111. Cyclometalation of Arylazo Compounds. Part 2[1]). Regioselectivity of the Cyclopalladation of Some Substituted 1-Arylazonaphthalenes

2nd Communication on Compounds with a Metal-Arene σ-Bond[1])

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Summary

A variety of cyclopalladated 1-arylazonaphthalenes is described, where *ortho*-palladation occurs at C(2) in the naphthyl ring or at C(2′ or 6′) in the phenyl moiety. Two examples of *peri*-cyclopalladation at C(8) in the naphthyl ring are presented. The electronic and steric influences of substituents at either arene moiety on the relative basicities of the azo-N-atoms and the relative nucleophilicities of the potential palladation sites C(2), C(2′ or 6′), and C(8) are discussed qualitatively in order to rationalize the observed regioselectivity.

Cyclopalladation of a 1-arylazonaphthalene could lead in principle to Pd(II)-azo complexes of the general types **A**–**D** *(Scheme)*.

In this paper we present a variety of 1-arylazonaphthalenes which on cyclopalladation lead to products of the types **A**, **B**, **C** or **D** *(Table)*. For some cases, a mixture of these types is formed.

We believe that the regioselectivity of the cyclopalladation of aromatic azo compounds is determined: *i)* by the relative values of the equilibrium constants of palladium pre-coordination at N_α and at N_β; *ii)* by the relative nucleophilicities of the aromatic palladation sites since these will determine the relative rates of the intrinsic substitution steps.

As a consequence, the cyclopalladation site can be altered: *i)* by the introduction of electron-withdrawing substituents in the naphthyl ring and of electron-releasing groups in the phenyl ring; *ii)* by the shielding of one of the two N-atoms of the azo-bridge by *ortho*-substituents thus making the pre-coordination of the Pd(II)-species more difficult or impossible; *iii)* by the blocking of the more easily accessible palladation sites by non-coordinating groups which cannot be readily replaced.

[1]) Part 1 and 1st communication see [1].

[2]) Results taken in part from the PhD. theses of *M. H.* [2] and of *A. J. K.* [3].

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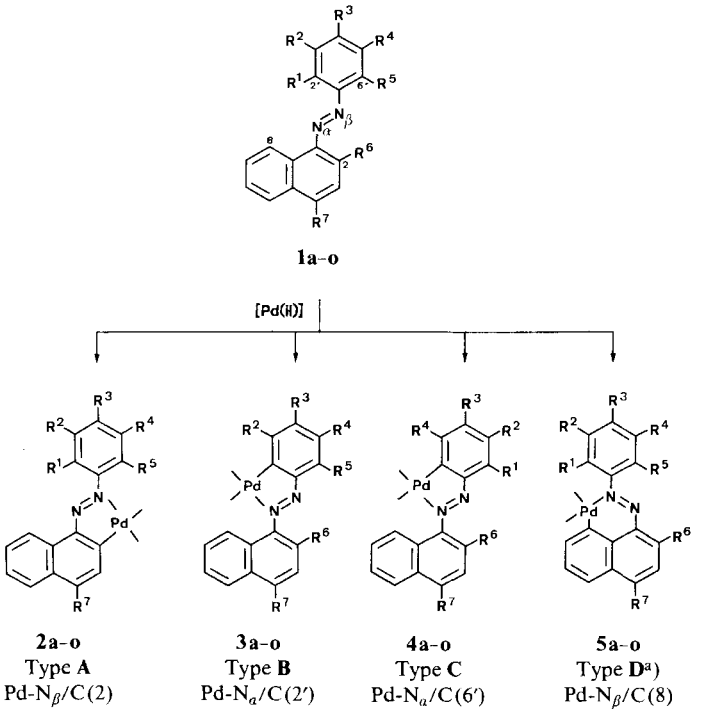
Scheme



[a]) According to *Cope & Friedrich* [4] a five-membered (Pd-N_α/C(8)) rather than a six-membered (Pd-N_β/C(8)) chelate ring is expected to be formed.

Cyclopalladation of the unsubstituted parent compound **1a** leads exclusively to the type-**A** complex [1]. As the naphthyl moiety is more nucleophilic than the phenyl ring, this result indicates that the palladation reaction is an electrophilic substitution [5] [6]. Despite the fact that the formation of type-**A** and type-**D** complexes meets the same mechanistic requirements (pre-coordination at N_β and subsequent formation of a Pd(II)-naphthyl bond), cyclopalladation at the *peri*-position is kinetically much less favourable than cyclopalladation at the *ortho*-position C(2). As the pre-coordination of the Pd(II) species at N_β is expected to decrease the nucleophilicity at C(2) more than at C(8), a topologically less favorable arrangement of the ligand (*e.g. endo*-form) seems to prevent the *peri*-C(8)-palladation. The substituents in the phenyl ring of the 1-arylazonaphthalenes **1b–1e** did not show any experimentally detectable effects on the regioselectivity of the palladation *(Table)*. Compared with the unsubstituted compound **1a**, the methoxy and hydroxy substituents at the phenylic *para*-position C(4′) in compounds **1d** and **1e** are expected to increase the basicity and thus the pre-coordination at N_α but decrease at the same time the rate of electrophilic palladation at C(2′). On the other hand, the methoxy substituent at C(5′) in compound **1c** should decrease the

Table. *Regioselectivity of the cyclopalladation of substituted 1-arylazonaphthalenes*

Compound		Regioselectivity (%) Type A	Type B	Type C	Type D	Pd(II)-source	Solv.	Ref.
1a:	$R^1=R^2=R^3=R^4=R^5=R^6=R^7=H$	100	0		0	Na_2PdCl_4 $Pd(OAc)_2$	CH_3OH $CHCl_3$	[1]
1b:	$R^1=R^2=R^3=R^5=R^6=R^7=H$, $R^4=CH_3$	100	0	0	0	Na_2PdCl_4 $Pd(OAc)_2$	CH_3OH $CHCl_3$	[1]
1c:	$R^1=R^2=R^3=R^5=R^6=R^7=H$, $R^4=OCH_3$	100	0	0	0	Na_2PdCl_4 $Pd(OAc)_2$	CH_3OH $CHCl_3$	[1]
1d:	$R^1=R^2=R^4=R^5=R^6=R^7=H$, $R^3=OCH_3$	100	0		0	Na_2PdCl_4 $Pd(OAc)_2$	CH_3OH $CHCl_3$	[1]
1e:	$R^1=R^2=R^4=R^5=R^6=R^7=H$, $R^3=OH$	100	0		0	Na_2PdCl_4	CH_3OH	This work
1f:	$R^1=R^2=R^4=R^5=R^7=H$, $R_3=OH$, $R^6=$ phenyl	0	detected[a])			Na_2PdCl_4	CH_3OH	This work
1g:	$R^1=R^2=R^4=R^5=R^7=H$ $R^3=OCH_3$, $R^6=CH_3$	0	100		0	$Pd(OAc)_2$	$CHCl_3$	This work
1h:	$R^2=R^4=R^6=R^7=H$, $R^3=OH$, $R^1=R^5=CH_3$	100	0		0	Na_2PdCl_4	CH_3OH	This work
1i:	$R^2=R^4=R^7=H$, $R^3=OH$, $R^1=R^5=R^6=CH_3$	0	0		100	Na_2PdCl_4	CH_3OH	This work
1j:	$R^1=R^2=R^4=R^5=R^6=H$, $R^3=OCH_3$, $R^7=NO_2$	33	67		0	Na_2PdCl_4	CH_3OH/ CH_2Cl_2	This work
1k:	$R^1=R^2=R^4=R^5=R^6=H$, $R^3=OH$, $R^7=NO_2$	100	0		0	Na_2PdCl_4	CH_3OH	This work
1l:	$R^1=R^2=R^5=R^6=H$, $R^3=OH$, $R^4=CH_3$, $R^7=NO_2$	75	25	0	0	Na_2PdCl_4	CH_3OH	This work
1m:	$R^1=R^2=R^5=R^6=H$, $R^3=OH$, $R^4=OCH_3$, $R^7=NO_2$	38	62	0	0	Na_2PdCl_4	CH_3OH	This work
1n:	$R^1=R^2=R^4=R^6=H$, $R^3=OH$, $R^5=CH_3$, $R^7=NO_2$	0	100		0	Na_2PdCl_4	CH_3OH	This work
1o:	$R^1=R^2=R^3=R^5=R^6=H$, $R^4=CH_3$, $R^7=NO_2$	detected[a])			0	Na_2PdCl_4	CH_3OH	This work

[a]) Due to separation- and solubility-problems the exact isomer ratio has not yet been determined.

basicity at N_a but increase the palladation rate. Only for the compound **1b**, with a methyl substituent at C(5'), is an increase of both the pre-coordination at N_a and the palladation rate at C(2') expected. However, this increase appears to be not sufficient to effect the palladation of the phenyl moiety, because exclusive naphthyl-C(2)-metalation is observed. Therefore, a nitro group was introduced at C(4) in order to deactivate the C(2)-position in the naphthyl ring for an electrophilic attack by the Pd(II)-species. Compared to the compounds **1b** and **1d**, the nitro-substituted analogues **1o** and **1j** show appreciable palladation at the phenyl ring. At first sight it is surprising that compound **1j** yields a mixture of type-**A** and type-**B** complexes, whereas compound **1k** forms only the type-**A** complex. However, this result can be rationalized by considering the σ-complex which is formed during the electrophilic palladation at the C(2)-site of compound **1k**. This intermediate can be further

stabilized by the release of the hydroxyl proton to give a dienone-type species[3]), and the gain in stabilization can lead to an increase of the palladation rate at C(2).

Compared with **1k**, the introduction of electron-releasing substituents at C(5′) enhances the palladation of the phenyl ring in the order H (**1k**) < CH_3 (**1l**) < OCH_3 (**1m**). Thus, with **1l** and **1m** a mixture of type-**A** and type-**B** complexes was formed. It is notable that no type-**C** complex was detected.

The influence of steric effects on the regioselectivity of the cyclopalladation is exemplified by the compound **1n**. On electronic grounds the preference for compounds to be palladated at the phenyl ring is expected to increase in the order **1k** < **1n** < **1l** < **1m**. However, the cyclopalladation of compound **1n** yields 100% type-**B** complex[4]). The methyl group at C(6′) appears to suppress the pre-coordination of the Pd(II) species at N_β. A study on *ortho*-methylated azobenzenes indicates that the methyl substituent in the C(6′)-position has a stronger shielding effect on N_β than on N_α [8]. Furthermore, we can deduce from that study, that a methyl group at C(6′) strongly increases the basicity of N_α, whereas a methyl group at C(2) would slightly decrease it. Both the shielding effect on N_β and the increase of the basicity of N_α are in agreement with the regioselectivity observed when **1n** was cyclopalladated.

Another way to preclude a cyclopalladation at C(2) in the naphthyl moiety is to introduce non-coordinating C(2)-substituents which cannot be easily replaced upon cyclopalladation. For this purpose **1g**, **1i** with a C(2)-methyl and **1f** with a C(2)-phenyl substituent were synthesized and cyclopalladated *(Table)*. Compounds **1g** and **1i** were prepared by cyclopalladating **1d** and **1h**, respectively, followed by cleaving the Pd, C-bond with methyllithium in the presence of triphenylphosphine. Similarly, **1f** was obtained from **1e** by cyclopalladation and subsequent reaction with phenyllithium.

The cyclopalladation of **1g** yields exclusively the phenyl-palladated complex **4g**. Apparently, the shielding of N_α and the expected [8] slight decrease of the basicity of N_α is not strong enough to shift the experimentally measured regioselectivity towards a palladation at C(8). Such a shift in regioselectivity was observed only after the methyl group at C(2) had been replaced by a phenyl group (**1f**) thus leading to a C(8)-palladated complex (**5f**).

Finally, an exclusive *peri*-palladation has been achieved by blocking the potential palladation sites C(2), C(2′) and C(6′) by methyl groups (**1i**). The palladation site in **5i** was determined by ^{1}H-NMR. spectroscopy and by reductive cleavage of the Pd, C-σ-bond with $NaBD_4$. It was shown by ^{15}N-NMR. that Pd(II) in **5i** is coordinated at N_β thus forming a six-membered chelate ring [9]. No palladation at the methyl groups was observed despite the fact that with 8-alkylquinolines [10] and *o*-*N*,*N*-dimethylaminotoluene [11] palladation of alkyl groups has been observed.

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[3]) The preponderance of the keto-hydrazone species in the tautomer equilibrium well known for hydroxy-azo compounds [7] leads to the same conclusions.

[4]) For compounds with symmetrically substituted phenyl rings type-**B** and type-**C** complexes are identical.

Conclusion. – The regioselectivity in the cyclopalladation reaction of substituted 1-arylazonaphthalenes is influenced by the electronic and steric effects exerted by the substituents. The site of palladation is determined by the pre-coordination of the Pd(II) species at either of the two azo-N-atoms as well as by the relative rates of the intrinsic palladation reaction. Whereas the pre-coordination is affected by the relative basicities of N_α and N_β, the relative palladation rates are governed by the nucleophilicities of the potential palladation sites. Both the basicity and the nucleophilicity are determined by the electronic effects of the substituents. In addition, substituents in *ortho*-positions to the azo bridge have a steric influence not only on the accessibility of the azo-N-atoms but also on their basicities, both factors which play a role during the pre-coordination. The extent to which the regioselectivity of cyclopalladations is influenced by the solvent, the reactivity of the Pd(II)-species and the geometric form *(cis/trans, endo/exo)* of the reacting azo compound remains to be explored.

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Experimental Part

General remarks. See [1]. The syntheses of the azo compounds **1a**–**1d** and of the corresponding complexes **2a**–**2d** (each chloro- and acetato-bridged) have been described previously [1]. The complexes of this work, too, were prepared by the general methods reported in [1].

1. *Synthesis of 1-(4′-hydroxyphenylazo)naphthalene* (**1e**). For the procedure and spectroscopic data *cf.* [1]; yield 50%, m.p. 136° ([12]: 136°).

1a. *Cyclopalladation of* **1e** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{1-(4′-hydroxyphenylazo)naphthyl-C(2),N_β]palladium(II)}* (**2e**). From 6.00 g (24.2 mmol) **1e** and 7.83 g (26.6 mmol) Na_2PdCl_4 in 250 ml CH_3OH, 120 h at r.t.; yield 8.68 g (92%). – UV./VIS. (DMF/HCl): 316 (8000), 398 (18300), 490 *S*, 515 (7900), 546 (7800). – ^{1}H-NMR. (90 MHz, D_7-DMF): 7.05 (*d* of the *AA′*-type, 2 H, H–C(3′ and 5′)); 7.5–7.7 (*m*, 3 H, H–C(5, 6 and 7)); 7.79 (*d*, *J* = 8.8, 1 H, H–C(4)); 8.01 (*d* of the *XX′*-type, 2 H, H–C(2′ and 6′)); 8.21 (*d*, *J* = 8.8, 1 H, H–C(3)); 8.6–8.8 (*m*, 1 H, H–C(8)); 10.56 (*s*, 1 H, OH).

2. *Synthesis of 1-(4′-hydroxyphenylazo)-2-phenylnaphthalene* (**1f**). A solution of 0.389 g (1.0 mmol) **2e** and 0.52 g (2.0 mmol) triphenylphosphine *(Fluka, puriss.)* in 15 ml ether was stirred at r.t. for 30 min, then cooled to 0° and 1.5 ml (3.0 mmol) phenyllithium (*Fluka*, 2M in benzene/ether) added. After 5 min the mixture was warmed to 7° and kept at that temp. for 100 min. Then the temp. was raised to r.t. and after 15 min the excess phenyllithium destroyed with diluted aq. HCl-solution. The mixture was filtered and then extracted with ether, the organic layer dried (Na_2SO_4) and evaporated. The crude product (0.475 g) was purified by prep. thick layer chromatography (silica gel, CH_2Cl_2/ethyl acetate 20:3); yield 0.090 g (28%). – UV./VIS. ($CHCl_3$): 290 (10800), 326 (10100), 363 (10600), 465 (1400). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 5.15 (*s*, 1 H, OH); 6.87 (*d* of the *AA′*-type, 2 H, H–C(3′ and 5′)); 7.25–7.38 (*m*, 5 H, H–C(6, 7 and 3″, 4″, 5″)); 7.49–7.57 (*m*, 2 H, H–C(2″ and 6″)); 7.62 (*d*, *J* = 8.5, 1 H, H–C(4)); 7.72 (*d* of the *XX′*-type, 2 H, H–C(2′ and 6′)); 7.86–7.94 (*m*, 1 H, H–C(5)); 7.89 (*d*, *J* = 8.5, 1 H, H–C(3)); 8.17–8.25 (*m*, 1 H, H–C(8)). – MS.: 324 (20, M^+), 323 (100), 295 (3), 248 (4), 217 (13), 216 (9), 204 (16), 203 (57), 202 (60), 201 (12), 200 (9), 189 (3), 176 (3), 127 (10), 121 (10), 93 (34), 65 (10), 39 (4).

2a. *Cyclopalladation of* **1f** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(4′-hydroxyphenylazo)-2-phenylnaphthyl-C(8),N_β]palladium(II)}* (**5f**)[5] *and Di-μ-chloro-bis{[1-(4′-hydroxyphenylazo)-2-phenylnaphthyl-*

[5]) The site of Pd,N-coordination has not yet been determined. In analogy to another *peri*-palladated complex (**5i**) [9], N_β-coordination and formation of a six-membered palladacycle is postulated.

C(2'),N$_a$]palladium(II)} (**3f**). A solution of 0.065 g (0.2 mmol) **1f** and 0.073 g (0.25 mmol) Na_2PdCl_4 in 5 ml CH_3OH was stirred at r.t. After 150 min the red crystals were collected on a funnel and identified as pure complex **5f**; yield 0.026 g (28%). The filtrate was concentrated *i.v.* at 75°, the residue dissolved in little CH_3OH and the clear solution kept at r.t. The precipitate of orange crystals was collected after 60 h and identified as pure complex **3f**; yield 0.040 g (43%).

Data of **5f**. – UV./VIS. (DMF/HCl): 290 (10800), 395 (21000), 500 *S*, 525 (17000). – ^{1}H-NMR. (360 MHz, D_7-DMF): 6.92 (*d* of the *AA'*-type, 2 H, H–C(3' and 5')); 7.33 (*t*, *J* = 7.1, 1 H, H–C(6)); 7.56–7.67 (*m*, 3 H, H–C(3'', 4'', and 5'')); 7.76 (*d*, *J* = 6.8, 2 H, H–C(2'' and 6'')); 7.81 (br. *d*, *J* = 7.1, 1 H, H–C(5)); 7.90 (*d*, *J* = 8.5, 1 H, H–C(4)); 7.96 (*d* of the *XX'*-type, 2 H, H–C(2' and 6')); 8.15 (br. *d*, *J* = 7.1, H–C(7)); 8.35 (*d*, *J* = 8.5, 1 H, H–C(3)); 10.48 (*s*, 1 H, OH).

Data of **3f**. – UV./VIS. (DMF/HCl): 327 (27300), 388 (16000), 462 (8000). – ^{1}H-NMR. (360 MHz, DMF-d_7): 6.71 (*d*×*d*, *J* = 8.5 and 2.5, 1 H, H–C(3')); 7.28 (*d*, *J* = 2.5, 1 H, H–C(5')); 7.33 (*t*, *J* = 8.5, 1 H, H–C(4'')); 7.41 (*t*, *J* = 8.5, 2 H, H–C(3'' and 5'')); 7.63 (br. *d*, *J* = 7.7, 2 H, H–C(2'' and 6'')); 7.59–7.68 (*m*, 2 H, H–C(6 and 7)); 7.70 (*d*, *J* = 8.5, 1 H, H–C(4)); 7.74 (*d*, *J* = 8.5, 1 H, H–C(2')); 8.10–8.15 (*m*, 2 H, H–C(5 and 8)); 8.17 (*d*, *J* = 8.5, 1 H, H–C(3)).

3. *Synthesis of 1-(4'-methoxyphenylazo)-2-methylnaphthalene* (**1g**). To 1.5 ml (3 mmol) of the solution of the *Grignard* reagent synthesized from 0.62 ml (10 mmol) methyl iodide and 0.24 g (10 mmol) magnesium turnings in 5 ml dry ether was added the solution of 0.25 g (0.59 mmol as the monomer) complex **2d** (acetato-bridged; synthesis see [1]) in 10 ml dry ether. Instantly, metallic Pd was precipitated. The mixture was kept boiling for 2 h, then cooled and hydrolyzed with 5 g ice and diluted aq. HCl-solution. The suspension was extracted with ether and the organic layer washed with water, dried and evaporated. The dark-red oily residue was chromatographed on a thick layer plate (silica gel, toluene) and 0.047 g (29%) of pure **1g** obtained as an orange-red oil. This was a (70:30)-mixture[6]) of *trans*-**1g** and *cis*-**1g**. – ^{1}H-NMR. (90 MHz, $CDCl_3$): 1.91 (*s*, rel. int. 15, CH_3 of the *cis*-isomer); 2.53 (*s*, rel. int. 36, CH_3 of the *trans*-isomer); 3.70 (*s*, rel. int. 15, OCH_3 of the *cis*-isomer); 3.92 (*s*, rel. int. 36, OCH_3 of the *trans*-isomer); 6.61 (*d*, of the *AA'*-type, H–C(3' and 5') of the *cis*-isomer); 6.96 (*d* of the *AA'*-type, H–C(3' and 5') of the *trans*-isomer); 7.08–7.95 (*m*); 8.02 (*d* of the *XX'*-type, H–C(2' and 6') of the *trans*-isomer); 8.15–8.35 (*m*, H–C(8)). – MS.: 276 (100, M^+), 275 (32), 262 (8), 261 (34), 260 (8), 245 (5), 233 (7), 142 (14), 141 (87), 140 (6), 139 (13), 138 (5), 135 (13), 127 (6), 116 (5), 115 (35), 108 (5), 107 (52), 97 (6), 92 (14), 91 (6), 83 (6), 77 (20), 69 (7), 64 (7), 63 (7), 57 (8), 55 (9), 43 (8), 41 (6).

3a. *Cyclopalladation of* **1g** *with Pd(OAc)$_2$ – Di-μ-acetato-bis*{*[1-(4'-methoxyphenylazo)-2-methylnaphthyl-C(2'),N$_a$]palladium(II)*} (**3g**). From 0.037 g (0.13 mmol) **1g** in 4 ml $CHCl_3$ and 0.030 g (0.13 mmol) $Pd(OAc)_2$ in 2 ml $CHCl_3$, 70 h at r.t.; yield 0.021 g (37%). – UV./VIS. (EtOH): 250 *S*, 310 (22600), 375 (16400), 455 (10600). – ^{1}H-NMR. (90 MHz, $CDBr_3$, 140°): 2.08 (*s*, 3 H, CH_3 of the acetato-group); 2.48 (*s*, 3 H, H_3C–C(2)); 3.87 (*s*, 3 H, OCH_3); 6.60–6.85, 7.18–7.58 and 7.60–8.00 (*m*, 9 H); additional small signals of the *cis*-dimer: 2.01 and 2.22 (*s*, non-equivalent CH_3 of the acetato-groups); 2.70 (*s*, H_3C–C(2)); 3.93 (*s*, OCH_3).

$[C_{20}H_{18}N_2O_3Pd]_2$ (881.6) Calc. C 54.46 H 4.11 N 6.35% Found C 50.96 H 4.06 N 5.65%

4. *Synthesis of 1-(2',6'-dimethyl-4'-hydroxyphenylazo)naphthalene* (**1h**). To a solution of 11 g (45.4 mmol) 1-naphthyldiazoniumtetrafluoroborate (see [13]) in 100 ml ice-cold aqueous acetonitrile were added slowly 5.5 g (45 mmol) 3,5-dimethylphenol (*EGA*, 98–99%) and 20 g Na_2CO_3 dissolved in aqueous acetonitrile. The reaction temperature was kept between 0–5°. After 2 h the mixture was neutralized with diluted aq. HCl-solution, the crude product collected on a funnel and purified by column chromatography (silica gel, CH_2Cl_2). One recrystallization from CH_2Cl_2/light petroleum ether yielded 4.83 g (39%) **1h** as yellowish-brown crystals, m.p. 139°. – UV./VIS. (EtOH): 259 *S*, 380 (21200). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.60 (*m*, CH_3); 4.86 (*s*, OH); 6.66 (*m*, H–C(3' and 5')); 7.76 (*d*×*d*, *J* = 7.5 and 1.5, H–C(2)); 7.45–8.05 (*m*); 8.75–8.90 (*m*, H–C(8)). – MS.: 276 (51, M^+), 149 (13), 143 (16), 128 (11), 127 (34), 122 (96), 121 (100), 115 (8), 107 (50), 91 (18), 79 (11), 77 (29), 43 (19), 41 (10), 39 (14), 27 (10).

$C_{18}H_{16}N_2O$ (276.3) Calc. C 78.24 H 5.84 N 10.14% Found C 78.00 H 5.87 N 10.02%

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[6]) Calculated on the basis of ^{1}H-NMR. singlet-intensities (rel. int.).

4a. *Cyclopalladation of* **1h** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(2′,6′-dimethyl-4′-hydroxyphenylazo)-naphthyl-C(2),N,β]palladium(II)}* (**2h**). From 2.0 g (7.2 mmol) **1h** and 2.3 g (7.8 mmol) Na_2PdCl_4 in 80 ml CH_3OH, 7 days at r.t.; yield 2.74 g (91%). – UV./VIS. (DMF): 311 (12000), 398 (18900), 500 (7000), 530 *S*. – ^{1}H-NMR. (90 MHz, D_7-DMF): 2.30 (*m*, CH_3); 6.73 (*m*, H–C(3′ and 5′)); 7.45–7.71 (*m*, H–C(5, 6, and 7)); 7.93 (*d*×*d*, *J* = 8.7 and 0.6, H–C(4)); 8.20 (*d*, *J* = 8.7, H–C(3)); 8.48–8.65 (*m*, H–C(8)); 9.87 (*s*, OH).

$[C_{18}H_{15}ClN_2OPd]_2$	Calc.	C 51.82	H 3.62	Cl 8.50	N 6.71%
(834.4)	Found	„ 51.51	„ 3.72	„ 8.05	„ 6.44%

5. *Synthesis of 1-(2′,6′-dimethyl-4′-hydroxyphenylazo)-2-methylnaphthalene* (**1i**). The suspension of 2.345 g (2.8 mmol) **2h** and 5.90 g (22.5 mmol) triphenylphosphine *(Fluka, puriss.)* in 100 ml dry ether was stirred under a N_2-atmosphere at r.t. After 30 min the solution was cooled to 0° and 11 ml (17 mmol) of a 5% solution of methyllithium in ether *(EGA)* were added slowly. The temperature was then raised to r.t., and after 60 min the excess methyllithium was carefully destroyed with water. The mixture was extracted with ether, the organic layer dried and evaporated. Column chromatography (silica gel, CH_2Cl_2) of the residue afforded a red oil which upon crystallization from toluene/light petroleum ether yielded 1.25 g (73%) **1i** as orange crystals, m.p. 106°. – UV./VIS. (EtOH): 355 (15100). – ^{1}H-NMR. (360 MHz, C_6D_6): 2.47 (*s*, H_3C–C(2)); 2.51 (*m*, H_3C–Ph); 4.10 (*s*, OH); 6.30 (*s*, H–C(3′ and 5′)); 7.16 (*d*, *J* = 8.2, H–C(3)); 7.26 (*m*, H–C(6)); 7.34 (*m*, H–C(7)); 7.52 (*d*, *J* = 8.1, H–C(4)); 7.65 (*d*, *J* = 8.3, H–C(5)); 8.57 (*d*, *J* = 8.3, H–C(8)). – ^{13}C-NMR. (D_7-DMF): 19.7 (*qa*, H_3C–C(2)); 21.2 (*qa*, H_3C–Ar), 117.7 (*d*, C(3′ and 5′)), 124.2 (*d*), 126.0 (*d*), 126.8 (*s*, C(2′ and 6′)), 127.4 (*d*), 128.4 (*d*), 130.6 (*d*), 133.6 (*d*), 136.6 (*s*), 144.1 (*s*, C(1′)), 148.5 (*s*, C(1)), 160.1 (*s*, C(4′)). – MS.: 290 (67, M^+), 275 (19), 262 (6), 247 (14), 149 (13), 142 (15), 141 (66), 139 (13), 122 (13), 121 (100), 120 (6), 115 (26), 91 (12), 77 (18), 28 (13).

$C_{19}H_{18}N_2O$ (290.4) Calc. C 78.59 H 6.25 N 9.65% Found C 78.14 H 6.26 N 9.43%

5a. *Cyclopalladation of* **1i** *with* Na_2PdCl_4: *Di-μ-chloro-bis{[1-(2′,6′-dimethyl-4′-hydroxyphenylazo)-2-methylnaphthyl-C(8),N,β]palladium(II)}* (**5i**). From 0.30 g (1.04 mmol) **1i** and 0.31 g (1.05 mmol) Na_2PdCl_4 in 30 ml CH_3OH, 24 h at r.t.; yield 0.34 g (76%), m.p. 283° (dec.). – UV./VIS. (DMF): 280 (29400), 385 (10500), 493 (13200). – ^{1}H-NMR. (90 MHz, D_6-DMSO): 2.29 (*m*, H_3C–Ph); 2.74 (*s*, H_3C–C(2)); 6.57 (*m*, H–C(3′ and 5′)); 7.22 (*t*, *J* = 7.6, H–C(6)); 7.60 (*d*, *J* = 8.3, H–C(3)); 7.64–7.73 (*m*, H–C(5)); 8.17 (*d*×*d*, *J* = 7.5 and 1.2, H–C(7)); 8.20 (*d*, *J* = 8.3, H–C(4)); 9.54 (*s*, OH).

6. *Synthesis of 1-(4′-hydroxyphenylazo)-4-nitronaphthalene* (**1k**). The suspension of 5.65 g (19.7 mmol) 4-nitro-1-naphthyldiazoniumtetrafluoroborate[7]) in diluted aq. HCl-solution was added dropwise to a cooled solution of 1.85 g (19.7 mmol) phenol (purified by sublimation) and 10 g sodium acetate in 50 ml diluted aq. NaOH-solution. The mixture was stirred at 0–5° for 3 h, then the red precipitate was collected and chromatographed (silica gel, CH_2Cl_2). Recrystallizations from CH_2Cl_2/light petroleum ether afforded 2.16 g (37%) **1k** as dark red crystals, m.p. 195° ([15]: 182–183°). – UV./VIS. (EtOH): 259 (16400), 405 (22000). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 5.24 (*s*, OH); 7.02 (*d* of the *AA′*-type, H–C(3′ and 5′)); 7.49 (*d*, *J* = 8.3, H–C(2)); 7.67–7.93 (*m*, H–C(6 and 7)); 8.05 (*d* of the *XX′*-type, H–C(2′ and 6′)); 8.31 (*d*, *J* = 8.4, H–C(3)); 8.56–8.70 (*m*, H–C(5)); 8.92–9.09 (*m*, H–C(8)). – MS.: 293 (63, M^+), 276 (26), 246 (16), 189 (10), 172 (15), 142 (10), 126 (45), 125 (16), 121 (45), 114 (10), 93 (100), 76 (10), 65 (53), 52 (11), 39 (31), 30 (10).

$C_{16}H_{11}N_3O_3$ (293.3) Calc. C 65.52 H 3.78 N 14.33% Found C 65.35 H 3.90 N 14.16%

6a. *Cyclopalladation of* **1k** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(4′-hydroxyphenylazo)-4-nitronaphthyl-C(2),N,β]palladium(II)}* (**2k**). From 0.233 g (0.80 mmol) **1k** and 0.235 g (0.80 mmol) Na_2PdCl_4 in 25 ml CH_3OH, 4 days at r.t.; yield 0.105 g (30%). – UV./VIS. (DMF): 313 (13700), 415 (28200), 523 (22100), 555 (22300). – ^{1}H-NMR. (90 MHz, D_7-DMF): 7.10 (*d* of the *AA′*-type, H–C(3′ and 5′)); 7.73–7.92 (*m*, H–C(6 and 7)); 8.16 (*d* of the *XX′*-type, H–C(2′ and 6′)); 8.26–8.37 (*m*, H–C(5)); 8.75 (*s*, H–C(3)); 8.84–8.95 (*m*, H–C(8)); 10.94 (*s*, OH).

$[C_{16}H_{10}ClN_3O_3Pd]_2$	Calc.	C 44.23	H 2.32	Cl 8.16	N 9.67%
(868.3)	Found	„ 44.33	„ 2.47	„ 8.00	„ 9.76%

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[7]) Synthesized by diazotization of 1-amino-4-nitronaphthalene with nitrosylsulfuric acid [14] and subsequent precipitation of the diazonium salt with aqueous HBF_4.

7. *Synthesis of 1-(4'-methoxyphenylazo)-4-nitronaphthalene* (**1j**) (by methylation of **1k** according to [16]). To the solution of 0.88 g (3 mmol) **1k** in a mixture of 0.16 g (4 mmol) NaOH in 8 ml HMPT were added carefully 0.75 ml (12 mmol) CH_3I. The mixture was kept for 30 min at r.t. Afterwards 30 ml 5% HCl-solution were given to the solution and the resulting orange precipitate filtered off, and washed with water and ethanol; yield 0.86 g (93%), m.p. 138–139°. – UV./VIS. (EtOH): 254 (16400), 400 (23100). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 3.94 (*s*, OCH_3); 7.08 (*d* of the *AA'*-type, H–C(3' and 5')); 7.75 (*d*, *J* = 8.2, H–C(2)); 7.66–7.92 (*m*, H–C(6 and 7)); 8.09 (*d* of the *XX'*-type, H–C(2' and 6')); 8.31 (*d*, *J* = 8.4, H–C(3)); 8.58–8.70 (*m*, H–C(5)); 8.85–9.07 (*m*, H–C(8)). – MS.: 307 (41, M^+), 290 (13), 172 (10), 149 (16), 142 (10), 135 (36), 126 (20), 107 (100), 92 (24), 77 (39), 64 (11).

$C_{17}H_{13}N_3O_3$ (307.3) Calc. C 66.44 H 4.26 N 13.67% Found C 66.27 H 4.25 N 13.62%

7a. *Cyclopalladation of* **1j** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(4'-methoxyphenylazo)-4-nitronaphthyl-C(2),N$_\beta$]palladium(II)}* (**2j**) *and di-μ-chloro-bis{[1-(4'-methoxyphenylazo)-4-nitronaphthyl-C(2'),N$_\alpha$]-palladium(II)}* (**3j**). From 0.46 g (1.5 mmol) **1j** and 0.44 g (1.5 mmol) Na_2PdCl_4 in 20 ml CH_3OH/CH_2Cl_2, 24 h at r.t.; yield 0.45 g (67%) of complexes **2j** and **3j** (33% **2j** + 67% **3j** in the mixture). The complex isomers could not be separated. – ^{1}H-NMR. (90 MHz, D_7-DMF) of **2j**: 7.24 (*d* of the *AA'*-type, H–C(3' and 5')); 8.24 (*d* of the *XX'*-type, H–C(2' and 6')); 8.77 (*s*, H–C(3)). – ^{1}H-NMR. (90 MHz, D_7-DMF) of **3j**: 6.97 (*d* × *d*, *J* = 8.7 and 2.6, H–C(5')); 7.44 (*d*, *J* = 2.6, H–C(3'**; 7.86 (*d*, *J* = 8.1, H–C(2)); 8.53 (*d*, *J* = 8.1, H–C(3)). Additional signals of either isomer: 7.75–8.65 (*m*); 8.84–8.96 (*m*).

$[C_{17}H_{12}ClN_3O_3Pd]_2$ (896.3) Calc. C 45.56 H 2.70 Cl 7.91 N 9.38%
Found „ 45.59 „ 3.19 „ 7.29 „ 9.75%

8. *Synthesis of 1-(4'-hydroxy-3'-methylphenylazo)-4-nitronaphthalene* (**1l**). To an ice-cold solution of 0.32 g (2.96 mmol) *o*-cresol and 5 g sodium acetate in 20 ml diluted aq. NaOH-solution was slowly added a solution of 0.78 g (2.72 mmol) 4-nitro-1-naphthyldiazoniumtetrafluoroborate[7]) in 20 ml diluted aq. HCl-solution. After 5 h the mixture was mixed with ice and extracted with ether. The organic layer was washed with diluted aq. NaOH-solution and water, dried and evaporated. Recrystallization of the crude product from acetone/light petroleum ether yielded 0.36 g (43%) **1l** as brown crystals, m.p. 194°. – UV./VIS. (EtOH): 262 (16300), 410 (21900). – ^{1}H-NMR. (360 MHz, $CDCl_3$): 2.40 (*s*, CH_3); 5.23 (*s*, OH); 6.94 (*d*, *J* = 8.6, H–C(5')); 7.72 (*d*, *J* = 8.4, H–C(2)); 7.70–7.85 (*m*, H–C(6 and 7)); 7.88 (*d* × *d*, *J* = 8.6 and 2.2, H–C(6')); 7.91 (br. *s*, H–C(2')); 8.29 (*d*, *J* = 8.4, H–C(3)); 8.62 (br. *d*, H–C(5)); 9.00 (br. *d*, H–C(8)). – MS.: 307 (73, M^+), 290 (17), 260 (11), 172 (12), 135 (23), 126 (24), 125 (12), 107 (100), 79 (13), 77 (21).

$C_{17}H_{13}N_3O_3$ (307.3) Calc. C 66.44 H 4.26 N 13.69% Found C 65.14 H 4.32 N 12.99%

8a. *Cyclopalladation of* **1l** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(4'-hydroxy-3'-methylphenylazo)-4-nitronaphthyl-C(2),N$_\beta$]palladium(II)}* (**2l**) *and di-μ-chloro-bis{[1-(4'-hydroxy-3'-methylphenylazo)-4-nitronaphthyl-C(6'),N$_\alpha$]palladium(II)}* (**3l**). From 0.104 g (0.34 mmol) **1l** and 0.105 g (0.36 mmol) Na_2PdCl_4 in 20 ml CH_3OH, 7 days under reflux; yield 0.112 g (74%) of the complexes **2l** and **3l** (75% **2l** + 25% **3l** in the mixture). The complex isomers could not be separated. – ^{1}H-NMR. (360 MHz, D_6-DMSO) of **2l**: 2.26 (*s*, CH_3); 6.97 (*d*, *J* = 8.9, H–C(5')); 7.93 (*d* × *d*, *J* = 8.9 and 2.3, H–C(6')); 8.01 (br. *s*, H–C(2')); 8.56 (*s*, H–C(3)). – ^{1}H-NMR. (360 MHz, D_6-DMSO) of **3l**: 2.13 (*d*, *J* = 0.6, CH_3); 7.20 (*s*, H–C(5')); 7.69 (*d*, *J* = 8.4, H–C(2)); 8.12 (*s*, H–C(2')); 8.44 (*d*, *J* = 8.4, H–C(3)). Additional signals of either isomer: 7.77–7.88 (*m*); 8.27 (*m*, H–C(5)); 8.42 (*m*); 8.82 (*m*, H–C(8)).

$[C_{17}H_{12}ClN_3O_3Pd]_2$ (896.3) Calc. C 45.56 H 2.70 Cl 7.91 N 9.38%
Found „ 45.01 „ 3.00 „ 7.21 „ 8.98%

9. *Synthesis of 1-(4'-hydroxy-3'-methoxyphenylazo)-4-nitronaphthalene* (**1m**), by coupling of 5.50 g (19 mmol) 4-nitro-1-naphthyldiazoniumtetrafluoroborate on 2.30 g (19.5 mmol) 2-methoxyphenol (*cf.* synthesis of **1l**, *Chapt. 8*). After purification of the crude product by chromatography (silica gel, CH_2Cl_2) and crystallization from CH_2Cl_2/light petroleum ether **1m** was obtained as dark-red crystals; yield 2.08 g (34%), m.p. 169°. – UV./VIS. (EtOH): 263 (16400), 420 (21700). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 4.07 (*s*, OCH_3); 6.60 (*s*, OH); 7.13 (*d*, *J* = 8.2, H–C(5')); 7.74 (*d*, *J* = 8.4, H–C(2)); 7.61–7.90 (*m*); 8.31 (*d*, *J* = 8.4, H–C(3)); 8.59–8.71 (*m*, H–C(5)); 8.93–9.05 (*m*, H–C(8)). – ^{1}H-NMR. (90 MHz, C_6D_6): 3.13 (*s*, OCH_3); 5.74 (*s*, OH); 7.02 (*d*, *J* = 8.4, H–C(5')); 7.22–7.34 (*m*, H–C(6 and 7)); 7.44

(*d*, J = 8.4, H–C(2)); 7.46 (*d*, J = 2.1, H–C(2')); 7.73 (*d* × *d*, J = 8.5 and 2.1, H–C(6')); 7.77 (*d*, J = 8.4, H–C(3)); 8.48–8.60 (*m*, H–C(5)); 8.94–9.06 (*m*, H–C(8)). – MS.: 323 (100, M^+), 307 (11), 306 (19), 293 (11), 276 (14), 172 (18), 151 (15), 142 (15), 126 (25), 125 (10), 123 (96), 108 (14).

$C_{17}H_{13}N_3O_4$ (323.3) Calc. C 63.16 H 4.05 N 13.01% Found C 63.04 H 4.05 N 12.84%

9a. *Cyclopalladation of* **1m** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(4'-hydroxy-3'-methoxyphenylazo)-4-nitronaphthyl-C(2),N_β]palladium(II)}* (**2m**) *and di-μ-chloro-bis{[1-(4'-hydroxy-3'-methoxyphenylazo)-4-nitronaphthyl-C(6'),N_α]palladium(II)}* (**3m**). From 0.45 g (1.40 mmol) **1m** and 0.43 g (1.46 mmol) Na_2PdCl_4 in 40 ml CH_3OH, 24 h at r.t.; yield 0.60 g (93%) of the mixture of **2m** and **3m** (38% **2m** and 62% **3m**). Recrystallizations from DMF/ether yielded pure **2m**. From the mother liquor **3m** was isolated in 90% purity.

Data of **2m**. – UV./VIS. (DMF): 410 (20400), 535 (28400), 563 (28400). – ^{1}H-NMR. (90 MHz, D_7-DMF): 4.03 (*s*, OCH_3); 7.10 (*d* × *d*, J = 8.0 and 0.7, H–C(5')); 7.76–7.97 (*m*); 8.28–8.38 (*m*, H–C(5)); 8.77 (*s*, H–C(3)); 8.89–8.99 (*m*, H–C(8)); 10.53 (*s*, OH).

$[C_{17}H_{12}ClN_3O_4Pd]_2$	Calc.	C 43.96	H 2.60	Cl 7.63	N 9.05%
(928.3)	Found	„ 42.62	„ 2.79	„ 7.63	„ 9.24%

Data of **3m**. – UV./VIS. (DMF): 346 *S*, 388 (24400), 536 (15400). – ^{1}H-NMR. (90 MHz, D_7-DMF): 3.92 (*s*, OCH_3); 7.34 (*s*, H–C(2')); 7.68 (*s*, H–C(5')); 7.82 (*d*, J = 8.3, H–C(2)); 7.76–7.97 (*m*); 8.52 (*d*, J = 8.3, H–C(3)); 8.42–8.68 (*m*, H–C(8 and 5)).

10. *Synthesis of 1-(3'-methylphenylazo)-4-nitronaphthalene* (**1o**), by the reaction of 4-nitro-1-naphthyldiazonium salt[7]) and 3-methylphenylmagnesium bromide according to [17]; average yield 0.8%, m.p. 104–105°. – UV./VIS. ($CHCl_3$): 322 (10600), 392 (14500); (DMF): 322 (10400), 391 (14000). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.52 (*s*, 3 H, CH_3); 7.35–7.85 (*m*, 7 H) including 7.75 (*d*, J = 8.4, H–C(2)); 8.30 (*d*, J = 8.4, 1 H, H–C(3)); 8.54–8.72 (*m*, 1 H, H–C(5)); 8.92–9.10 (*m*, 1 H, H–C(8)). – ^{1}H-NMR. (90 MHz, C_6D_6): 2.13 (*s*, 3 H, CH_3); 6.96–7.30 (*m*, 4 H); 7.38 (*d*, J = 8.1, 1 H, H–C(2)); 7.69 (*d*, J = 8.4, 1 H, H–C(3)); 7.86–7.93 (*m*, 2 H); 8.42–8.53 (*m*, 1 H, H–C(5)); 8.87–8.98 (*m*, 1 H, H–C(8)).

10a. *Cyclopalladation of* **1o** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(3'-methylphenylazo)-4-nitronaphthyl-C(2),N_β]palladium(II)}* (**2o**) *and di-μ-chloro-bis{[1-(3'-methylphenylazo)-4-nitronaphthyl-C(2' or 6'),N_α]palladium(II)}* (**3o**). From 0.050 g (0.17 mmol) **1o** in 7 ml CH_3OH and 0.050 g (0.17 mmol) Na_2PdCl_4 in 3 ml CH_3OH, 6 days at r.t.; yield 0.071 g (95%) of a mixture of complexes **2o**, **3o** and a non-cyclometalated Pd/azo ligand (1:2)-complex; the mixture could not be separated. – ^{1}H-NMR. (90 MHz, D_7-DMF): 2.43, 2.51 and 2.53 (*s*, CH_3 of different complex species); 7.24–7.60 (*m*, 2 H); 7.76–8.35 (*m*); 8.48–8.60 (*m*, *ca.* 1.3 H, H–C(5) of **2o** and **3o**) including 8.54 (*d*, J = 8.2, H–C(3) of **3o**); 8.75 (*s*, *ca.* 0.65 H, H–C(3) of **2o**); 8.84–9.20 (*m*, 1 H, H–C(8) of **2o** and **3o**).

11. *Synthesis of 1-(4'-hydroxy-2'-methylphenylazo)-4-nitronaphthalene* (**1n**). Azo compound **1n** was a by-product of the synthesis of **1o** (see above), when the double salt with $ZnCl_2$ instead of the tetrafluoroborate of the diazonium ion was used[8]); m.p. 194–195°. – UV./VIS. (EtOH): 263 (15500), 416 (20700). – ^{1}H-NMR. (90 MHz, $CDCl_3$): 2.79 (*s*, 3 H, CH_3); 5.16 (*s*, 1 H, OH); 6.73–6.85 (*m*, 2 H, H–C(3' and 5')); 7.67–7.94 (*m*, 4 H) including 7.72 (*d*, J = 8.2, H–C(2)); 8.32 (*d*, J = 8.2, 1 H, H–C(3)); 8.59–8.71 (*m*, 1 H, H–C(5)); 8.90–9.11 (*m*, 1 H, H–C(8)). – ^{1}H-NMR. (90 MHz, C_6D_6): 2.59 (*s*, 3 H, CH_3); 4.32 (*s*, 1 H, OH); 6.35–6.43 (*m*, 2 H, H–C(3' and 5')); 7.12–7.37 (*m*, 3 H) including 7.30 (*d*, J = 8.2, H–C(2)); 7.73–7.88 (*m*, 2 H) including 7.78 (*d*, J = 8.4, H–C(3)); 8.49–8.61 (*m*, 1 H, H–C(5)); 8.90–9.03 (*m*, 1 H, H–C(8)). – MS.: 308 (31), 307 (100, M^+), 306 (6), 291 (6), 290 (17), 277 (6), 262 (6), 261 (10), 260 (16), 232 (6), 172 (11), 135 (35), 126 (22), 125 (8), 108 (10), 107 (78), 79 (11), 77 (31); m^* 58 (m/z 107 → m/z 79), m^* 85 (m/z 135 → m/z 107), m^* 274 (m/z 307 → m/z 290).

11a. *Cyclopalladation of* **1n** *with* Na_2PdCl_4. – *Di-μ-chloro-bis{[1-(4'-hydroxy-2'-methylphenylazo)-4-nitronaphthyl-C(6'),N_α]palladium(II)}* (**3n**). From 0.032 g (0.1 mmol) **1n** in 8 ml CH_3OH and 0.031 g (0.1 mmol) Na_2PdCl_4 in 1.5 ml CH_3OH, 3 days at r.t.; yield 0.038 g of a (2:1)-mixture of **3n** and $PdCl_2$ that could not be separated. – UV./VIS. (EtOH): 251 (40500), 333 (22500), 376 (21500), 490 (19500). – ^{1}H-NMR. (90 MHz, D_7-DMF): 2.51 (*s*, 3 H, CH_3); 6.54–6.57 (*m*, 1 H, H–C(3')); 7.37–7.39 (*m*, 1 H, H–C(5')); 7.69–7.87 (*m*, 3 H) including 7.74 (*d*, J = 8.2, H–C(2)); 8.35–8.52 (*m*, 3 H, H–C(5 and 8) including 8.44 (*d*, J = 8.1, H–C(3)); 10.89 (*m*, 1 H, OH).

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8) The formation of **1n** is explained by the diazonium/$ZnCl_2$ double salt containing water that could not be removed completely for safety reasons.

REFERENCES

[1] *A.J. Klaus & P. Rys*, Helv. Chim. Acta *64*, 1452 (1981).
[2] *M. Hugentobler*, PhD. thesis No. 7020, ETH Zürich 1982.
[3] *A.J. Klaus*, PhD. thesis No. 6607, ETH Zürich 1980.
[4] *A.C. Cope & E.C. Friedrich*, J. Am. Chem. Soc. *90*, 909 (1968).
[5] *G.W. Parshall*, Acc. Chem. Res. *3*, 139 (1970).
[6] *M.I. Bruce, B.L. Goodall & F.G.A. Stone*, J. Chem. Soc., Dalton Trans. *1978*, 687.
[7] *A. Burawoy & A.R. Thompson*, J. Chem. Soc. *1953*, 1443; *H. Zollinger*, 'Azo & Diazo Chemistry', Interscience, London 1961, p.322; *J.E. Kuder*, Tetrahedron *28*, 1973 (1972); *J. Griffiths*, J. Soc. Dyers Colour. *1972*, 106.
[8] *J.E. Haselbach*, Helv. Chim. Acta *53*, 1526 (1970).
[9] *K. Gehrig, M. Hugentobler, A.J. Klaus & P. Rys*, Inorg. Chem. *21(6)* (1982), in press.
[10] *G.E. Hartwell, R.V. Lawrence & M.J. Smas*, J. Chem. Soc., Chem. Commun. *1970*, 912; *A.J. Deeming & I.P. Rothwell*, J. Organomet. Chem. *205*, 117 (1981).
[11] *C. Mutet & M. Pfeffer*, J. Organomet. Chem. *171*, C34 (1979); *J. Dehand, C. Mutet & M. Pfeffer*, J. Organomet. Chem. *209*, 255 (1981).
[12] *W. McPherson & H.C. Gore*, Am. Chem. J. *25*, 485 (1901).
[13] *M.F.W. Dunker, E.B. Starkey & G.L. Jenkins*, J. Am. Chem. Soc. *58*, 2308 (1936).
[14] *H.H. Hodgson et al.*, Org. Synth. Coll. Vol. III, 341 (1955).
[15] *A.C. Sircar*, J. Chem. Soc., Dalton Trans. *1916*, 772.
[16] *J.E. Shaw, D.C. Kunerth & J.J. Sherry*, Tetrahedron Lett. *1973*, 689.
[17] *Y. Nomura & H. Anzai*, Bull. Chem. Soc. Jpn. *37*, 970 (1964).