Multiple Functionalization of Bis(2-pyridylimino)isoindole (BPI) Ligands: Their Modular Synthesis and Coordination to Palladium(II)

Bettina A. Siggelkow and Lutz H. Gade*

Heidelberg/Germany, Anorganisch-Chemisches Institut der Universität

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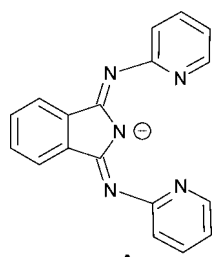
Dedicated to Professor Herbert W. Roesky on the Occasion of his 70th Birthday

Abstract. Polyether dendritic wedges have been attached to bis(2-pyridylimino)isoindole (BPI) ligands, and the corresponding Pd^{II} complexes have been synthesized and studied as hydrogenation catalysts. The fixation of dendrons at the ligand framework was carried out at the stage of the phthalodinitrile precursor of the BPI ligands by nucleophilic substitution of 4-nitrophthalodinitrile with the in situ generated alcoholates. Reaction of 1,3-dibenzyloxy-2-propanol [G-1] and the coupling of Fréchet's first and second generation arylether dendrons [(3,5)-G-1]-OH, [*t*-Bu-(3,5)-G-1]-OH and [(3,5)-G-2]-OH with 4-nitrophthalodinitrile gave the corresponding O-coupled phthalodinitrile derivatives. The synthesis of the BPI ligands was achieved by reaction with two molar equivalents of 2-amino-5-bromopyridine to give the protioligands (11-Br)-BPI-[G-1] (**4**) and (11-Br)-BPI-[R-(3,5)-G-1] (R = H: **5a**, tBu: **5b**) whereas the reaction of compound **5a** with Me_3SiCCH, Ph_3SiCCH and PhCCH, using Sonogashira's $[Pd(PPh_3)_4]$/CuI catalyst, gave the corresponding bis(alkynyl)-derivatives. All the protioligands were cleanly metallated to give the corresponding palladium(II) complexes. In contrast to the unsubstituted complex, its dendrimer functionalized derivatives [(11-Br)-BPI-[R-(3,5)-G-1]-PdCl] (R = H: **9a**, *t*Bu : **9b**) and [(11-Br)-BPI-[(3,5)-G-2]-PdCl] (**11**) hydrogenated styrene and 1-octene without decomposition (TOF = 5 h^{-1} at T = 295 K, $p(H_2)$ = 1 bar, 2 mol% cat.) and among these, catalyst **11**, carrying the 2nd generation dendron displayed sufficient stability to be isolated and reused several times.

Keywords: Palladium; N-Donor Ligands; Dendrimer; Sonogashira Coupling

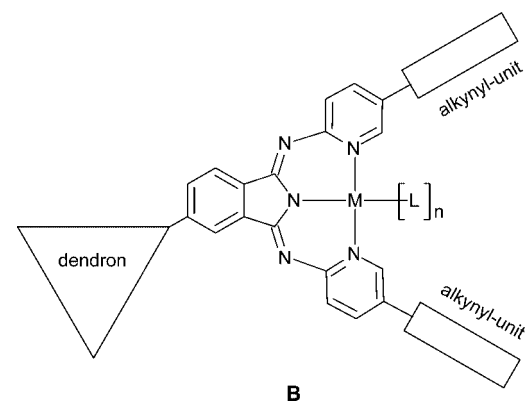
Introduction

We have recently begun to study the catalytic activity of palladium complexes containing derivatives of the well established bis(2-pyridylimino)isoindolate (BPI) ligands (**A**) [1]. These BPI-palladium compounds have proved to be a promising new non-phosphine based class of molecular hydrogenation catalysts for alkenes. Prior to this work, the tridentate BPI ligands have been extensively studied in oxidation catalysis induced by the middle and late transition metals [2−10].



A

The protonated neutral precursors of the formally anionic BPI ligands are readily accessible in a one-step condensation reaction of a phthalodinitrile derivative with two molar equivalents of 2-aminopyridine [4]. This simplicity of their assembly makes them promising candidates as core molecules within complex structural architectures. In particular, it was of interest to assess whether the introduction of larger peripheral structural units was possible after the initial assembly of the BPI core. Such novel ligand systems might confer significantly different chemical properties upon their complexes, affecting for instance their kinetic stability and solubility.



B

In this work we report the synthesis of BPI derivatives (**B**) containing polyether dendritic wedges [11, 12] attached to the ligand backbone, as well as alkynyl units of variable steric bulk coupled to the pyridyl groups. By way of the chosen synthetic strategy a modular assembly of a wide variety of such derivatives is feasible. As examples for their

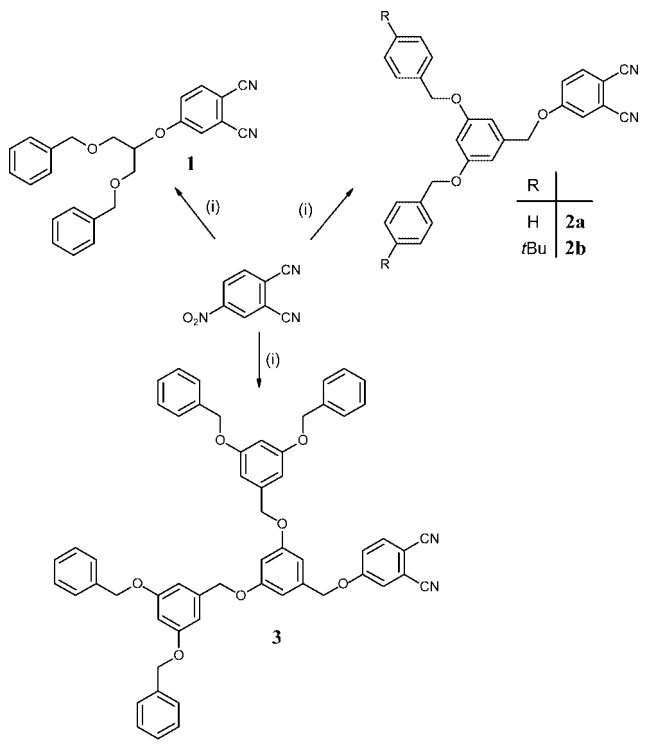
* Prof. Dr. L. H. Gade
Anorganisch-Chemisches Institut, Universität Heidelberg
Im Neuenheimer Feld 270
D-69120 Heidelberg/Germany
Fax: +49-(0)6221-545609
E-mail: lutz.gade@uni-hd.de

complexation to transition metals, the synthesis of several new dendritic BPI-Pd complexes will be described.

Results and Discussion

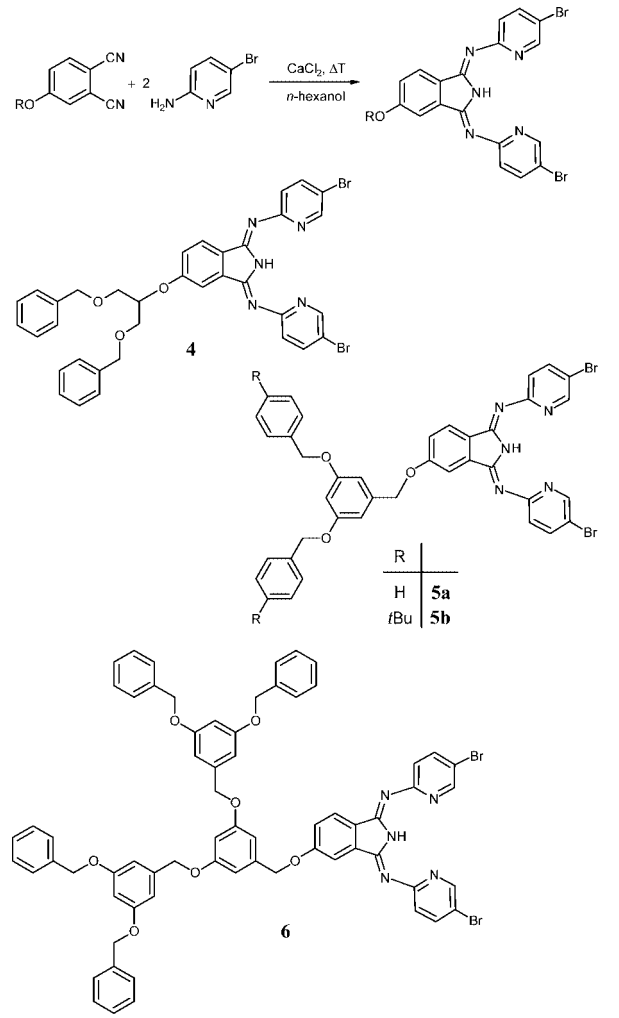
Synthesis of Bis(2-pyridylimino)isoindole Containing Polyether Dendritic Wedges Attached to the Ligand Framework

The fixation of polyether dendritic wedges at the ligand framework of bis(2-pyridylimino)isoindole was carried out at the stage of the phthalodinitrile precursor. As *Brewis* et al. have shown in their synthesis of phthalocyanines at the core of polyarylether dendrimers [13], the coupling of the dendrons with the ligand or dendrimer core is readily achieved by the nucleophilic substitution of 4-nitrophthalodinitrile with the in situ generated alcoholates. This strategy was chosen since *Siegl* et al. had previously found that the substitution of a nitro function in the backbone of BPI derivatives is not feasible [4d].



Scheme 1 Fixation of polyether dendrons to phthalodinitrile. (i) K_2CO_3, DMF, ΔT.

Reaction of 1,3-dibenzyloxy-2-propanol [G-1] [14] with 4-nitrophthalodinitrile in dimethylformamide (DMF) using K_2CO_3 as auxiliary base, cleanly gave the O-coupled phthalodinitrile derivative 4-[G-1]-phthalodinitrile (**1**) (Scheme 1). In a similar way, the reaction of Fréchet's first and second generation arylether dendrons [(3,5)-G-1]-OH, [*t*-Bu-(3,5)-G-1]-OH and [(3,5)-G-2]-OH [11] with 4-nitrophthalodinitrile gave the ligand precursors **2a**, **2b** and **3**. Whereas **1**, **2a** and **2b** were obtained in good yield after stirring at 60 °C for two days, the fixation of the second generation dendron in **3** required an extended reaction time of eight days.

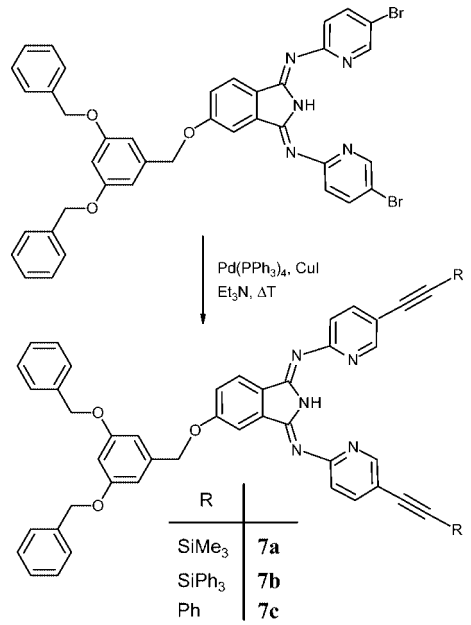


Scheme 2 Synthesis of 1,4-bis{2-(4-bromopyridyl)imino}isoindole derivatives containing dendritic polyether wedges.

The synthesis of the BPI ligands derived from **1** and **2a,b** was achieved by stirring the dendron-functionalized phthalodinitriles with two molar equivalents of 2-amino-5-bromopyridine in the presence of $CaCl_2$ in hexanol under reflux for 20 − 25 h. This gave the protioligands (11-Br)-BPI-[G-1] (**4**) and (11-Br)-BPI-[R-(3,5)-G-1] (R = H: **5a**, ^{t}Bu: **5b**) as yellow microcrystalline solids (Scheme 2). The preparation of the BPI derivative containing the second generation arylether dendron required more forcing reaction conditions. Refluxing compound **3** with two equivalents of 2-amino-5-bromopyridine in the presence of $CaCl_2$ in a 2:3 mixture of mesitylene/hexanol for 10 days gave the corresponding BPI ligand (11-Br)-BPI-[(3,5)-G-2] (**6**) which was purified by column chromatography.

Sonogashira Coupling of a Dendritic Bis(2-pyridylimino)isoindole with Terminal Alkynes to give the 11-Alkynylpyridyl Derivatives

We have previously found that BPI ligands are stable with respect to the conditions of palladium catalyzed Sonoga-



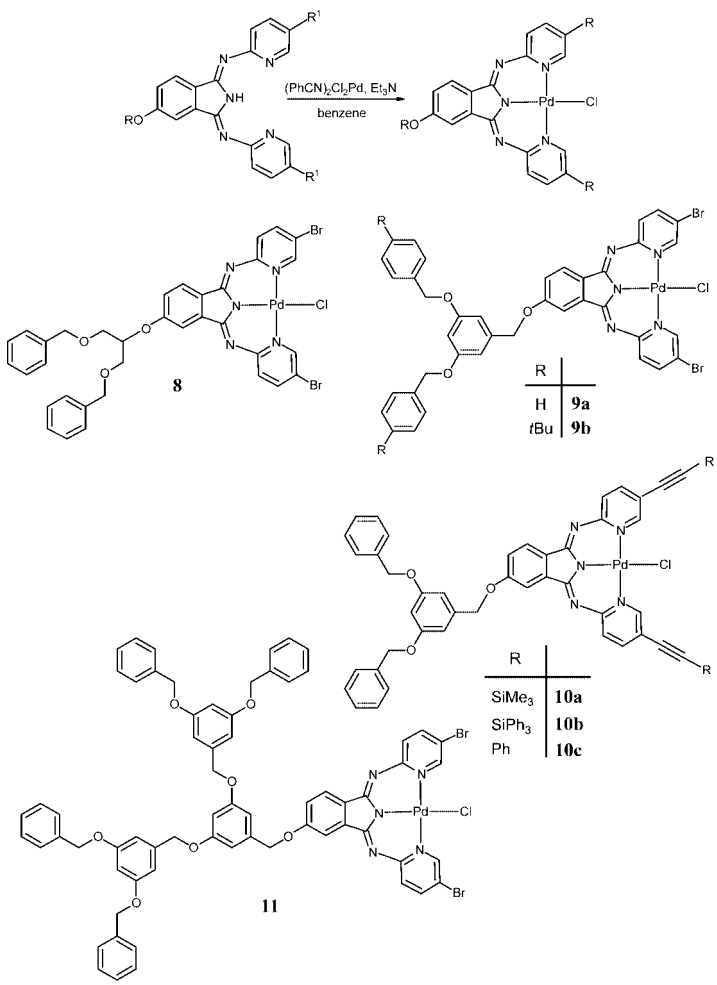
Scheme 3 Alkynylation of a 1,4-bis{2-(4-bromopyridyl)imino}-isoindole by Sonogashira coupling

shira type couplings. This opened up the possibility of an "a posteriori" functionalization of the dendritic BPI derivatives discussed above. The reaction of compound **5a** with Me_3SiCCH, Ph_3SiCCH and PhCCH using Sonogashira's $[Pd(PPh_3)_4]$/CuI catalyst [15] gave the highly functionalized BPI ligand precursors **7a** − **7c** in good yields (Scheme 3).

The reaction products precipitated as orange (**7a,b**) and red (**7c**) microcrystalline solids during the course of the conversion. Their formulation as represented in Scheme 3 was confirmed by elemental analysis, the observation of the molecular ion peaks in their FAB mass spectra, the ν(CC) infrared bands at 2135 − 2155 cm^{-1} as well as the ^1H and ^{13}C NMR data.

Synthesis of Highly Functionalized Dendritic BPI-Palladium Complexes

The preparation of the dendrimer-functionalized square planar palladium(II) complexes **8** − **11** was carried out by reaction of the protioligands with $[(PhCN)_2PdCl_2]$ as Pd^{II} precursor in benzene and with triethylamine as an auxiliary base (Scheme 4). The reaction products precipitated directly



Scheme 4 Synthesis of BPI-palladium(II) complexes with dendritic wedges attached to the ligand backbone.

from the reaction mixture as orange-red microcrystalline solids which were isolated by filtration and were obtained as analytically pure compounds after extraction from dichloromethane/water.

The metallation was monitored by ^{1}H-NMR spectroscopy, the most characteristic change being the coordination shift of the 6-pyridyl protons from ca. 8.4 ppm in the protioligands to ca. 9.5 ppm in the palladium complexes and the disappearance of the NH-resonance of the isoindole unit. In all the dendrimer-functionalized complexes the BPI-unit has lost the C_s-symmetry of the parent compound leading to two sets of signals for the pyridyl-units and their attached functional groups. The FAB mass spectra of all the palladium(II) complexes displayed the characteristic $[M\text{-}Cl]^+$ fragment which, together with the elemental analyses establishes the formulation of the compounds given in Scheme 4. For the silylated complexes [(11-TMS-ethynyl)-BPI-{(3,5)-G-1}PdCl] (**10a**) and [(11-Ph_3Si-ethinyl)-BPI-{(3,5)-G-1}PdCl] (**10b**) the ^{29}Si NMR resonances (**10a**: −22.1, **10b**: −22.3 ppm) are shifted with respected to those of the protioligands **7a** and **7b** (−16.9 and −28.5 ppm, respectively).

Catalytic Hydrogenation of Styrene and 1-Octene with the Dendron-Functionalized Palladium Complexes 9b and 11

There is a substantial interest in the development of molecular non-phosphine containing palladium catalysts for homogeneous hydrogenations. *Costa*, *Pelagatti* et al. have studied the hydrogenation activity of palladium(II) complexes stabilized inter alia by polydentate N∩N∩S [16] and N∩N∩N ligands [17]. In particular, the use of tridentate nitrogen donor ligands gave rise to relatively efficient Pd^{II}-hydrogenation catalysts. The activation of dihydrogen is thought to involve the protonation of a basic site in the polydentate N-ligand and this formally protonated site in subsequently involved in the elimination of the saturated reaction product. We have recently shown that some BPI-palladium complexes hydrogenate alkenes without decomposition provided they do not carry electron withdrawing substituents at the pyridyl units [2].

The latter is the case for [(11-Br)-BPI-PdCl] [2] which is degraded during the course of catalytic hydrogenations under atmospheric pressures of H_2. In contrast to the unsubstituted complex, its dendrimer functionalized derivatives [(11-Br)-BPI-[R-(3,5)-G-1]-PdCl] (R = H: **9a**, *t*Bu : **9b**) and [(11-Br)-BPI-[(3,5)-G-2]-PdCl] (**11**) hydrogenate styrene without decomposition (TOF = 5 h^{-1} at T = 295 K, $p(H_2)$ = 1 bar, 2 mol% cat.) and among these, catalyst **11**, carrying the second generation dendron displays sufficient stability to be isolated at the end of a catalytic run and reused several times. This behaviour is similar to that observed for the stable BPI-derivatives which are alkylated at the pyridyl units.

The stabilization of the hydrogenation catalyst upon going from **9a,b** to **11** is also apparent in the hydrogenation of 1-octene depicted in Figure 1.

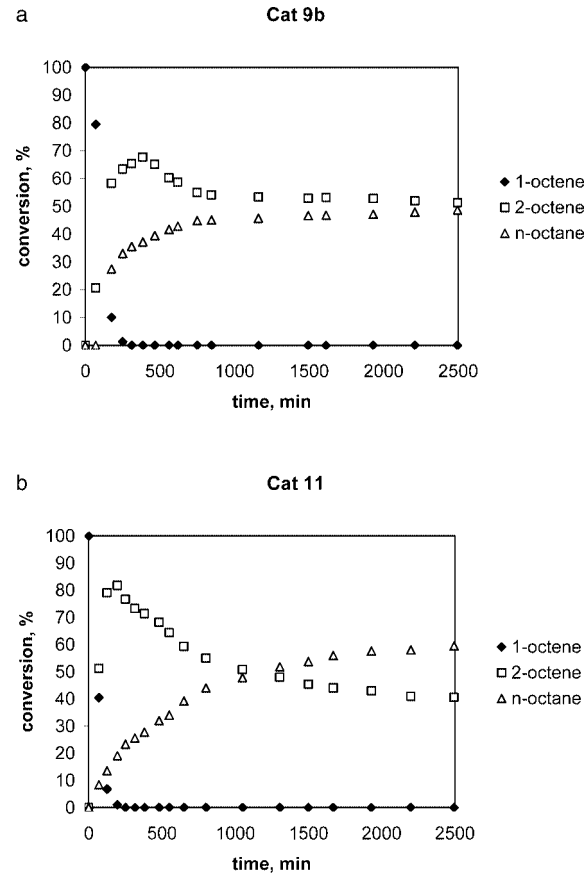


Figure 1 Hydrogenation of 1-octene catalyzed by **9b** (a) and **11** (b) and the concomitant isomerization of the alkene to a mixture of *E*- and *Z*-2-octene as followed by GC-MS.

A remarkable feature of both catalysts carrying the dendritic wedges is the rapid isomerization of 1-octene to 2-octene which for the second generation dendrimer catalyst **11** leads initially to an almost complete shift of the C=C double bond (> 80 %) before the hydrogenation of the olefin(s) leads to a steady generation of *n*-octane.

Conclusion

In this paper we have devised a straightforward strategy which allows for the combination of the well established BPI ligand systems with large structural building blocks leading to the modular assembly of systems of greater complexity. Such modifications may influence the reactive or − as in the case at hand − catalytic properties of the coordination compounds. The observation of a greater stability of the dendrimer-functionalized catalysts is in line with previous observations in dendrimer catalysis [18]. The key may be small changes in catalyst solubility and solvation and thus a modification of the microenviroment of the reactive sites.

Experimental Part

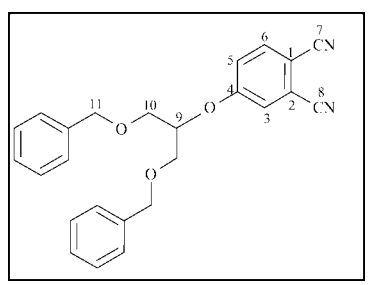
All manipulations were performed under nitrogen. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and stored over 4-Å molecular sieves. Solids were separated from suspensions by filtration through dried Celite or by centrifugation. The ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker AC 200, Bruker Avance 250 and Bruker AMX 400 FT-NMR spectrometers. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the chemistry department at Strasbourg. $[(PhCN)_2PdCl_2]$ [19] was prepared according to a published procedure. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of the phthalonitrile derivatives 1, 2a,b and 3

The coupling of 4-nitrophthalonitrile with the dendritic alcohols was carried out as described by *McKeown* et al. [13] who reported the synthesis of **2a** and **3**. The analytical and spectroscopic data of **1** and **2b** are given below. The yields refer to the preparation on a 5 mmol scale.

4-[G-1]-phthalodinitrile (1)

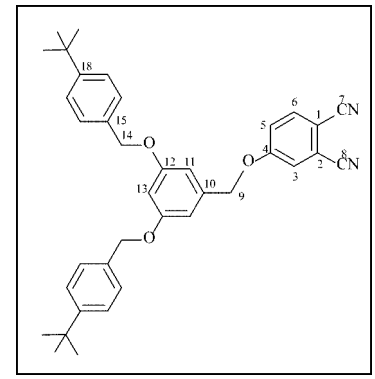
Yield: 63 % (colourless oil). $C_{25}H_{22}N_2O_3$ (398.46 g.mol^{-1}): calcd.: C 75.36, H 5.57, N 7.03; found: C 75.17, H 5.61, N 6.76 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.65−3.76 (m, 4 H, H-10), 4.53 (s, 4 H, H-11), 4.67−4.70 (m, 1 H, H-9), 7.24−7.36 (m, 12 H, H-Ph, H-3,5), 7.62 (d, $^{3}J_{HH}$ = 8.8 Hz, 1 H, H-6). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 69.1 (C-10,11), 73.0 (C-10, 11), 77.9 (C-9), 106.9 (C-1), 115.1 (C-7/8), 115.6 (C-7/8), 116.8 (C-2), 120.5 (C-3/5), 120.8 (C-3/5), 127.2 (C-Ph), 127.7 (C-Ph), 128.3 (C-Ph), 134.8 (C-6), 137.2 (C-12), 161.6 (C-4). **IR** (neat): ν = 3063 (w), 2866 (s), 2601 (vw), 2230 (vs), 1722 (s), 1596 (s), 1562 (s), 1494 (s), 1453 (s), 1425 (w), 1366 (s), 1252 (vs), 1206 (s), 1097 (vs), 1027 (s) cm^{-1}.

4-[*t*-Bu-(3,5)-G-1]-phthalodinitrile (2b)

Yield: 89 %. M.p.: 149 °C. $C_{37}H_{38}N_2O_3$ (558.72 g.mol^{-1}): calcd.: C 79.54, H 6.85, N 5.01; found: C 79.27, H 6.96, N 4.65 %.



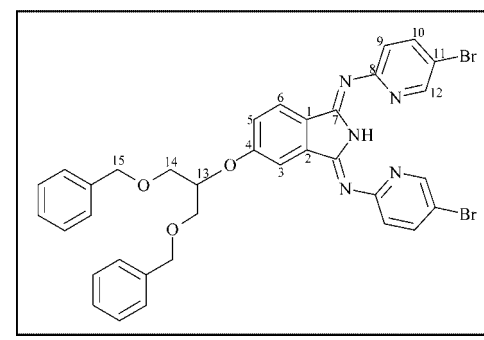
^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 1.31 (s, 18 H, CH_3), 4.97 (s, 4 H, H-14), 5.08 (s, 2 H, H-9), 6.59 (s, 3 H, H-11,13), 7.21 (dd, $^{4}J_{HH}$ = 2.8 Hz, $^{3}J_{HH}$ = 8.8 Hz, 1 H, H-5), 7.29 (d, $^{4}J_{HH}$ = 2.8 Hz, 1 H, H-3), 7.32−7.41 (m, 8 H, H-16,17), 7.67 (d, $^{3}J_{HH}$ = 8.8 Hz, 1 H, H-6). **{^{1}H}^{13}C-NMR** (75.48 MHz, $CDCl_3$, 295 K): δ = 31.1 (**C**H_3), 34.6 (C_q), 70.1 (C-14), 70.9 (C-9), 101.8 (C-13), 106.2 (C-11), 107.6 (C-1), 115.2 (C-7,8), 117.4 (C-2), 119.7 (C-3, 5), 120.0 (C-3, 5), 125.6 (C-Ph), 127.5 (C-Ph), 133.4 (C-10/15), 135.2 (C-6), 136.8 (C-10/15), 151.8 (C-18), 160.5 (C-12), 161.6 (C-4). **IR** (KBr): ν = 3054 (w), 2959 (s), 2229(s), 1594 (s), 1504 (s), 1454 (s), 1412 (w), 1362 (s), 1319 (s), 1257 (s), 1166 (vs), 1030 (s), 857 (w), 817 (s), 544 (w), 522(s) cm^{-1}.

General procedure for the preparation of the functionalized bis(pyridylimino)isoindol ligands 4 − 6. (11-Br)-BPI-[G-1] (4)

The phthalodinitriles **1** − **3** (1.5 mmol), 2-amino-5-bromopyridine (552 mg = 2.3 mmol) and $CaCl_2$ (70.0 mg = 0.63 mmol) were heated in 15 ml of *n*-hexanol under reflux (**4, 5a**: 24 h, **5b**: 48 h, **6**: 10 d). Upon cooling to room temperature, the respective BPI-derivatives precipitated and were isolated by filtration. After extraction with ca 100 ml of water, the yellow solids were dried in a dessiccator over P_4O_{10}.

(11-Br)-BPI-[G-1] (4)

Yield: 53 %. M.p.: 88 °C. $C_{35}H_{29}Br_2N_5O_3$ (727.45 g.mol^{-1}) calcd.: C 57.79, H4.02, N 9.63; found: C 57.31, H 3.61, N 9.15 %.

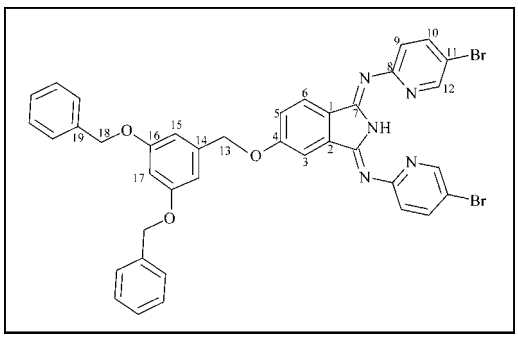


^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.68−3.78 (m, 4 H, H-14), 4.57 (s, 4 H, H-15), 4.81 (m, 1 H, H-13), 7.21-7.48 (m, 13 H, Ph-H, H-5, H-9), 7.60 (s, 1 H, H-3), 7.79 (s, 2 H, H-10), 7.89 (s, 1 H, H-6), 8.56 (s, 2 H, H-12), 13.46 (s, 1 H, N-H). {^{1}H}^{13}C-NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 69.2/69.3 (C-14), 73.5/73.6 (C-15), 78.2 (CH), 108.6 (C-3), 116.0/116.3 (C-11), 119.9 (C-5), 124.2 (C-6), 124.4/124.6 (C-9), 127.6 (C-Ph), 127.9 (C-Ph), 128.5 (C-Ph), 137.3/137.5 (C-1,2), 137.8 (C-Ph), 140.5 (C-10), 148.4/148.5 (C-12), 153.6 (C-7), 158.7 (C-8), 161.9 (C-4). IR (KBr): ν = 1718 (w), 1623 (s), 1560

(vs), 1480 (w), 1449 (s), 1354 (w), 1324 (vw), 1265 (w), 1229 (s), 1090 (s), 1019 (w) cm^{-1}.

(11-Br)-BPI-[(3,5)-G-1] (5a)

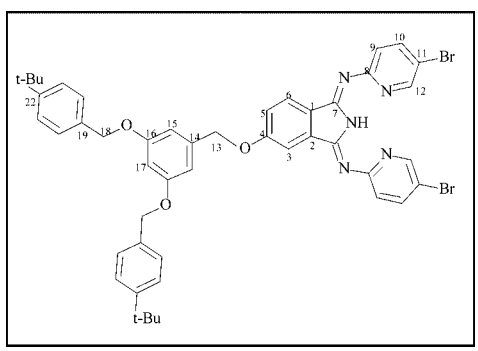
Yield: 97 %. M.p.: 224 °C. $C_{39}H_{29}Br_2N_5O_3$ (775.50 $g.mol^{-1}$): calcd.: C 60.40, H3.77, N 9.03; found: C 60.57, H3.95, N 8.70 %.



^{1}H-NMR (300.18 MHz, $CDCl_3$, 295 K): δ = 5.03 (s, 4 H, H-18), 5.10 (s, 2 H, H-13), 6.58 (s, 1 H, H-17), 6.70 (s, 2 H, H-15), 7.15 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H-5), 7.30-7.33 (pseudo-t, 2 H, H-9), 7.36−7.49 (m, 10 H, H-Ph), 7.52 (s, 1 H, H-3), 7.80 (pseudo-t/d, $^4J_{HH}$ = 2.2 Hz, 2 H, H-10), 7.90 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H-6), 8.54 (pseudo-dd, $^4J_{HH}$ = 2.2 Hz, 2 H, H-12), 13.48 (s, 1 H, N-H). **{^{1}H}^{13}C-NMR** (75.48 MHz, $CDCl_3$, 295 K): δ = 70.2 (C-13/18), 70.4 (C-13/18), 101.7 (C-17), 106.3 (C-15), 107.2 (C-3), 116.0/116.4 (C-11), 119.9 (C-5), 124.1 (C-9), 124.6 (C-6), 127.5 C-Ph), 128.0 (C-Ph), 128.6 (C-Ph), 136.7 (C-19), 137.6 (C-1,2), 138.5 (C-14), 140.5 (C-10), 148.5/148.6 (C-12), 153.6 (C-7), 158.6/158.8 (C-8), 160.2 (C-16), 162.1 (C-4). **IR** (KBr): ν = 3422 (br), 1625 (s), 1560 (s), 1489 (vw), 1448 (m), 1355 (w), 1292 (w), 1228 (w), 1154 (w), 1089 (w), 1027 (w), 835 (w), 732 (vw), 526 (vw) cm^{-1}.

(11-Br)-BPI-[*t*-Bu-(3,5)-G-1] (5b)

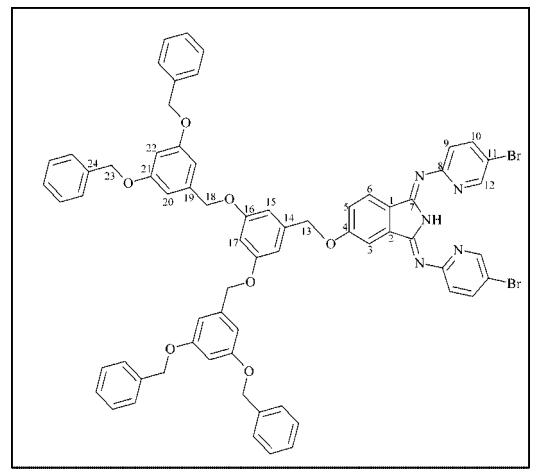
Yield: 45 %. m.p.: 118 °C. $C_{47}H_{45}Br_2N_5O_3$ (887.71 $g.mol^{-1}$): calcd.: C 63.59, H 5.11, N 7.89; found: C 63.50, H 5.43, N 7.78 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 1.33 (s, 18 H, CH_3), 5.01 (s, 4 H, H-18), 5.11 (s, 2 H, H-13), 6.61 (s, 1 H, H-17), 6.72 (s, 2 H, H-15), 7.16 (d, $^3J_{HH}$ = 8.8 Hz, 1 H, H-5), 7.27−7.43 (m, 10 H, Ph-H, H-9), 7.53 (s, 1 H, H-3), 7.79 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, H-10), 7.88 (d, $^3J_{HH}$ = 8.8 Hz, 1 H, H-6), 8.56 (s, 2 H, H-12), 13.46 (s, 1 H, N-H). {^{1}H}^{13}C-NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 31.3 (CH_3), 34.6 ($\mathbf{C}CH_3$), 70.0 (C-13/18), 70.4 (C-13/18), 101.7 (C-17), 106.3 (C-15), 107.3 (C-3), 116.1/116.4 (C-11), 120.1 (C-5), 124.4 (C-9), 124.6 (C-6), 125.5 (C-Ph), 127.6 (C-Ph), 133.6 (C-19), 137.6 (C-1,2), 138.4 (C-14), 140.6 (C-10), 148.6 (C-12), 151.1 (C-22), 153.6 (C-7), 158.6 (C-8), 160.3 (C-16), 162.3 (C-4). IR (KBr): ν = 2959 (w), 1624 (s), 1563 (s), 1448 (s), 1352 (w), 1228 (w), 1159 (w), 1028 (w), 831 (w) cm^{-1}.

(11-Br)-BPI-[(3,5)-G-2] (6)

Yield: 8 %. M.p.: 57 °C. $C_{67}H_{53}Br_2N_5O_7$ (1200.0 $g.mol^{-1}$): calcd.: C 67.06, H 4.45, N 5.84; found: C 67.05, H 4.86, N 5.17 %.



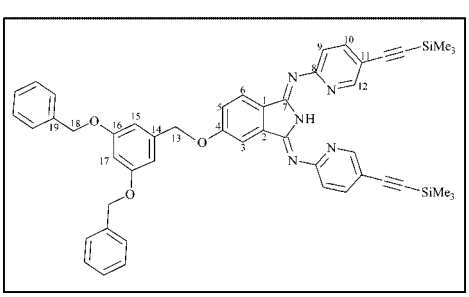
^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 4.95 (s, 2 H, H-13), 4.99 (s, 8 H, H-23), 5.01 (s, 4 H, H-18), 6.55−6.67 (m, 9 H, H-15, 17, 20, 22), 7.07 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.2 Hz, 1 H, H-5), 7.27 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, H-9), 7.29−7.43 (m, 20 H, H-Ph), 7.44 (s, 1 H, H-3), 7.69 (m, 2 H, H-10), 7.80 (d, 1 H, H-6), 8.48 (m, 2 H, H-12), 13.42 (s, 1 H, N-H). {^{1}H}^{13}C-NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 69.9, 70.0, 70.2 (C-13/18/23), 101.5 (C-22), 101.7 (C-17), 106.3 (C-20), 107.3 (C-3), 116.2/116.4 (C-11), 119.9 (C-5), 124.3/124.6 (C-9), 126.4 (C-6), 127.5 (C-Ph), 127.9 (C-Ph), 128.5 (C-Ph), 136.7 (C-19,24), 137.4 (C-1), 138.4 (C-14/15), 139.1 (C-14/15), 140.5 (C-10), 148.4 (C-12), 153.4/153.6 (C-7), 158.3 (C-8), 160.0 (C-16/21), 160.1 (C-16/21), 162.2 (C-4).MS (FAB): 1199 $[M+H]^+$. IR (KBr): ν = 3294 (br), 2921 (w), 1735 (s), 1647 (s), 1595 (vs), 1451 (s), 1292 (w), 1155(s), 1028 (s) cm^{-1}.

Preparation of alkynyl-substituted BPI ligands 7a−c

The BPI-derivative **5a** (0.5 mmol), 6 molar equivalents of the substituted acetylene, 0.12 molar equivalents of CuI and 0.12 molar equivalents of tetrakis(triphenylphosphine)-palladium(0) were stirred in 10 ml of triethylamine at 60 °C. The reaction time was 8 d for **7a**, 5 d for **7b** and 24 h for **7c**. After cooling the reaction mixture to ambient temperature, the solvent was removed *in vacuo*. The residue was redissolved in 10 ml of CH_2Cl_2 the solution extracted with 10 ml of water and then dried over magnesium sulfate. The evaporation of the solvent *in vacuo* yielded the reaction products as pure yellow microcristalline solids.

(11-TMS-acetylen)-BPI-[(3,5)-G-1] (7a)

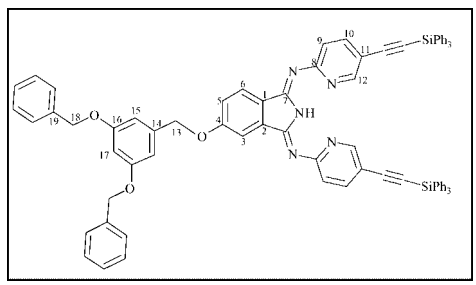
Yield: 72 %. M.p.: 153 °C. $C_{49}H_{47}N_5O_3Si_2$ (810.12 $g.mol^{-1}$): calcd.: C 75.26, H6.06, N8.96; found: C 75.13, H5.79, N 8.15 %.



^{1}H-NMR (300.18 MHz, $CDCl_3$, 295 K): δ = 5.04 (s, 4 H, H-18), 5.10 (s, 2 H, H-13), 6.58 (s, 1 H, H-17), 6.70 (s, 1 H, H-15), 7.16 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, H-9), 7.25-7.40 (m, 11 H, Ph-H, H-5), 7.54 (s, 1 H, H-3), 7.76 (d, $^3J_{HH}$ = 7.4 Hz, 2 H, H-10), 7.88 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H-6), 8.69 (s, 2 H, H-12), 13.66 (s, 1 H, N-H). **{^{1}H}^{13}C-NMR** (75.48 MHz, $CDCl_3$, 295 K): δ = 0.9 (CH_3), 70.1 (C-13/18), 70.4 (C-13/18), 98.0 (**C**≡CSi),101.8 (C-17), 102.2 (C≡**C**Si), 106.4 (C-15), 107.1 (C-3), 116.1/116.3 (C-11), 119.9 (C-5), 122.4 (C-9), 124.0 (C-6), 127.5 (C-Ph), 128.0 (C-Ph), 128.6 (C-Ph), 136.7 (C-19), 137.7 (C-1,2), 138.5 (C-14), 140.8 (C-10), 151.0 (C-12), 153.7 (C-7), 159.2/159.3 (C-8), 160.2 (C-16), 162.1 (C-4). **^{29}Si-NMR** (79.5 MHz, $CDCl_3$, 295 K): δ = −17.0. **IR** (KBr): ν = 2948 (w), 2156 (s), 1623 (vs), 1565 (vs), 1485 (w), 1458 (w), 1379 (w), 1357 (w), 1218 (s), 1155 (s), 1062 (w), 1025 (w) cm^{-1}.

(11-Ph$_3$Si-acetylen)-BPI-[(3,5)-G-1] (7b)

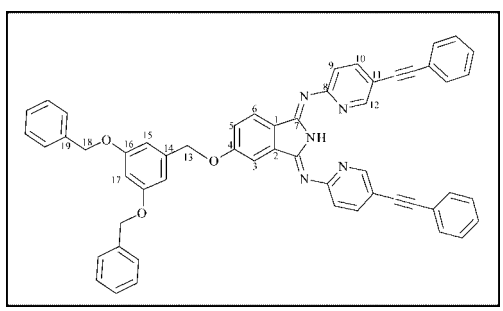
Yield: 84 %. M.p.: 134 °C (dec.). $C_{79}H_{59}N_5O_3Si_2$ (1182.54 $g.mol^{-1}$): calcd.: C 80.24, H 5.03, N 5.03; found: C 80.67, H 4.94, N 4.94 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 5.05 (s, 4 H, H-18), 5.18 (s, 2 H, H-13), 6.59 (s, 1 H, H-17), 6.71 (s, 2 H, H-15), 7.34−7.71 (m, 46 H, Ph-H, H-5, H-9, H-3), 7.93 (d, $^3J_{HH}$ = 7.0 Hz, 1 H, H-6), 8.80 (m, 2 H, H-12), 13.73 (s, 1 H, N-H). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 70.2 (C-13/18), 70.4 (C-13/18), 82.2 (**C**≡CSi), 91.9 (C≡**C**Si), 101.8 (C-14), 106.4 (C-15), 107.1 (C-3), 116.1 (C-11), 120.1 (C-5), 122.6 (C-9), 126.9 (C-6), 127.5 (C-Ph), 128.1 (C-Ph), 128.5 (C-Ph), 130.0 (C-Ph), 130.2 (C-Ph), 132.1 (C-Ph), 135.5 (C-Ph), 136.7 (C-19), 137.7 (C-1,2), 138.4 (C-14), 141.2 (C-10), 151.2 (C-12), 153.8 (C-7), 159.3 (C-8), 160.2 (C-16), 162.1 (C-4). **^{29}Si-NMR** (79.5 MHz, $CDCl_3$, 295 K): δ = −28.5. MS (FAB): 1182 $[M+H]^+$. **IR** (KBr): ν = 3062 (w), 3016 (w), 2153 (s), 1624 (s), 1565 (vs), 1483 (w), 1459 (s), 1428 (s), 1355 (w), 1323 (w), 1269 (w), 1221 (w), 1151 (vw), 1112 (vs), 1028 (s), 819 (s) cm^{-1}.

(11-Ph-acetylen)-BPI-[(3,5)-G-1] (7c)

Yield:75 %. M.p.: 188 °C. $C_{55}H_{39}N_5O_3$ (817.94 $g.mol^{-1}$): calcd.: C 80.76, H 4.81, N 8.56; found: C 80.27, H 4.64, N 9.07 %.



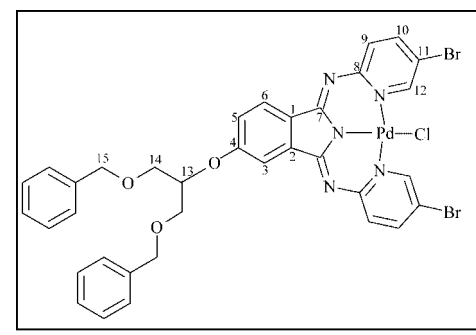
^{1}H-NMR (400.13 MHz, $CDCl_3$, 295 K): δ = 5.03 (s, 4 H, H-18), 5.14 (s, 2 H, H-13), 6.57 (s, 1 H, H-17), 6.70 (s, 2 H, H-15), 7.24-7.55 (m, 26 H, Ph-H, H-5, H-9, H-3), 7.85 (s(br), 1 H, H-6), 8.78 (s(br), 2 H, H-12), 13.93 (s, 1 H, N-H). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 69.3 (C-13,18), 79.0 (**C**≡CSi), 92.8 0 (C≡**C**Si), 100.9 (C-14), 106.5 (C-15), 108.1 (C-3), 115.5 (C-11), 118.4 (C-5/9), 119.6 (C-5/9), 125.5 (C-6), 126.7 (C-Ph), 126.9 (C-Ph), 127.3 (C-Ph), 127.6 (C-Ph), 135.7 (C-Ph/C-19), 136.5 (C-Ph/C-19), 137.9 (C-1,2), 138.5 (C-14/10), 139.7 (C-14/10), 152.1 (C-12,7), 159.3 (C-8), 159.9 (C-16), 161.2 (C-4). MS (FAB): 818 $[M+H]^+$. **IR** (KBr): ν = 3264 (br), 2961 (w), 2135 (vw), 1629 (s), 1567 (s), 1489 (s), 1469 (s), 1352 (w), 1261 (s), 1215 (w), 1101 (s), 1025 (s), 802 (w), 752 (vw), 689 (w) cm^{-1}.

General procedure for the preparation of the palladium(II) complexes 8−11

The bis(pyridyl)isoindole (BPI) derivative (in general 0.3 mmol) and together with 1.1 molar equivalents of $[PdCl_2(PhCN)_2]$ and 1.1 molar equivalents of NEt_3 were dissolved in benzene and stirred at room temperature for 2 days. Depending on the substitution pattern of the ligand, the palladium complex precipitated directly from the reaction mixture or remained in solution. In the case of compound **10b** direct precipitation of the reaction product was observed and the resulting solid was separated by filtration. The co-product $[NEt_3H]Cl$ was extracted from the solid by extraction with 3 x 50 ml of water and the crude product thus obtained was recrystallized from CH_2Cl_2/*n*-hexane. For all other complexes the reaction product remained in solution. After removal of the solvent and the volatiles *in vacuo*, the solid residue was extracted with 10 ml of benzene and the solvent of the extract evaporated *in vacuo*. After washing with 3 x 50 ml of water and 10 ml of hexane, the crude product thus obtained was recrystallized from CH_2Cl_2/*n*-hexane. All compounds are deep yellow-range crystalline solids.

[(11-Br)-BPI-[G-1]-PdCl] (8)

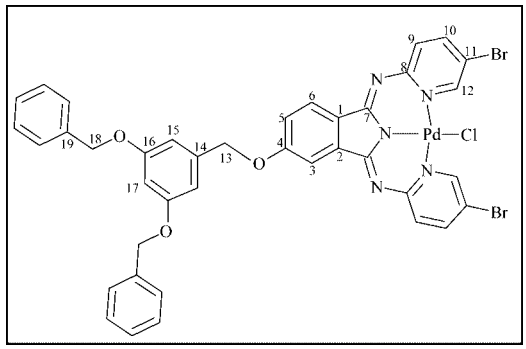
Yield: 58 %. M.p.: 147 °C (dec.). $C_{35}H_{28}Br_2ClN_5O_3Pd$ (868.32 $g.mol^{-1}$): calcd.: C 48.41, H 3.25; N 8.07; found: C 47.94, H 3.88, N 7.89 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 3.78−3.79 (m, 4 H, H-14), 4.57 (s, 4 H, H-15), 4.79 (m, 1 H, H-13), 7.12 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H-5), 7.26−7.37 (m, 12 H, H-Ph, H-9), 7.56 (s, 1 H, H-3), 7.79 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, H-6), 7.89 (m, 2 H, H-10), 9.95 (pseudo-d, 2 H, H-12). {^{1}H}^{13}C-NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 69.3 (C-14), 73.5 (C-15), 108.7 (C-3), 114.4/114.7 (C-11), 120.1 (C-5), 123.9 (C-6/9), 127.4 (C-6/9), 127.6 (C-Ph), 128.3 (C-Ph), 128.4 (C-Ph), 137.9 (C-1,2), 139.3 (C-Ph), 141.8 (C-10), 150.5 (C-7/8), 153.2 (C-7/8), 153.5/153.6 (C-12), 161.6 (C-4). MS (FAB): 832 $[M-Cl]^+$. IR (KBr): ν = 2962 (w), 2855 (w), 1602 (w), 1569 (s), 1515 (w), 1482 (s), 1451 (vs), 1360 (w), 1261 (s), 1219 (s), 1186 (s), 1105 (vs), 1068 (s), 1022 (s) cm^{-1}.

[(11-Br)-BPI-[(3,5)-G-1]-PdCl] (9a)

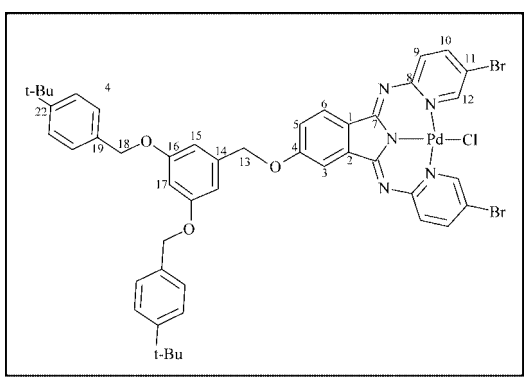
Yield: 43 %. M.p.: 85 °C. $C_{39}H_{28}Br_2ClO_3N_5Pd$ (917.37 g.mol^{-1}): calcd.: C 51.12, H 3.08, N 7.64; found: C 50.98, H 3.88, N 7.33 %.



^{1}H-NMR (300.18 MHz, $CDCl_3$, 295 K): δ = 5.04 (s, 4 H, H-18), 5.09 (s, 2 H, H-13), 6.59 (s, 1 H, H-17), 6.71 (s, 2 H, H-15), 7.07 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 2.2 Hz, 1 H, H-5), 7.11−7.39 (m, 13 H, H-Ph, H-3, H-9), 7.76 (d, $^3J_{HH}$ = 8.4 Hz, 2 H, H-10), 7.83 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H-6), 9.90 (pseudo-d/d, $^4J_{HH}$ = 1.8 Hz, 2 H, H-12). {^{1}H}^{13}C-NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 70.2 (C-13,18), 101.6 (C-17), 106.4 (C-15), 107.4 (C-3), 114.4/114.7 (C-11), 119.1 (C-5), 122.0 (C-6,9), 123.9 (C-6,9), 127.5 (C-C-Ph), 128.0 (C-Ph), 128.6 (C-Ph), 136.7(C-1,2/14/19), 138.5(C-1,2/14/19), 139.4 (C-1,2/14/19), 141.7 (C-10), 150.4/150.5 (C-12), 153.2(C-7/8), 153.6 (C-7/8), 160.8 (C-16), 162.0 (C-4). **MS (FAB)**: 880 [M-Cl]$^+$. **IR** (KBr): ν = 3405 (br), 2932 (w), 2676 (w), 1725 (vw), 1641 (vw), 1602 (s), 156 (s), 1517 (w), 1485 (w), 1451 (s), 1360 (w), 1324 (vw), 1282 (vw), 1218 (w), 1139 (w), 1107 (s), 1067 (s), 833 (w) cm^{-1}.

[(11-Br)-BPI-[*t*-Bu-(3,5)-G-1]-PdCl] (9b)

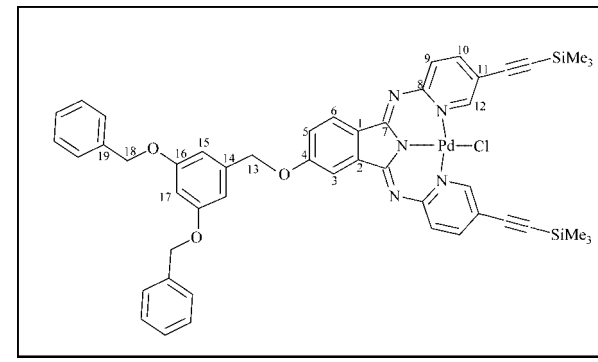
Yield: 38 %. M.p.: 111 °C. $C_{47}H_{44}Br_2ClN_5O_3Pd$ (1028.58 g.mol^{-1}): calcd.: C 54.88, H 4.31, N 6.80; found: C 54.74, H 4.65, N 6.53 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 1.31 (s, 9 H, CH_3), 4.99 (s, 4 H, H-18), 5.09 (s, 2 H, H-13), 6.59 (s, 1 H, H-17), 6.70 (s, 2 H, H-15), 7.07 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H-5), 7.29−7.44 (m, 13 H, H-Ph, H-3, H-9), 7.74 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, H-6), 7.81 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, H-10), 9.90 (pseudo-d, 2 H, H-12). {^{1}H}^{13}C-NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 31.3 (CH_3), 34.6 (CCH_3), 70.0 (C-13/18), 70.3 (C-13/18), 101.6 (C-17), 106.3 (C-15), 107.4 (C-3), 114.4 (C-11), 119.1 (C-5), 123.8 (C-6, 9), 124.5 (C-6,9), 125.5 (C-Ph), 126.5 (C-Ph), 127.5 (C-Ph), 133.6 (C-19), 138.4 (C-1,2/14), 139.4 (C-1,2/14), 141.7 (C-10), 150.5 (C-7/8), 151.1 (C-7/8), 153.3/153.6 (C-12), 160.3 (C-16), 161.9 (C-4). MS(FAB): 991 [M-Cl]$^+$. IR (KBr): ν = 3086 (w), 2959 (vs), 2855 (vw), 1601 (s), 1573 (s), 1517 (w), 1486 (w), 1452 (s), 1361 (s), 1329 (w), 1283 (w), 1218 (w), 1186 (w), 1153 (w), 1107 (s), 1073 (w), 1016 (vw) cm^{-1}.

[(11-TMS-acetylen)-BPI-[(3,5)-G-1]-PdCl] (10a)

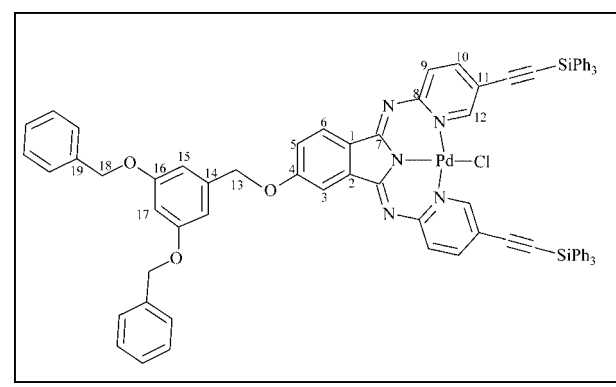
Yield: 34 %. M.p.: 108 °C (dec.). $C_{49}H_{46}ClN_5O_3PdSi_2$ (950.98 g.mol^{-1}): calcd.: C 61.89, H 4.88, N 7.36; found: C 61.27, H 4.31, N 7.17 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 0.26 (s, 18 H, CH_3), 5.04 (s, 4 H, H-18), 5.13 (s, 2 H, H-13), 6.59 (s, 1 H, H-17), 6.70 (s, 2 H, H-15), 7.13 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H-5), 7.39−7.47 (m, 12 H, H-Ph, H-9), 7.54 (s, 1 H, H-3), 7.80 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, H-10), 7.89 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, H-6), 9.92 (pseudo-d, 2 H, H-12). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 1.0 (CH_3), 70.1 (C-13/18), 70.3 (C-13/18), 84.6 (C≡C), 99.8 (C≡C), 101.7 (C-17), 106.4 (C-15), 107.5 (C-3), 116.4 (C-11), 119.1 (C-5), 123.9 (C-9), 125.8 (C-6), 127.5 (C-Ph), 128.3 (C-Ph), 128.6 (C-Ph), 136.7 (C-19), 138.5 (C-1,2/14), 139.7 (C-1,2/14), 141.4 (C-10), 150.8 (C-12), 153.9 (C-7), 156.6 (C-8), 160.2 (C-16), 162.0 (C-4). ^{29}Si-NMR (79.5 MHz, $CDCl_3$, 295 K): δ = −22.1. MS (FAB): 914 [M-Cl]$^+$. IR (KBr): ν = 2962 (s), 2160 (w), 1596 (w), 1560 (w), 1459 (w), 1384 (w), 1363 (w), 1331 (vw), 1261 (s), 1098 (vs), 1023 (vs) cm^{-1}.

[(11-Ph$_3$Si-acetylen)-BPI-[(3,5)-G-1]-PdCl] (10b)

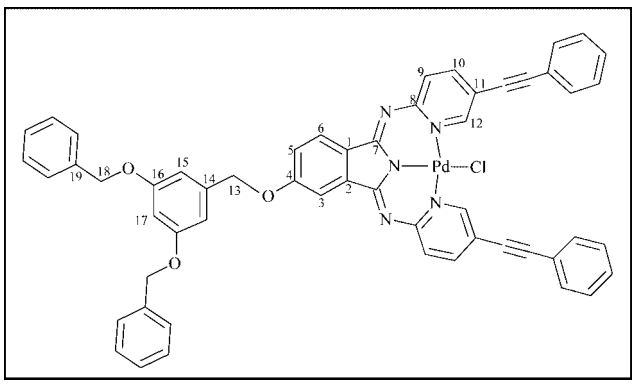
Yield: 61 %. M.p.: 156 °C (dec.). $C_{79}H_{58}ClN_5O_3PdSi_2$ (1320.38 g.mol^{-1}): calcd.: C 71.70, H 4.42, N 5.30; found: C 71.25, H 3.81, N 4.97 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 5.04 (s, 4 H, H-18), 5.15 (s, 2 H, H-13), 6.59 (s, 1 H, H-17), 6.71 (s, 2 H, H-15), 7.16-7.71 (m, 44 H, H-Ph, H-3, H-5, H-9), 7.91-7.94 (m, 3 H, H-6, H-10), 10.10 (pseudo-d, 2 H, H-12). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 70.2 (C-13/18), 70.5 (C-13/18), 82.2 (C≡C), 92.0 (C≡C), 101.8 (C-14), 104.5 (C-15), 106.4 (C-3), 119.5 (C-5), 125.9 (C-9), 127.5 (C-6), 128.6 (C-Ph), 129.9 (C-Ph), 130.3 (C-Ph), 132.2 (C-Ph), 132.8 (C-Ph), 136.0 (C-Ph), 136.5 (C-Ph), 136.7 (C-19), 138.5 (C-1,2), 141.7 (C-10), 150.9/151.2 (C-12), 154.2 (C-7), 157.1 (C-8), 159.1 (C-16), 160.2 (C-4). ^{29}Si-NMR (79.5 MHz, $CDCl_3$, 295 K): δ = −22.3. MS (FAB): 1286 [M-Cl]$^+$. IR (KBr): ν = 3201 (vw), 2959 (w), 2071 (s), 1586 (w), 1560 (s), 1458 (s), 1428 (vs), 1385 (w), 1359 (w), 1258 (w), 1183 (w), 1113 (vs), 1056 (w) cm^{-1}.

[(11-Ph-acetylen)-BPI-[(3,5)-G-1]-PdCl] (10c)

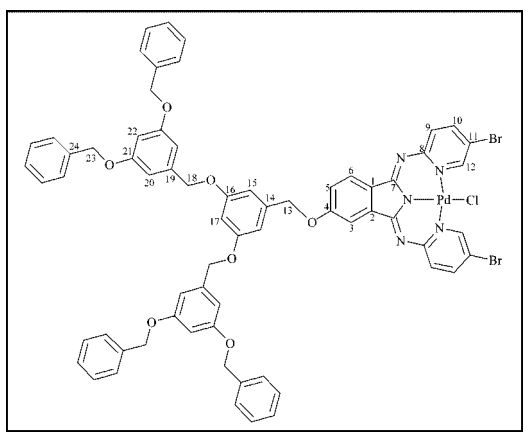
Yield: 55 %. M.p.: 108 °C (dec.). $C_{55}H_{38}ClN_5O_3Pd$ (958.81 g.mol^{-1}): calcd.: C 68.90, H 3.99, N 7.30; found: C 68.63, H 3.41, N 6.82 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 5.01 (s, 4 H, H-18), 5.09 (s, 2 H, H-13), 6.57 (s, 1 H, H-17), 6.69 (s, 2 H, H-15), 7.05 (s, 1 H, H-5), 7.33−7.51 (m, 22 H, H-Ph, H-9), 7.51 (s, 1 H, H-3), 7.83 (s, 2 H, H-10), 7.98 (s, 1 H, H-6), 10.06 (s, 2 H, H-12). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 70.0 (C-12, 14), 85.2 (C≡C), 94.0(C≡C), 101.6 (C-17), 106.3 (C-15), 107.1 (C-3), 116.5 (C-11), 119.0 (C-5), 122.3 (C-9), 125.4 (C-6), 127.5 (C-Ph), 128.0 (C-Ph), 128.1 (C-Ph), 128.3 (C-Ph), 128.5 (C-Ph), 128.7 (C-Ph), 130.1 (C-Ph), 131.7 (C-Ph), 136.6 (C-19), 138.5 (C-1,2/14), 139.7 (C-1,2/14), 140.4 (C-10), 150.6 (C-12), 153.2 (C-7), 156.1 (C-8), 160.1 (C-16), 161.7 (C-4). **MS (FAB)**: 922 [M-Cl]$^+$. **IR** (KBr): ν [$^{-1}$] = 2959 (w), 2217 (vw), 1594 (s), 1560 (s), 1486 (s), 1460 (s), 1378 (w), 1354 (w), 1261 (s), 1187 (w), 1100 (vs), 1019 (vs).

[(11-Br)-BPI-[(3,5)-G-2]-PdCl] (11)

Yield: 46 %. M.p.: 66 °C. $C_{67}H_{52}Br_2ClN_5O_7Pd$ (1340.86 g.mol^{-1}): calcd.: C 60.02, H 3.91, N 5.22; found: C 60.87, H 4.83, N 4.81 %.



^{1}H-NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 4.95 (s, 2 H, H-13), 4.98 (s, 8 H, H-23), 5.01 (s, 4 H, H-18), 6.53-6.97 (m, 9 H, H-15, 17, 20, 22), 7.18 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 3.7 Hz, 1 H, H-5), 7.28−7.38 (m, 20 H, H-Ph), 7.52 (s, 1 H, H-3), 7.63 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, H-10), 7.72 (m, 1 H, H-6), 9.83 (m, 2 H, H-12). **{^{1}H}^{13}C-NMR** (100.61 MHz, $CDCl_3$, 295 K): δ = 70.0 (C-13,18,23), 101.5 (C-22), 101.7 (C-17), 106.3 (C-20), 107.4 (C-3), 114.4 (C-11), 119.1 (C-5), 126.5 (C-6/9), 126.9 (C-6/9), 127.5 (C-Ph), 127.9 (C-Ph), 128.5 (C-Ph), 136.7 (C-19,24), 138.5 (C-1), 139.1 (C-14/15), 139.4 (C-14/15), 141.7 (C-10), 150.5 (C-12), 153.2 (C-7/8), 153.5 (C-7/8), 160.1 (C-16,21), 161.8 (C-4). **MS (FAB)**: 1304 [M+H]$^+$. **IR** (KBr): ν [$^{-1}$] = 3024 (vw), 2921 (vw), 1595 (vs), 1451 (s), 1369 (w), 1317 (w), 1288 (w), 1262 (w), 1213 (vw), 1152 (vs), 1104 (s), 1050 (s), 1027 (s), 828 (s).

Catalyst Testing of 9b and 11

The catalyst tests were carried out in thf at 1 bar H_2 pressure using 2 mol% of palladium catalyst (the catalyst concentration being ca. 1.5 μmol.mL^{-1}). The course of the catalytic hydrogenations was monitored by GC/MS-spectrometry performed with a Shimadzu GC-17A/GCMS-QP5050A. Column: SGE BPX5, 5 % phenyl, polysilyphenylene-siloxane, nonpolar, 30 m, 0.22 mm, carrier gas He. The products were analyzed by comparison of the recorded mass spectra and retention times with those of authentic samples. The measured relative ratio of the products was calibrated by comparative measurements with known substance ratios using pure substances. The data displayed are average values of two runs.

GC/MS-parameters (styrene hydrogenation): T (start) = 50 °C, T (injector) = 250 °C, T (interface) = 280 °C, 30.0 m (0.22 mm), 0.7 ml/min He (flow rate), 66.3 kPa (column pressure), temperature program: 5.0 min, 50 °C; 2 °C.min^{-1}, 80 °C; 20 °C.min^{-1}, 250 °C; retention times: t_R (ethyl benzene) = 7.84 min, t_R (styrene) = 9.12 min,

GC/MS-parameters (1-octene hydrogenation): T (start) = 35 °C, T (injektor) = 250 °C, T (interface) = 280 °C, 30.0 m (0.22 mm), 1.5 ml/min He (flow rate), 133.2 kPa (column pressure), temperature program: 8.0 min, 35 °C; 30 °C.min^{-1}, 250 °C; t_R (1-octene) = 5.62 min, t_R (*n*-octane) = 5.93 min, t_R ((cis/trans)-2-octene) = 6.35 min.

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