	„ 24.84%[11])

Di-μ-chloro-bis(1-phenylazonaphthyl-C(2),N$_\beta$)dipalladium(II) (**2e**). From 0.120 g (0.52 mmol) **1a** in 100 ml methanol and 0.116 g (0.52 mmol) Na_2PdCl_4 in 5 ml methanol, 2 h at 60–65° and 17 h at RT. (yield 0.186 g (96%)) or from 3.85 g (16.6 mmol) **1a** in 125 ml methanol and 4.88 g (16.6 mmol) Na_2PdCl_4 in 100 ml methanol, 100 h at RT. (yield 5.81 g (94%)), m.p. > 300°. – UV./VIS.(DMF): 399 (18200), 512 (10300), 527 (10300). – IR.: 3055*m*, 1680*m*, 1636*w* br., 1618*m*, 1567*s*, 1499*s*, 1482*m*, 1460*m*, 1427*w*, 1390*m*, 1378*s*, 1333*vs*, 1302 sh, 1268*w*, 1238*w*, 1193*s*, 1172*w*, 1155*w*, 1129*w*, 1070*m*, 1027*w*, 1002*w*, 980*vw*, 960*w*, 942*w*, 912*m*, 884*w*, 860*w*, 830*w*, 810*s*, 772*s* sh, 768*s*, 754*s*, 740*s*, 690*vs*, 660*s*, 632 *w* br., 577*m*, 549*m*, 520*m*, 444*w*, 430*m*, 400*w*, 349*w* br., 319*s*, 280*s*, 269*m* sh, 229*m* sh, 218*m*. – ^{1}H-NMR. (90 MHz, DMF-d_7): 7.50–7.80 (*m*, 5H); 7.89 (*d* × *d*, *J*=8.8 and 0.6, 1H, H–C(4)); 7.98–8.10 *(m)*; 8.24 (*d*, *J*=8.8, 1H, H–C(3)); 8.63–8.76 (*m*, 1H, H–C(8)).

$[C_{16}H_{11}ClN_2Pd]_2$	Calc.	C 51.50	H 2.97	Cl 9.50	N 7.51	Pd 28.51%
(746.3)	Found	„ 51.17	„ 3.20	„ 9.49	„ 7.68	„ 27.06%

Di-μ-bromo-bis(1-phenylazonaphthyl-C(2),N$_\beta$)dipalladium(II) (**2i**). To a methanolic solution of the ethylenediamine complex **5** (see below) were added a few drops of 48% aq. HBr-solution. The bromo-bridged complex **2i** was precipitated immediately, filtered off and washed with water, methanol, and ether. – UV./VIS.(DMF): 306 (13600), 395 (12700), 510 (7100), 532 (7300). – IR.: 3060*m* br., 1621*m*, 1589*w S*, 1570*s*, 1546*w*, 1502*s*, 1487*m*, 1460*m*, 1438*w*, 1429*w*, 1392*m*, 1381*m*, 1335*s*, 1270*w*, 1230*w*, 1222*w*, 1199*s*, 1176*w*, 1158*w* br., 1146*w*, 1130*w*, 1072*m*, 1030*w*, 1006*w*, 958*w* br., 942*w*, 918*w*, 886*w*, 862*w*, 842*w S*, 812*s*, 775*s S*, 770*s*, 758*s*, 744*s*, 732*w S*, 696*s*, 663*m*, 633*w* br., 579*m*, 551*m*, 522*w*, 448*vw*, 432*w*, 271*w*, 260*w*. – ^{1}H-NMR. (90 MHz, DMF-d_7): 7.38–7.69 (*m*, 5H); 7.85 (*d* × *d*, *J*=8.8 and < 1.0, 1H, H–C(4)); 7.95–8.06 *(m)*; 8.52 (br. *d*, *J*=8.4, 1H, H–C(3)); 8.63–8.74 (*m*, 1H, H–C(8)).

$[C_{16}H_{11}BrN_2Pd]_2$	Calc.	C 45.98	H 2.65	Br 19.12	N 6.70%	
(835.2)	Found	„ 46.09	„ 2.77	„ 19.03	„ 6.88%	

Di-μ-iodo-bis(1-phenylazonaphthyl-C(2),N$_\beta$)dipalladium(II) (**2l**). The solution of 0.090 g (0.113 mmol as dimer) complex **2a** in 10 ml acetone was added dropwise to a solution of 0.045 g (0.303 mmol) NaI in 5 ml acetone. After 10 h the brown-red precipitate was collected on a funnel, rinsed with little acetone, and with methanol, water, methanol, and ether, and dried; yield 0.056 g (53%). – ^{1}H-NMR. (90 MHz, DMF-d_7): 7.10–7.50 *(m)*; 7.50–7.84 *(m)*, including 7.75 (*dxd*, *J*=8.6 and 0.9, H–C(4)); 7.84–8.20 *(m)*; 8.58–8.76 (*m*, H–C(8)); 8.97 (*d*, *J*=8.6, H–C(3)).

$[C_{16}H_{11}IN_2Pd]_2$ (929.2) Found C : N : I = 16 : 2.1 : 1.2

(Ethylenediamino)(1-phenylazonaphthyl-C(2),N$_\beta$)palladium(II) chloride (**5**). To a suspension of 0.080 g (0.1 mmol) complex **2e** in 10 ml methanol a few drops of freshly distilled ethylenediamine were added. The precipitate dissolved to a clear red solution. After 18 h the solvent was removed by distillation, and the residue recrystallized from methanol/water; yield 0.078 g (90%). – ^{1}H-NMR. (90 MHz, DMSO-d_6): 2.72 (br.

[11]) Determined as residue of combustion.

m, 4H, CH_2CH_2); 4.60 (br., 2H, NH_2); 5.75 (br., 2H, NH_2); 7.5–8.1 (*m*, 10H); 8.55–8.70 (*m*, 1H, H–C(8)). – ^{1}H-NMR. (360 MHz, CD_3OD); 2.69–2.88 (*m*, 4H, CH_2CH_2); 7.38 (*d*, *J*=8.4, 1H, H–C(3)); 7.48 (*m*, 1H); 7.55–7.61 (*m*, 4H); 7.740 (*d*, *J*=7.8, 1H); 7.745 (*d*, *J*=8.4, 1H); 7.83 (br. *d*, *J*=8.2, 1H, H–C(4)); 7.86 (*d*, *J*=8.4, 1H); 8.62 (*d*, *J*=8.2, 1H, H–C(8)).

$C_{18}H_{19}ClN_4Pd$ (433.2) Found C : H : Cl : N = 18 : 21 : 1 : 4

*Di-μ-acetato-bis[1-(3′-methylphenylazo)naphthyl-*C(2),N*β*]*dipalladium(II)* (**2b**). From 0.493 g (2 mmol) **1b** in 6 ml $CHCl_3$ and 0.468 g (2.1 mmol) $Pd(OAc)_2$ in 10 ml $CHCl_3$, 5 days at RT.; yield 0.621 g (76%), m.p. 198–200° (dec.). – UV./VIS.($CHCl_3$): 306 (15800), 365 (14200), 402 (14900), 420 *S*, 510 (13700), 550 *S*. – IR.: 3060*m*, 3040*w S*, *2930w*, 1621*m*, 1580*vs* br., 1565*vs* br., 1504*s*, 1490*s*, 1420*vs* br., 1372*s*, 1350*s*, 1340*s*, 1270*w*, 1250*w* br., 1071*w*, 1042*w* br., 1025*w*, 1005*w*, 975*w* br., 956*w* br., 914*w*, 897*w*, 870*m*, 825*s*, 808*m*, 791*s*, 782*s*, 749*s*, 692*s*, 670*s*, 636*m* br., 585*m*, 550*w* br., 508*w*, 440*m*, 410*w* br., 378*w*, 331*s*, 298*w*, 270*w*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.17 (*s*, $COCH_3$); 2.19 (*s*, CH_3 of the tolyl ring); 6.78 (*d*, *J*=8.6, 1H, H–C(3)); 6.87–7.56 *(m)*; 7.68–7.84 *(m)*; 8.13–8.33 (*m*, 1H, H–C(8)); additional signals of the *cis*-dimer: 1.86 (*s*, one CH_3CO), 2.30 (*s*, CH_3 of the tolyl ring), 2.40 (*s*, the other CH_3CO). – ^{1}H-NMR. (90 MHz, DMF-d_7): 2.14 (*s*, CH_3CO); 2.20 (br. *s*, CH_3 of the tolyl ring); 6.81 (*d*, *J*=8.6, 1H, H–C(3)); 6.98 (br. *s*, 1H); 7.08–7.71 (*m*, 8H); 7.90–8.05 *(m)*; 8.13–8.36 (*m*, 1H, H–C(8)); additional signals of the *cis*-dimer: 1.85 (*s*, one CH_3CO), 2.31 (*s*, CH_3 of the tolyl ring), 2.38 (*s*, the other CH_3CO). – ^{13}C-NMR. ($CDCl_3$): 21.4 (*qa*, CH_3 of the tolyl ring), 24.8 (*qa*, CH_3CO), 121.1 *(d)*, 123.8 *(d)*, 125.7 *(d)*, 127.8 *(d)*, 128.0 *(d)*, 128.6 *(d)*, 130.4 *(d)*, 131.3 *(d)*, 131.4 *(d)*, 132.0 *(d)*, 132.1 *(d)*, 137.8 (*s*, C(3′)), 151.7 *(s)*, 157.2 *(s)*, 161.2 (*s*, Pd-C(2)), 181.2 (*s*, C=O). – ^{13}C-NMR.(DMF-d_7): 21.2 (*qa*, CH_3 of the tolyl ring), 24.6 (*qa*, CH_3CO), 123.6 *(d)*, 123.8 *(d)*, 126.4 *(d)*, 128.6 *(d)*, 129.0 *(d)*, 129.5 *(d)*, 130.7 *(d)*, 132.2 *(d)*, 132.7 *(d)*, 133.2 *(d)*, 138.7 (*s*, C(3′)), 152.1 *(s)*, 157.3 *(s)*, 166.5 (*s*, Pd-C(2)), 181.3 (*s*, C=O). – MS.: 414 (8), 413 (4), 412 (18), 411 (5), 410 (M^+ of the monomer, 20), 409 (16), 408 (8), 372 (9), 371 (25), 370 (4), 369 (6), 368 (6), 367 (5), 366 (9), 365 (6), 355 (10), 354 (4), 353 (20), 352 (5), 351 (24), 350 (19), 349 (9), 336 (10), 335 (27), 260 (13), 259 (4), 252 (4), 247 (6), 246 (30), 245 (19), 234 (5), 233 (6), 232 (9), 231 (8), 230 (5), 218 (11), 217 (50), 216 (48), 215 (100), 214 (7), 213 (9), 203 (17), 202 (74), 201 (6), 189 (9), 185 (4), 178 (6), 177.5 (5), 176.5 (7), 175.5 (7), 175 (6), 165 (4), 141 (37), 140 (6), 139 (5), 128 (12), 127 (75), 126 (19), 119 (4), 115 (16), 113 (4), 108 (8), 107 (12), 106 (11), 105 (6), 101 (5), 92 (8), 91 (85), 89 (7), 77 (11), 75 (5), 65 (24), 63 (8), 60 (44), 51 (7), 45 (54), 44 (10), 43 (61), 42 (9), 41 (6), 39 (11), 29 (6), 28 (21); *m** 176.5 (*m/z* 231 → *m/z* 203), *m** 185 (*m/z* 366 → *m/z* 260), *m** 201 (*m/z* 336 → *m/z* 260).

$[C_{19}H_{16}N_2O_2Pd]_2$ (821.5) Calc. C 55.56 H 3.93 N 6.82% Found C 55.66 H 4.00 N 6.89%

*Di-μ-chloro-bis[1-(3′-methylphenylazo)naphthyl-*C(2),N*β*]*dipalladium(II)* (**2f**). From 0.246 g (1 mmol) **1b** in 30 ml methanol and 0.303 g (1.02 mmol) Na_2PdCl_4 in 10 ml methanol, 18 h at RT.; yield 0.329 g (85%), m.p. 274–276° (dec.). – UV./VIS. (DMF): 309 (18900), 395 (18500), 510 (11100), 530 *S*. – IR.: 3060*m*, 3040*w S*, 2920*w*, 1620*m*, 1610*w*, 1587*w*, 1572*s* br., 1549*w*, 1502*s*, 1488*m S*, 1458*w* br., 1437*w*, 1429*w*, 1392*m*, 1380*m*, 1350*w*, 1338*s*, 1321*m S*, 1270*w*, 1222*w*, 1202*s*, 1162*w*, 1145*w*, 1130*m*, 1088*w*, 1070*m* br., 1040*w* br., 1002*w*, 910*m*, 898*w*, 882*w*, 870*w*, 862*w*, 814*s*, 804*s*, 787*s*, 774*vs*, 744*s*, 698*s*, 662*s*, 634*w* br., 580*m* br., 551*m*, 539*w*, 522*w*, 461*w*, 442*w*, 432*m*, 408*w* br., 372*w* br., 345*m*, 320*m*, 282*m*, 230*w S*, 212*m*. – ^{1}H-NMR. (360 MHz, DMF-d_7); 2.49 (*s*, CH_3); 7.44 (*d*, H–C(4′)); 7.52 *(t)*; 7.66 *(t)*; 7.82 (≈ *d*, H–C(2′ and 6′)); 7.89 (*d*, H–C(4)); 8.24 (*d*, H–C(3)); 8.69 (*d*, H–C(8)).

$[C_{17}H_{13}ClN_2Pd]_2$ (774.3) Calc. C 52.74 H 3.38 Cl 9.16 N 7.24%
Found „ 51.61 „ 4.84 „ 8.62 „ 7.45%

*Di-μ-acetato-bis[1-(4′-methoxyphenylazo)naphthyl-*C(2),N*β*]*dipalladium(II)* (**2c**). From 1.50 g (5.73 mmol) **1c** in 15 ml $CHCl_3$ and 1.29 g (5.75 mmol) $Pd(OAc)_2$ in 10 ml $CHCl_3$, 90 h at RT.; yield 1.53 g (63%), m.p. 196.5° (dec.). – UV./VIS. (EtOH): 308 (12200), 382 (20900), 398 *S*, 513 (15200). – IR.: 3070*w S*, 3050*w*, 3000*w*, 2960*w*, 2930*w*, 2840*w*, 1589*s*, 1580*s S*, 1573*s*, 1560*s*, 1502*s*, 1495*s S*, 1460*m S*, 1413*s*, 1366*m*, 1342*m S*, 1331*m*, 1321*m S*, 1303*m*, 1282*w S*, 1254*s*, 1230*m S*, 1215*w S*, 1194*m*, 1180*w*, 1164*s*, 1155*m S*, 1139*w*, 1130*w*, 1112*w*, 1070*w*, 1029*m*, 885*w*, 832*s*, 818*m*, 796*w*, 775*m*, 740*m*, 720*w*, 685*m*, 663*m*, 620*w*, 570*m*, 525*m*, 505*w*, 470*w*, 430*w*, 352*w*, 332*w*, 310*w*, 252*w*. – ^{1}H-NMR. (360 MHz, $CDCl_3$): 2.20 (*s*, 3H, CH_3 of the acetato-group); 3.84 (*s*, 3H, OCH_3); 6.47 (*d*, *J*=9, 2H, H–C(3′ and 5′); 6.78 (*d*, *J*=8, 1H, H–C(3)); 7.18 (*d*, *J*=8, 1H, H–C(4)); 7.23 (*d*, *J*=9, 2H, H–C(2′ and 6′)); 7.43–7.48 (*m*, 2H); 7.69–7.74 (*m*, 1H); 8.22–8.24 (*m*, 1H, H–C(8)). – ^{13}C-NMR. ($CDCl_3$): 24.7 (*qa*, CH_3 of the acetato-group), 55.6 (*qa*, OCH_3),112.9 (*d*, 2C, C(3′)

and C(5')), 123.6 *(d)*, 124.9 (*d*, 2C, C(2') and C(6')), 125.3 *(d)*, 127.5 *(d)*, 128.1 *(d)*, 130.2 *(d)*, 130.8 *(d)*, 132.0 *(d)*, 145.9 *(s)*, 160.0 (*s*, C(4')), 161.4 (*s*, Pd–C(2)), 181.0 (*s*, C=O).

$[C_{19}H_{16}N_2O_3Pd]_2$ (853.5) Calc. C 53.44 H 3.78 N 6.56% Found C 52.25 H 3.93 N 6.48%

*Di-μ-chloro-bis[1-(4'-methoxyphenylazo)naphthyl-*C(2),N_β*]dipalladium(II)* (**2g**). From 0.500 g (1.9 mmol) **1c** in 27 ml methanol/ether 25 : 2 and 0.561 g (1.9 mmol) Na_2PdCl_4 in 12 ml methanol, 2 h at RT., recrystallization from DMF/methanol/ether, yield 0.365 g (47%), m.p. 285° (dec.). – UV./VIS. (DMF): 313 (15800), 398 (29400), 515 (18100), 540 (17500). – IR.: 3065*w*, 3050*w*, 3030*w*, 3000*w*, 2960*w*, 2922*w*, 2840*w*, 1600*s*, 1581*m*, 1570*m*, 1548*w*, 1505*s*, 1500*s*, 1465*w*, 1452*w*, 1425*w*, 1377*w*, 1333*m*, 1320*m*, 1304*m*, 1260*s*, 1199*m*, 1170*s*, 1155*w*, 1128*w*, 1115*w*, 1070*s*, 1040*m*, 1035*m* sh, 884*w*, 832*s*, 812*m*, 796*w*, 771*w*, 740*m*, 661*w*, 610*w*, 566*w*, 550*m*, 528*m*, 505*w*, 470*w*, 445*w*, 425*w*, 388*w*, 355*w*, 334*m*, 278*m*. – ^{1}H-NMR. (90 MHz, DMF-d_7): 3.96 (*s*, 3H, OCH_3); 7.20 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.50–7.75 (*m*, 2H); 7.83 (br. *d*, *J*=8.7, 1H, H–C(4)); 7.92–8.15 *(m)*, including 8.09 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 8.22 (*d*, *J*=8.7, 1H, H–C(3)); 8.62–8.77 (*m*, 1H, H–C(8)).

$[C_{17}H_{13}ClN_2OPd]_2$	Calc.	C 50.61	H 3.25	Cl 8.79	N 6.94%
(806.3)	Found	„ 50.80	„ 3.38	„ 8.51	„ 7.10%

*Di-μ-bromo-bis[1-(4'-methoxyphenylazo)naphthyl-*C(2)N_β*]dipalladium(II)* (**2k**). The solution of 0.050 g (0.12 mmol) **2c** in 4 ml ether was combined with 1 ml of an ethereal solution containing 1.2 mmol *t*-butylmagnesium bromide. Gradually a precipitate of red crystals was deposited. The mixture was stirred for 15 h at RT. The suspension was acidified with diluted HCl-solution, the ether layer separated, and the precipitate of **2k** collected on a funnel; yield 0.034 g (32%), m.p. 246.5° (dec.). – UV./VIS. (DMF): 313 (14800), 400 (27200), 514 (16700), 540 (16500). – IR.: 3060*w*, 3020*w*, 3010*w*, 2970*w*, 2940*w*, 2850*w*, 1610*s*, 1591*m*, 1580*m*, 1515*s*, 1510*s*, 1472*w*, 1465*w*, 1450*w*, 1435*w*, 1385*w*, 1340*m*, 1328*m*, 1312*m*, 1270*s*, 1208*m*, 1178*s*, 1162*w*, 1135*w*, 1122*w*, 1080*w*, 1050*m*, 1040*m*, 895*w*, 841*s*, 820*m*, 805*w*, 781*m*, 750*m*, 730*w*, 670*w*, 620*w*, 574*m*, 555*m*, 535*m*, 435*w*. – ^{1}H-NMR. (90 MHz, DMF-d_7): 3.95 (*s*, 3H, OCH_3); 7.18 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.52–7.69 *(m)*; 7.78 (*d*, *J*=8.5, 1H, H–C(4)); 7.96–8.00 *(m)*; 8.06 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 8.50 (br. *d*, *J*=8.5, 1H, H–C(3)); 8.62–8.84 (*m*, 1H, H–C(8)).

$[C_{17}H_{13}BrN_2OPd]_2$	Calc.	C 45.58	H 2.93	Br 17.84	N 6.25%
(895.2)	Found	„ 44.08	„ 3.11	„ 17.23	„ 5.92%

*Di-μ-iodo-bis[1-(4'-methoxyphenylazo)naphthyl-*C(2),N_β*]dipalladium(II)* (**2m**). The solutions of 0.040 g (0.09 mmol) complex **2c** in 20 ml acetone and 0.1 g (0.67 mmol) NaI in 10 ml acetone were combined at RT. After 20 h the solvent was distilled off, and the solid residue recrystallized from acetone/ether. The crude product was washed with water, methanol, and ether to give 0.031 g (67%) **2m**, m.p. 235° (dec.). – UV./VIS. (DMF): 310 *S*, 399 (26700), 512 (16900), 538 (15900). – IR.: 3060*w*, 3018*w*, 3003*w*, 2960*w*, 2930*w*, 2840*m*, 1600*s*, 1582*m*, 1570*s*, 1545*w*, 1505*s*, 1500*s*, 1461*w*, 1440*w*, 1423*w*, 1340*w*, 1330*s*, 1328*s*, 1318*s*, 1304*m*, 1260*s*, 1195*m*, 1170*s*, 1150*w*, 1123*w*, 1111*w*, 1070*w*, 1036*m*, 955*w*, 882*w*, 832*s*, 811*s*, 772*m*, 740*m*, 721*w*, 660*w*, 608*w*, 561*w*, 545*w*, 526*m*, 505*w*, 463*w*, 373*w*, 352*w*, 330*w*, 305*w*, 270*w*, 245*w*, 228*w*. – ^{1}H-NMR. (90 MHz, DMF-d_7): 3.95 (*s*, 3H, OCH_3); 7.20 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.43–7.68 *(m)*; 7.68 (*d*, *J*=9, 1H, H–C(4)); 7.90–8.01 *(m)*; 8.02 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 8.62–8.77 (*m*, 1H, H–C(8)); 8.95 (*d*, *J*=9, 1H, H–C(3)).

$[C_{17}H_{13}IN_2OPd]_2$	Calc.	C 41.25	H 2.65	I 25.65	N 5.66%
(989.2)	Found	„ 41.13	„ 2.76	„ 25.42	„ 5.49%

*Di-μ-acetato-bis[1-(3'-methoxyphenylazo)naphthyl-*C(2)N_β*]dipalladium(II)* (**2d**). From 0.048 g (0.18 mmol) **1d** in 1 ml $CHCl_3$ and 0.050 g (0.22 mmol) $Pd(OAc)_2$ in 1.5 ml $CHCl_3$, 40 h at RT.; yield 0.070 g (91%). – UV./VIS. ($CHCl_3$): 303 (15400), 355 *S*, 405 (15600), 420 *S*, 515 (13700), *ca.* 560 *S*. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.22 (*s*, 3H, CH_3 of the acetato-group); 3.58 (*s*, 3H, OCH_3); 6.78 (*d*, *J*=8.7, 1H, H–C(3)); 6.84–6.97 (*m*, *ca.* 3H); *ca.* 7.22 (br. *d*, *J*=9, H–C(4)); 7.39–7.53 (*m*, 2H); 7.70–7.81 (*m*, 1H); 8.21–8.33 (*m*, *ca.* 1H, H–C(8)).

$[C_{19}H_{16}N_2O_3Pd]_2$ (853.5) Calc. C 53.48 H 3.78 N 6.56% Found C 53.37 H 3.93 N 6.47%

*Di-μ-chloro-bis[1-(3'-methoxyphenylazo)naphthyl-*C(2),N_β*]dipalladium(II)* (**2h**). From 0.034 g (0.13 mmol) **1d** in 2 ml methanol and 0.043 g (0.15 mmol) Na_2PdCl_4 in 10 ml methanol, 26 h at RT.; yield 0.044 g (84%), m.p. 306–307° (dec.). – UV./VIS. (DMF): 308 (19300), 400 (19300), 518 (11400), 530 *S*. – IR.: 3080*w*, 3065*w* sh, 2998*w*, 2965*w*, 2845*w*, 1622*m*, 1608*s*, 1573*s*, 1505*s*, 1493*s*, 1474*m*, 1464*m*, 1455*w*, 1439*m*, 1391*m*, 1382*m*, 1340*vs*, 1324*s* *S*, 1292*w*, 1270*s* br., 1230*m*, 1212*m*, 1200*m*, 1178*m*, 1155*m*, 1131*w*, 1075*w*, 1050*m*,

1001*w*, 908*m*, 868*s*, 820*s*, 814*s*, 778*s*, 747*m*, 694*s*, 668*m*, 581*w* br., 549*w* br., 510*w* br., 480*w*, 435*w*, 410*w*, 356*w*, 322*m*, 281*m*, 222*w*. – ^{1}H-NMR. (90 MHz, DMF-d_7): 3.96 (*s*, 3H, OCH_3); 6.99–7.27 (*m*, 1H, H–C(4′)); 7.54–7.76 (*m*, *ca.* 5H); 7.89 (br. *d*, *J*=8.7, 1H, H–C(4)); 7.95–8.11 *(m)*; 8.25 (*d*, *J*=8.7, 1H, H–C(3)); 8.64–8.76 (*m*, 1H, H–C(8)).

$[C_{17}H_{13}ClN_2OPd]_2$	Calc.	C 50.65	H 3.25	Cl 8.79	N 6.95%
(806.3)	Found	„ 50.47	„ 3.41	„ 8.70	„ 6.81%

*Di-μ-chloro-bis[1-(4′-sulfophenylazo)naphthyl-*C(2),N_β*]dipalladium(II)* (**4a**). From 0.060 g (0.18 mmol) **3a** in 10 ml methanol/1 ml water and 0.054 g (0.18 mmol) Na_2PdCl_4 in 10 ml methanol, 140 h at RT.; yield 0.063 g (74%). – UV./VIS. (H_2O): 300 (20400), 411 (13500), 527 (12100). – ^{1}H-NMR. (90 MHz, DMSO-d_6, 61°): 7.50–7.65 (*m*, 2H); 7.69–7.77 (*m*, 1H); 7.78–7.94 (*m*, *ca.* 4H, phenyl protons); 7.94–8.02 (*m*, 1H); 8.08 (*d*, *J*=8.7, 1H, H–C(3)); 8.54–8.69 (*m*, 1H, H–C(8)). – ^{1}H-NMR. (90 MHz, DMF-d_7): 7.32–7.80 (*m*, 2H, H–C(6 and 7)); 7.87 (br. *d*, *J*=8.7, 1H, H–C(4)); 7.94–8.09 *(m)*; 8.24 (*d*, *J*=8.7, 1H, H–C(3)); 8.60–8.79 (*m*, 1H, H–C(8)).

$[C_{16}H_{10}ClN_2NaO_3PdS]_2$	Calc.	C 40.44	H 2.12	Cl 7.46	N 5.90	S 6.75%
(950.3)	Found	„ 38.62	„ 2.38	„ 7.74	„ 5.40	„ 6.87%

*Di-μ-chloro-bis(1-phenylazo-7-sulfonaphthyl-*C(2),N_β*)dipalladium(II)* (**4b**). From 0.035 g (0.10 mmol) **3b** in 3 ml methanol and 0.035 g (0.12 mmol) Na_2PdCl_4 in 2.5 ml methanol, 18 h at RT.; yield 0.039 g (79%). – ^{1}H-NMR. (90 MHz, DMF-d_7): 7.55–7.72 (*m*, 3H); 7.85 (*d*×*d*, *J*=8.7 and 0.8, 1H, H–C(4)); 7.92–8.08 *(m)*; 8.24 (*d*, *J*=8.7, 1H, H–C(3)); 9.10–9.16 (*m*, 1H, H–C(8)).

$[C_{16}H_{10}ClN_2NaO_3PdS]_2$	Calc.	C 40.44	H 2.12	Cl 7.46	N 5.90	S 6.75%
(950.3)	Found	„ 38.02	„ 1.99	„ 6.92	„ 5.44	„ 6.05%

C : H : Cl : N : S = 16 : 10 : 1 : 2 : 1

*Di-μ-chloro-bis[1-(4′-sulfophenylazo)-6-sulfonaphthyl-*C(2),N_β*]dipalladium(II)* (**4c**). From 0.030 g (0.045 mmol) **3c** in 3 ml methanol and 0.019 g (0.065 mmol) Na_2PdCl_4 in 2 ml methanol, 20 min. at 80° and 14 h at RT.; yield 0.017 g (67%). – UV./VIS. (H_2O): 303 (27500), 401 (16400), 509 (12000). – ^{1}H-NMR. (90 MHz, DMF-d_7): 7.88 (*d*×*d*, *J*=8.8 and < 1.0, *ca.* 1H, H–C(4)); 7.94–8.10 *(m)*; 8.24 (*d*, *J*=8.7, 1H, H–C(3)); 8.31–8.34 (br. *d*, *J*=1.4, 1H, H–C(5)); 8.67 (br. *d*, *J*=8.5, 1H, H–C(8)).

$[C_{16}H_9ClN_2Na_2O_6PdS_2]_2$ (1154.4) Found C : Cl : N = 16 : 0.8 : 2

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