260. Cyclometalated Arylazo Compounds

Part 4[1])

ortho-Cyano-1-arylazonaphthalenes and 3-Amino-2-arylbenzo[*g*]indazoles from Cyclopalladated 1-Arylazonaphthalenes

4th Communication on Compounds with a Metal-Arene σ-Bond[1])

by **Kurt Gehrig, Alfred J. Klaus** and **Paul Rys***

Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule Zürich, CH-8092 Zürich

(9.XI.83)

Summary

The reaction of a cyclopalladated 1-arylazonaphthalene with tetrabutylammonium cyanide leads to an *ortho*-cyano-1-arylazonaphthalene and a 3-amino-arylbenzo[*g*]indazole, depending upon whether triphenylphosphine or 1,2-bis(diphenylphosphino)ethane (DIPHOS) is used to monomerize the binuclear Pd(II)-complex. In a similar insertion reaction with cyclohexyl isocyanide the corresponding 3-(*N*-cyclohexyl)-aminoindazole is formed. A Pd(II)-isocyano complex is shown to be a possible intermediate in that conversion.

Cyclometalated complexes appear to be frequent intermediates of metal-catalyzed aromatic substitution reactions [2–6]. These cyclometalated compounds provide a suitable tool for studying the chemism of the cleavage of metal-arene σ-bonds with various reagents.

The direct introduction of CN-substituents into aromatic systems may be important for the syntheses of certain dyestuffs because of the marked influence of that CN-group on their absorption characteristics [7]. In addition, conversion of the CN-group into a carboxylic substituent allows the syntheses of arylazoaryl carboxylic acids and esters. Furthermore, *ortho*-cyano-azoarenes can undergo cyclization to indazoles[2]) or indazolines[2]) [8].

To our knowledge the insertion of an isocyanide into a Pd-C bond seems to be the first example for the synthesis of indazolines *via* cyclometalation [10] [11].

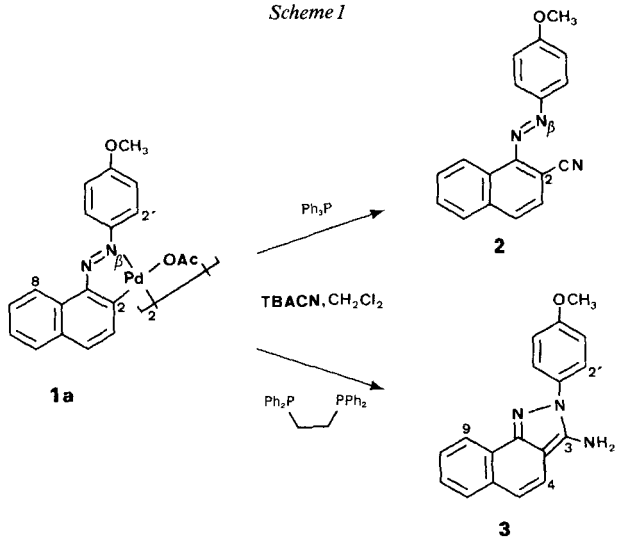
The reaction of the acetato-bridged Pd(II)-azo complex **1a** with tetrabutylammonium cyanide (TBACN) in the presence of excess Ph_3P yielded the *ortho*-cyano-azo derivative **2**. When an excess of the chelating ligand 1,2-bis(diphenylphosphino)ethane (DIPHOS)

[1]) Part 3 and 3rd Communication see [1].

[2]) For the differentiation between '-ole' and '-oline' see IUPAC-nomenclature [9].

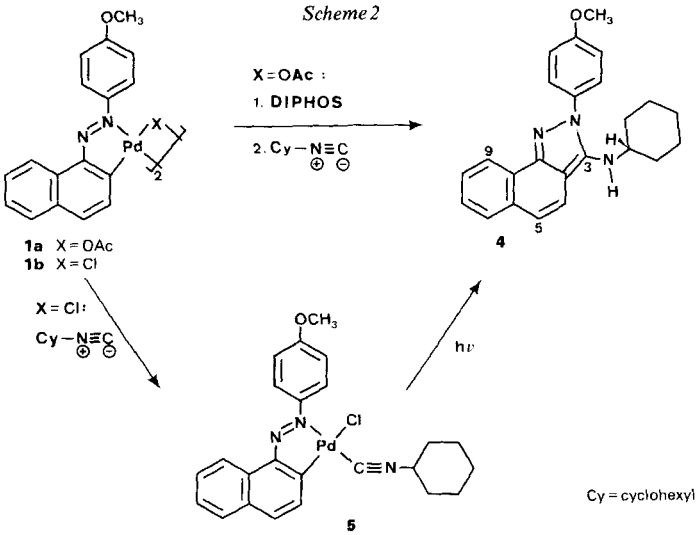
instead of the monodentate Ph_3P was used, the 3-aminoindazole derivative **3** was isolated in good yield. The presence of water favours the formation of the aminoindazole **3** over the *ortho*-cyanated azo compound **2** *(Scheme 1)*. In the absence of a monomerizing phosphine the reaction of complex **1a** with TBACN leads to the cyano-bridged analogue of complex **1a** and no insertion of the cyanide into the Pd-C bond occurs.

Scheme 1



The synthesis of *N*-monosubstituted 3-amino-2-aryl-benzo[*g*]indazoles is achieved easily by the method described by *Yamamoto and Yamazaki* [10]: the acetato-bridged complex **1a** reacts with *e.g.* cyclohexyl isocyanide in the presence of DIPHOS to the 3-(*N*-cyclohexyl)amino-2-aryl-benzo[*g*]indazole **4** *(Scheme 2)*. The reaction of the

Scheme 2



Cl-bridged complex **1b** with cyclohexyl isocyanide in the absence of phosphine leads to the monomeric isocyano complex **5**. Preliminary experiments showed that complex **5** is readily converted into the 3-(*N*-cyclohexyl)aminoindazole **4** *(Scheme 2)*. Light and a certain amount of water seem to be necessary for this insertion reaction to proceed.

The structures of the cyanated azonaphthalene **2** and for the aminoindazole **3** are established by ^{1}H-NMR spectroscopy[3]). The *ortho*-cyano substituent in **2** generates an *AB*-coupling system for H–C(3) and H–C(4) represented by a pair of doublets at 7.69 and 7.90 ppm, respectively, where the latter is broadened slightly by long-range interactions of H–C(4) with the *peri*-proton H–C(8)[4]). Because of the C(2)-substituent the azo bridge is twisted out of the plane of the naphthyl moiety somewhat. This reduces the deshielding of the *peri*-proton and its resonance is observed at higher field (at about 8.67 ppm) compared with the resonance at about 9.0 ppm for H–C(8) in azonaphthalenes without C(2)-substituents [12] [13].

In the ^{1}H-NMR spectrum of the aminoindazole **3** the *AB*-coupling pattern for H–C(4) and H–C(5) manifests itself in a pair of doublets at 7.30 ppm and 7.16 ppm, where the latter is broadened by long-range interactions of H–C(5) with H–C(9)[4]). ^{1}H-NMR data assign the indazole[5]) structure **4** to the product of the isocyanide insertion: in (D_6)DMSO (360 MHz) the NH-proton appears as a doublet at 5.37 ppm which couples with the neighbouring cyclohexyl proton attached to the tertiary C-centre. This coupling interaction was confirmed by decoupling experiments.

Conclusion. – *ortho*-Cyanated 1-arylazonaphthalenes can be obtained by cleavage of the Pd-C bond of a cyclopalladated complex with tetrabutylammonium cyanide in the presence of phosphine. The amount of 3-amino-benzo[*g*]indazole **3** formed depends upon the reaction conditions and the nature of the phosphine (triphenylphosphine *vs.* DIPHOS). The aminoindazole **3** is isolated almost exclusively when DIPHOS is used to monomerize the dimeric Pd(II)-azo complex **1a** and when water is present in the reaction mixture. The mechanism of the cleavage reaction to the cyano-azo compound **2** and of the cyclization to the aminoindazole **3** is not clear yet and has to be elucidated by additional experiments. It can be assumed that prior to the insertion the cyanide is coordinated at the Pd(II)-centre, but such a complex could not be detected yet. Analogous intermediate complexes with coordinated isocyanide (complex **5**) or carbon monoxide [14] have been isolated and were shown to undergo the insertion reaction.

Partial financial support of this work by *Ciba-Geigy AG*, Basel and by the *Eidgenössische Technische Hochschule* (project No. 0.330.082.09/0) is gratefully acknowledged.

Experimental Part

General. See [12]. The syntheses of the complexes **1a** and **1b** have been described earlier [12]. The IR spectra were recorded on the *Perkin Elmer 1430* spectrophotometer of the Dept. of Inorganic Chemistry, ETHZ. Yields are not optimized. Abbreviations: r. t. = room temperature; *i.v.* = in vacuum.

---

[3]) We acknowledge gratefully the invaluable NMR work of Mr. *F. Bangerter.*

[4]) This long-range coupling was confirmed by decoupling experiments.

[5]) *Yamamoto and Yamazaki* [10] claimed that they had obtained the tautomeric indazoline from a Pd(II)-azobenzene complex and isocyanides.

Tetrabutylammonium Cyanide (TBACN). Tetrabutylammonium hydrogensulfate (3.40 g, 10 mmol; *Fluka, purum*) was dissolved in 10 ml CH_2Cl_2. After addition of 1.0 ml 10 M KOH and cooling of the mixture to r.t. a solution of 0.749 g (11.5 mmol) KCN in 1.5 ml H_2O was added. The two-phase mixture was stirred for 5 min at r.t., the org. layer separated, dried ($MgSO_4$), evaporated, and the residue dried *i.v.*, yield 2.375 g (88%) TBACN which is dissolved in CH_2Cl_2 for use[6]).

2-Cyano-1-(4'-methoxyphenylazo)naphthalene (**2**). The mixture of 0.171 g (0.2 mmol) **1a** and 0.424 g (1.6 mmol) Ph_3P *(Fluka, puriss.)* dissolved in 2 ml dry CH_2Cl_2 was stirred at r.t. After 30 min 1.8 ml (0.8 mmol) of freshly prepared 0.441 M TBACN-solution were added and the mixture was kept at r.t. overnight. The crude product was chromatographed (silica gel, CH_2Cl_2), yield 0.054 g (47%) **2**, m.p. 141°. IR (CsBr): 3100*w*, 3075*w*, 3050 w, 3020 w, 3000 w, 2975 w, 2955 w, 2845 w, 2215 m, 1904 w, 1601 s, 1578 s, 1557 w, 1510 m sh, 1503 *s*, 1470 *m*, 1465 *w* sh, 1453 *w*, 1445 *m*, 1417 *m*, 1380 *w*, 1344 *w*, 1330 w, 1319 w, 1300 m, 1258 s, 1225 m sh, 1192 *w*, 1170 *w* sh, 1155 *m*, 1149 *m*, 1137 *s*, 1105 *m*, 1073 *w*, 1021 *m*, 955 *w* sh, 948 *w*, 892 *w*, 860 *w*, 836 *s*, 815 *s*, 805 *w* sh, 705 *w* sh, 690 *w*, 672 *w*, 665 *w*, 633 w, 587 *w*, 540 *w*, 515 *w*, 432 *w*, 415 *w* sh, 368 *w*, 358 *w*, 272 *w*, 240 *w*. ^{1}H-NMR (360 MHz, $CDCl_3$): 3.94 (*s*, 3H, OCH_3); 7.08 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.64–7.71 (*m*, 3H, H–C(6 and 7), including 7.69 *d*, $J = 8.4$, H–C(3)); 7.89–7.94 (*m*, 2H, H–C(5), including 7.90 br. *d*, $J = 8.2$, H–C(4)); 8.13 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 8.66–8.69 (*m*, 1H, H–C(8)). MS: 288 (8), 287 (38, M^+), 153 (4), 152 (19), 136 (4), 135 (42), 125 (5), 108 (8), 107 (100), 92 (24), 78 (4), 77 (34), 64 (14), 63 (8), 51 (5).

3-Amino-2-(4'-methoxyphenyl)benzo[g]indazole (**3**). The mixture of 1.024 g (1.2 mmol) **1a** and 2.88 g (7.2 mmol) DIPHOS *(Fluka, purum)* dissolved in 10 ml CH_2Cl_2 was stirred for 30 min at r.t. Then a mixture of 1 ml H_2O and 9.6 ml (4.8 mmol) of a freshly prepared 0.5 M TBACN-solution in CH_2Cl_2 was added. The two-phase mixture was kept at r.t. overnight, the org. layer separated, concentrated *i.v.*, and the residue chromatographed on silica gel with 20:1 CH_2Cl_2/AcOEt. A recrystallization from CH_2Cl_2/hexane yielded 0.610 g (82%) **3** as slightly greyish crystals, m.p. 206°. IR (CsBr): 3415 *m*, 3405 *m*, 3275 *m*, 3240–2900 br. *s*, 3040 *m*, 2995 *m*, 2960 *w*, 2935 *w*, 2905 *w*, 1647–1641 br. *s*, 1604 *m*, 1584 *w*, 1560 *s*, 1548 *s*, 1532 *s*, 1512 *s*, 1474 *w*, 1463 *w*, 1452 *m*, 1442 *m*, 1428 *w*, 1407–1400 br. *m*, 1397 *m*, 1252 *m*, 1203 *w*, 1184 *w*, 1166 *m*, 1139 *m*, 1103 *w*, 1090 *w*, 1057 *w*, 1027 *m*, 1008 *w*, 985 *w*, 953 *w*, 931 *w*, 886 *m*, 867 *w*, 836 *s*, 812 *w*, 804 *m*, 760 *w*, 753 *w*, 737 *w*, 700 *w*, 598 *w*, 584 *w*, 567 *w*, 520 *w*, 442 *w*. ^{1}H-NMR (360 MHz, $CDCl_3$): 3.86 (*s*, 3H, OCH_3); 4.18 (br. *s*, 2H, NH_2); 7.03 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.16 (br. *d*, $J = 8.9$, 1H, H–C(5)); 7.30 (*d*, $J = 9.0$, 1H, H–C(4)); 7.48–7.52 (*symm. signal with 8 lines*, 2H, H–C(7 and 8)); 7.57 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 7.73–7.76 (*m*, 1H, H–C(6)); 8.52–8.55 (*m*, 1H, H–C(9)). MS: 290 (21), 289 (100, M^+), 288 (6), 275 (5), 274 (24), 247 (5), 246 (17), 153 (6), 152 (6), 149 (6), 140 (7), 126 (7), 122 (7), 108 (6), 77 (7), 64 (5), 63 (5).

3-(N-Cyclohexyl)amino-2-(4'-methoxyphenyl)benzo[g]indazole (**4**). The mixture of 0.171 g (0.2 mmol) **1a** and 0.480 g (1.2 mmol) DIPHOS *(Fluka, purum)* dissolved in 5 ml CH_2Cl_2 was stirred for 30 min at r.t. Then 0.1 ml (0.8 mmol) cyclohexyl isocyanide *(Fluka, purum)* were added and the mixture kept at r.t. for 30 min. Column chromatography (silica gel, 19:1 CH_2Cl_2/AcOEt) and recrystallization from CH_2Cl_2/hexane yielded 0.112 g (75%) **4**, mp. 125°. UV/VIS ($CHCl_3$): 240 (21 800), 272 (25 500), 335 (9500). ^{1}H-NMR (360 MHz, C_6D_6): 0.75–1.86 (*m*, 10H, cyclohexyl-H); 3.31–3.45 (*m*, 1H, H-cyclohexyl at tertiary C); 3.28 (*s*, 3H, OCH_3); 3.55 (br. *d*, $J = 9$, 1H, NH); 6.73 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.24 (*d*, $J = 9.0$, 1H, H–C(5)); 7.34–7.39 (*m*, 1H, H–C(7)); 7.39–7.43 (*m*, 1H, H–C(8)); 7.48 (*d*, $J = 9.1$, 1H, H–C(4)); 7.58 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 7.72 (*d* × *d*, $J = 7.6$ and 1.5, 1H, H–C(6)); 9.10 (*d* × *d*, $J = 7.7$ and 1.5, 1H, H–C(9)). ^{1}H-NMR (360 MHz, (D_6)DMSO): 1.08–1.90 (*m*, 10H, cyclohexyl-H); 3.25–3.31 (*m*, 1H, H-cyclohexyl at tertiary C); 5.37 (*d*, $J = 8.8$, 1H, NH); 7.13 (*d* of the *AA'*-type, 2H, H–C(3' and 5')); 7.15 (*d*, $J = 9.0$, 1H, H–C(5)); 7.48–7.52 (*m*, 2H, H–C(7 and 8)); 7.59 (*d*, $J = 9.0$, 1H, H–C(4)); 7.65 (*d* of the *XX'*-type, 2H, H–C(2' and 6')); 7.77–7.80 (*m*, 1H, H–C(6)); 8.29–8.32 (*m*, 1H, H–C(9)). MS: 372 (28), 371 (100, M^+), 290 (9), 289 (43), 288 (16), 274 (9), 260 (4), 257 (4), 246 (5), 153 (7), 152 (22), 140 (6), 126 (7), 122 (10), 107 (5), 92 (6), 83 (4), 77 (9), 55 (16), 41 (13); *m** 225 (*m/z* 371 → *m/z* 289), *m** 260 (*m/z* 289 → *m/z* 274).

Chloro(cyclohexylisocyano)[1-(4'-methoxyphenylazo)naphthyl-C(2), N_β]palladium(II) (**5**). The suspension of 0.161 g (0.2 mmol) **1b** in 5 ml CH_2Cl_2 turned clear after 0.1 ml (0.8 mmol) cyclohexyl isocyanide *(Fluka, purum)* had been added. The mixture was stirred for 1 h at r.t. and the solvent distilled off. After column chromatography (silica gel, 4:1 CH_2Cl_2/AcOEt) and recrystallization from CH_2Cl_2/light petroleum ether 0.118 g (58%) **5** were obtained as bright red crystals, m.p. 147–149° (dec.)[7]). IR (CsBr): 3060 *w*, 2940 *m*, 2865 *w*, 2845 *w*, 2230 *s*, 1599 *s*, 1583 *s*, 1570 *m*, 1547 *w*, 1506 *s*, 1465 *w*, 1455 *w*, 1445 *w*, 1427 *w*, 1370 *w*, 1353 *w*, 1320 *m*, 1308 *w*, 1257 *s*, 1200 *w*, 1168 *s*, 1155 *w*, 1130 *w*, 1117 *w*, 1073 *w*, 1034 *m*, 895 *w*, 885 *w*, 835 *m*, 813 *m*, 778 *w*, 745 *w*, 725 *w*, 552 *w*, 530 *w*, 428 *w*, 290 *w*.

---

[6]) The solution of TBACN in CH_2Cl_2 is not stable and has to be used readily.

[7]) Determined in a sealed capillary.

^{1}H-NMR (90 MHz, $CDCl_3$): 1.45–2.20 (*m*, 10H, cyclohexyl-H); 3.89 (*s*, 3H, OCH_3); 3.90–4.20 (*m*, 1H, H-cyclohexyl at tertiary C); 6.98 (*d* of the *AA'*-type, 2H, H–C(3′ and 5′)); 7.45–7.64 (*m*, 4H, H–C(3, 4, 6 and 7)); 7.71–7.85 (*m*, 1H, H–C(5)); 8.21 (*d* of the *XX'*-type, 2H, H–C(2′ and 6′)); 8.64–8.75 (*m*, 1H, H–C(8)).

Reaction of **1a** *with TBACN in the Absence of Phosphine.* The suspension of 0.17 g (0.2 mmol) **1a** in 2 ml CH_3CN was combined with 1.6 ml (0.8 mmol) of a 0.5 M TBACN-solution in CH_3CN and the mixture stirred at r. t. overnight. The precipitate was filtered off and washed with Et_2O. After drying 0.144 g of practically insoluble di-μ-cyano-bis{[1-(4′-methoxyphenylazo)naphthyl-C(2),N_β]palladium(II)} were obtained. IR (CsBr): among other absorptions 2175*s* for $\nu(CN)_{bt}$.

$[C_{18}H_{13}N_3OPd]_2$ (787.4) Calc. C 54.92 H 3.33 N 10.67% Found C 54.96 H 4.01 N 9.91%

REFERENCES

[1] *K. Gehrig, M. Hugentobler, A.J. Klaus & P. Rys*, Inorg. Chem. *21*, 2493 (1982).
[2] *D.R. Fahey*, J. Organomet. Chem. *27*, 283 (1971).
[3] *M. Mori, K. Chiba & Y. Ban*, Heterocycles *6*, 1841 (1977).
[4] *C.H. Chao, D.W. Hart, R. Bau & R.F. Heck*, J. Organomet. Chem. *179*, 301 (1979).
[5] *G.D. Pandey & K.P. Tiwari*, Tetrahedron *37*, 1213 (1981).
[6] *M. Ishikura, M. Mori, T. Ikeda, M. Terashima & Y. Ban*, J. Org. Chem. *47*, 2456 (1982).
[7] a) *A. Gotteschlich & K. Leverenz*, U.S.P. 3962209 (1976); b) *G.L.A. Belfort*, U.S.P. 4165297 (1979); c) *R. Price & N. Hall*, U.S.P. 4192800 (1980); *K.H. Schündehütte*, Chem. Rundschau (CR-Magazin No. 25), 8 (1981).
[8] *R. Price*, Dyes Pigm. *2*, 11 (1981).
[9] *J. Rigaudy & S.P. Klesney* (Editors), 'IUPAC-Nomenclature of Organic Chemistry', Pergamon Press, Oxford (1979), p. 53-4.
[10] *Y. Yamamoto & H. Yamazaki*, Synthesis *1976*, 750.
[11] *Y. Yamamoto & H. Yamazaki*, J. Org. Chem. *42*, 4136 (1977).
[12] *A.J. Klaus & P. Rys*, Helv. Chim. Acta *64*, 1452 (1981).
[13] *M. Hugentobler, A.J. Klaus, H. Mettler, P. Rys & G. Wehrle*, Helv. Chim. Acta *65*, 1202 (1982).
[14] *E. Steiner & F.A. L'Eplattenier*, Helv. Chim. Acta *61*, 2264 (1978).