Monatshefte für Chemie 136, 1693–1706 (2005)
DOI 10.1007/s00706-005-0368-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Bis(2-pyridylimino)isoindole (*BPI*) Ligands with Novel Linker Units: Synthesis and Characterization of Their Palladium and Platinum Complexes

Markus Meder, Christian H. Galka, and **Lutz H. Gade***

Anorganisch-Chemisches Institut, Universität Heidelberg, 69120 Heidelberg, Germany

Received March 9, 2005; accepted March 22, 2005
Published online September 26, 2005

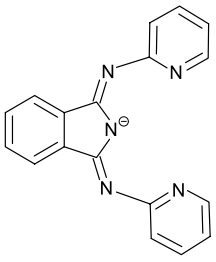
Summary. With the aim of immobilizing bis(2-pyridylimino)isoindolate (*BPI*) ligands their backbone structure has been functionalized with several linker units. Their fixation was carried out at the stage of the phthalodinitrile precursor by nucleophilic *ipso*-substitution of 4-nitrophthalodinitrile. Subsequent synthesis of the functionalized phthalodinitriles with two molar equivalents of the 2-aminopyridine derivatives gave the corresponding *BPI* ligands. Reaction of the ethyleneglycol functionalized *BPI* derivative with the zeroth generation carbosilane dendrimer $[G\text{-}0]_{4\text{-}exo}$-Cl yielded the functionalized dendrimer $[G\text{-}0]_{4\text{-}exo}$-$[O(CH_2)_2O]$-10-*MeBPI* (**7**). The synthesis of the palladium complexes was carried out by reaction of the protioligands with $[(PhCN)_2PdCl_2]$ in benzene using triethylamine as auxiliary base whereas the first examples of *BPI*-platinum complexes were prepared using $[(COD)PtCl_2]$ as starting material.

Keywords. Palladium; Platinum; Ligand design; Dendrimers.

Introduction

The aim of the extensive studies towards the immobilization of molecular catalysts has been the development of catalytic phases which combine the virtues of homogeneous catalysis (high activity and selectivity, directed catalyst design) with those of heterogeneous catalysts (*e.g.* facile catalyst separation and recycling) [1]. The results obtained in this field have revealed that leaching of the metal is a major practical problem, regardless of the method of catalyst fixation and the nature of the support material [2]. This may be suppressed to various degrees by using polydentate ligands which form thermally and kinetically stable complexes with the catalyst metal. A second problem frequently encountered when using immobilized phosphorus-based ligands is their propensity to be oxidized if exposed to air

* Corresponding author. E-mail: lutz.gade@uni-hd.de



Formula 1

over extended periods of time. This has set limits to their recycling potential and has encouraged research into non-phosphorus-containing (in particular, hydrogenation) catalysts which combine molecular stability with sufficient activity [3].

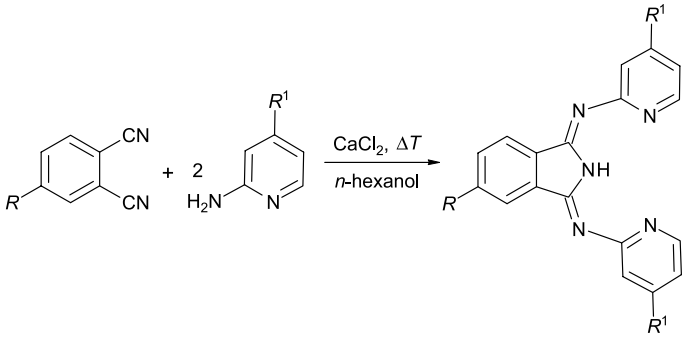
We have recently begun to study the catalytic activity of palladium complexes containing derivatives of the well established bis(2-pyridylimino)isoindolate (*BPI*) ligands (Formula 1) [4]. These *BPI*-palladium compounds have proved to be a promising new non-phosphine based class of molecular hydrogenation 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 [5–13]. However, the use of such systems in heterogenized metal catalysts requires the functionalization of their backbone structure, introducing an appropriate linker unit. In this work we report the preparation of such modified *BPI* ligands and the synthesis of their palladium and platinum complexes.

Results and Discussion

Synthesis of the Bis(2-pyridylimino)isoindole (BPI) Ligands with Linker Units

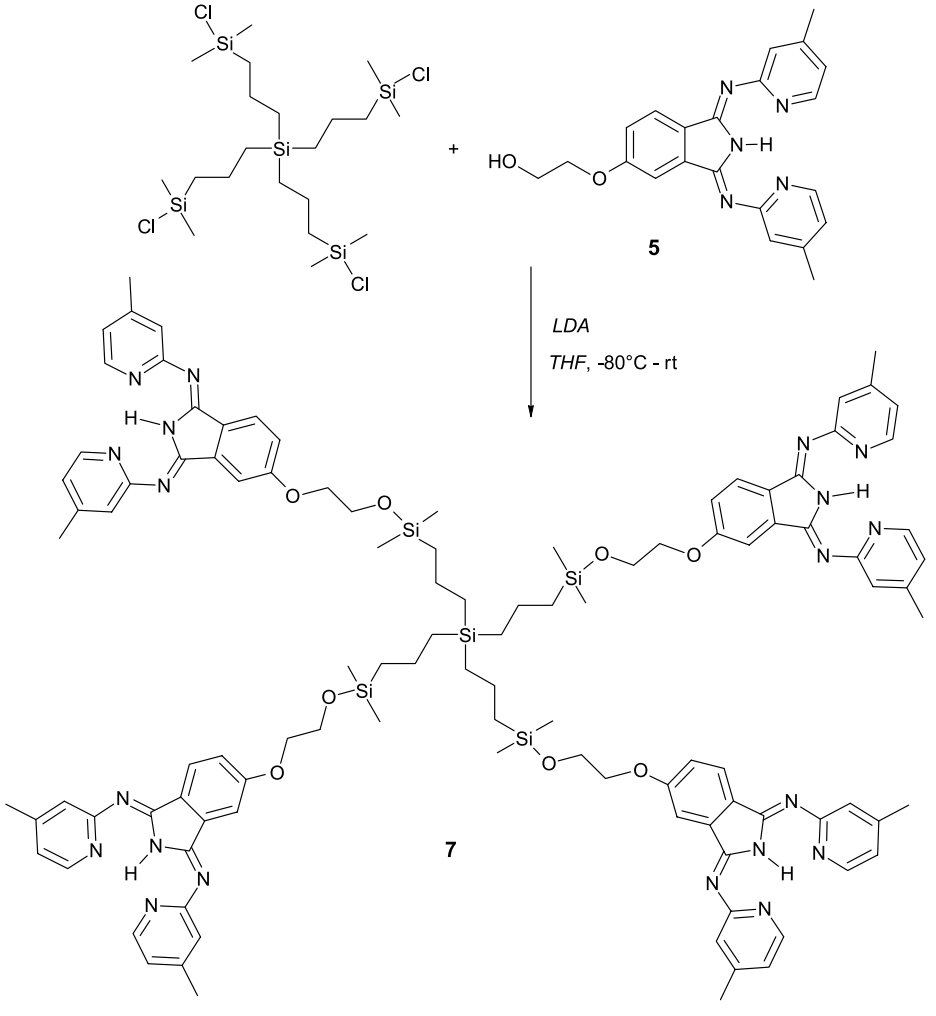
The fixation of linker units at the ligand framework of bis(2-pyridylimino)isoindole was carried out at the stage of the phthalodinitrile precursor. As *Brewis et al.* have shown in their synthesis of phthalocyanines at the core of polyarylether dendrimers [14], the introduction of such linkers is readily achieved by the nucleophilic substitution of 4-nitrophthalodinitrile with the *in situ* generated alcoholates. The synthesis of the *BPI* ligands was subsequently achieved by stirring the functionalized phthalodinitriles with two molar equivalents of the 2-aminopyridine derivatives in the presence of $CaCl_2$ in hexanol under reflux for 20–25 h to give the protioligands displayed in Scheme 1 as yellow microcrystalline solids.

Reaction of the ethyleneglycol functionalized *BPI* derivative **5** with the zeroth generation carbosilane dendrimer $[G\text{-}0]_{4\text{-}exo}$-Cl [15] using *LDA* as a base in *THF* cleanly yielded the functionalized dendrimer $[G\text{-}0]_{4\text{-}exo}$-$[O(CH_2)_2O]$-10-*MeBPI* (**7**) (Scheme 2). The base *LDA* was employed due to the instability of the *BPI* ligands towards alkyllithium reagents and the non-reactivity of NaH towards **5**. With the preparation of compound **7** we have shown the possibility of attaching *BPI* systems to carbosilane dendrimers similar to the immobilization of polydentate phosphines which we reported previously [16].



R	R^1	
H	H	Ref. [5]
Me	H	Ref. [5]
Me	*t*Bu	**3**
3-butenoxy	*Me*	**4**
$HOCH_2CH_2O$-	*Me*	**5**
$HOCH_2CH_2O$-	*t*Bu	**6**

Scheme 1



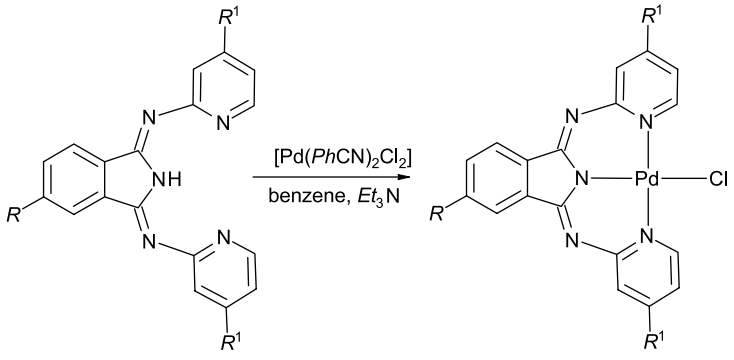
Scheme 2

In the ^{1}H NMR spectrum of the dendritic compound the resonance of the $Si(CH_3)_2$ groups is detected at 0.14 ppm, the corresponding ^{13}C NMR chemical shift being −1.8 ppm while there are practically no coordination shifts of the

signals assigned to the *BPI* units. The ^{29}Si NMR signals were observed at $\delta = 0.4$ (core) and 18.8 ppm [$Si(CH_3)_2$]. The molecular ion peak in the FAB mass spectrum of **7** was found at $m/z = 1974.9$ confirming the completeness of the ligand fixation to the [G-0] carbosilane dendrimer.

Synthesis and Structural Characterization of BPI-Palladium Complexes with Linker Units

The synthesis of the palladium complexes was carried out as reported previously by reaction of the protioligands with [$(PhCN)_2PdCl_2$] in benzene using triethylamine as auxiliary base (Scheme 3). The metallation of the *BPI* protioligands is conveniently followed by ^{1}H and ^{13}C NMR spectroscopy. The coordination shift of the signals attributed to the protons in α-position of the pyridyl substituents from around 8.4 to *ca.* 9.5 ppm along with the disappearance of the NH-resonance of the isoindol unit are particularly diagnostic.



R	R^1	
3-butenoxy	*Me*	**8**
$HOCH_2CH_2O$-	*Me*	**9**
$HOCH_2CH_2O$-	*tBu*	**10**

Scheme 3

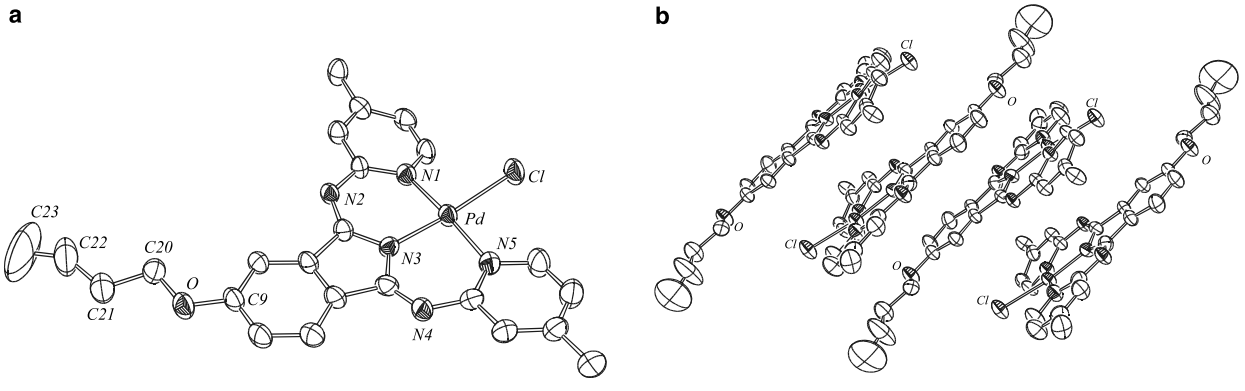


Fig. 1. a) Molecular structure of complex **8**; principal bond lengths (Å) and angles (°): Pd–N3 1.965(5), N3–Pd–N5 89.7(2), Pd–N5 2.068(6), N3–Pd–N1 88.5(2), Pd–N1 2.057(6), N5–Pd–N1 175.1(2), Pd–Cl 2.332(2), N3–Pd–Cl 173.1(1), C9–O 1.369(8), N5–Pd–Cl 91.4(2), O–C20 1.459(9), N1–Pd–Cl 90.9(2), C20–C21 1.48(1), C9–O–C20 118.0(6), C22–C23 1.18(2), C21–C22–C23 140(1); b) view of the packing of compound **8** in the crystal

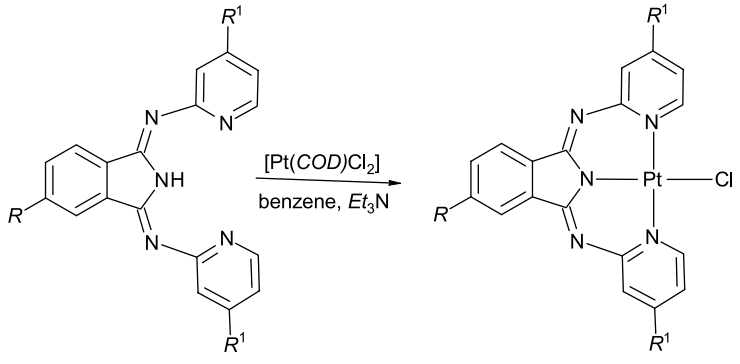
In order to establish the structural details of the palladium complexes a single crystal X-ray diffraction study of one derivative, complex **8**, was carried out. Its molecular structure is displayed in Fig. 1a along with the principal bond lengths and angles. As we have found previously, the amido-type Pd–N3 bond [1.957(6) Å] is *ca.* 0.1 Å shorted than the metal–nitrogen bonds of the neutral pyridyl donor units, while the Pd–Cl bond length of 2.332(3) Å is comparable to palladium–Cl distances reported in the literature [17].

The coordination geometry around the metal centre deviates slightly from the ideal square planar arrangement as reflected in the N3–Pd–Cl angle of 173.1(1)°. A closer inspection of the molecular packing of the complexes in the unit cell in Fig. 1b reveals the formation of a stacked arrangement of a type not observed for other *BPI* complexes.

Synthesis and Structural Characterization of BPI-Platinum Complexes

The extension of the synthetic method employed for the palladium complexes to their heavier Pt congeners by reaction of the protioligands with $[(Ph\mathrm{CN})_2\mathrm{PtCl}_2]$ proved to be hampered by the greater kinetic inertness of the precursor complex. However, using $[(COD)\mathrm{PtCl}_2]$ as an alternative starting material led to the preparation of the first *BPI*-platinum complexes (Scheme 4).

As previously observed for the *BPI*-palladium complexes the platinum analogues with no or only small substituents at the *BPI* ligands proved to be only sparingly soluble. It was therefore not possible to record a ^{13}C NMR spectrum of the unsubstituted derivative **11** even at 353 K in *DMSO*. Complex **11** was nevertheless adequately characterized by the usual analytical and spectroscopic methods. A useful spectroscopic probe is again the significant coordination shift of the α-pyridyl protons from 8.5 ppm in the protioligand to values around 10 ppm observed for the complexes, as well as their $^3J(^{195}\mathrm{Pt}-^1\mathrm{H})$ coupling of *ca.* 19 Hz with the metal nucleus. In order to establish the structural details of these first examples of *BPI*-platinum complexes, a single crystal X-ray structure analysis of compound **13** was carried out. Its molecular structure is displayed in Fig. 2 along with the principal bond lengths and angles.



R	R^1	
H	H	**11**
Me	H	**12**
Me	*tBu*	**13**
3-butenoxy	*Me*	**14**

Scheme 4

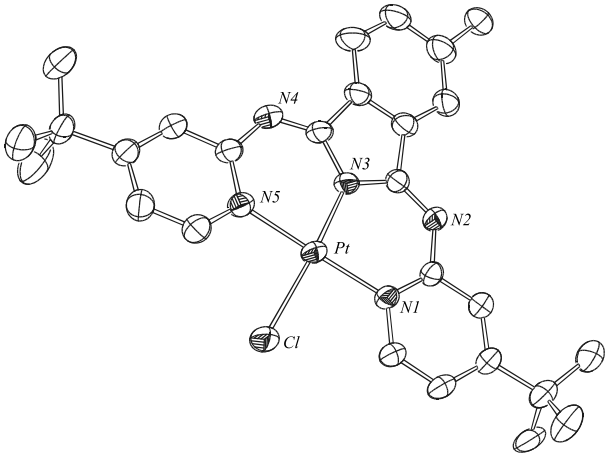


Fig. 2. Molecular structure of complex **13**; principal bond lengths (Å) and angles (°): Pt–N3 1.966(3), N3–Pt–N5 89.50(15), Pt–N5 2.049(4), N3–Pt–N1 88.65(15), Pt–N1 2.060(4), N5–Pt–N1 178.57(13), Pt–Cl 2.335(2), N3–Pt–Cl 170.14(12), N5–Pt–Cl 89.12(11), N1–Pt–Cl 91.92(11)

Complex **13** possesses the expected square planar geometry with Pt–N distances of *ca.* 2 Å and a Pt–Cl bond length of 2.335(2) Å which is comparable to the literature data for platinium(II) complexes [18].

Conclusions

The attachment of linkers to the *BPI* ligand system by nucleophilic ipso-substitution at the 4-nitrophthalodinitrile precursor stage has proved to be straightforward and may serve as a general approach to the immobilization of their complexes. This is of considerable interest due to the observed activity of the palladium complexes in the hydrogenation of olefins at ambient dihydrogen pressure [4a, c] and thus the possibility of recycling such catalysts at the end of the conversion. Our current and future activities in this area are aimed at the development of recyclable *BPI*-Pd catalysts based on the methodology presented in this paper.

Experimental Section

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; results agreed favourably with calculated values. [(*Ph*CN)$_2$PdCl$_2$] [19], [(COD)PtCl$_2$] [20], THP–OCH$_2$CH$_2$OH [21] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

4-(3-Butenoxy)phthalodinitrile (**1**, $C_{12}H_{10}N_2O$)

4-Nitrophthalodinitrile (1.00 g, 5.77 mmol) and K_2CO_3 (1.59 g, 11.5 mmol) were dissolved in *DMF* (25 cm^3) and heated to 50°C. 3-Butenol (0.83 g, 11.5 mmol) was added over a period of 30 min, the

reaction mixture was stirred at 50°C for another 20 h and then cooled to room temperature. After the addition of water (100 cm^3) the mixture was extracted with toluene, the extract dried over $MgSO_4$, and the reaction product obtained as a colourless solid after removal of the solvent in vacuo. Yield 1.02 g (5.14 mmol, 89%); mp 49°C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 2.56$ (dt, $^3J_{HH} = 6.5$ Hz, 2H, $OCH_2C\underline{H}_2$), 4.01 (t, $^3J_{HH} = 6.5$ Hz, 2H, OCH_2), 5.15 (m, 2H, $=CH_2$), 5.83 (m, 1H, =CH–), 7.19 (dd, $^3J_{HH} = 8.8$ Hz, $^4J_{HH} = 2.8$ Hz, 1H, 5-H), 7.22 (d, $^4J_{HH} = 2.8$ Hz, 1H, 3-H), 7.69 (d, $^3J_{HH} = 8.8$ Hz, 1H, 6-H) ppm; {^{1}H}^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 32.9$ ($OCH_2\underline{C}H_2$), 68.3 (OCH_2), 106.8 (C-1), 115.2 (C-7), 115.6 (C-7), 117.1 (C-2), 117.8 ($=CH_2$), 119.2 (C-3), 119.6 (C-5), 133.1 (=$\underline{C}$(H)–), 135.1 (C-6), 161.9 (C-4) ppm; IR (KBr): $\bar{\nu} = 3080$ (w), 2990 (w), 2933 (m), 2896 (w), 2229 (s), 1644 (m), 1602 (s), 1562 (s), 1486 (s), 1465 (m), 1430 (w), 1397 (m), 1309 (s), 1251 (s), 1172 (m), 1095 (s), 1009 (m), 988 (m), 923 (m), 884 (m), 840 (m), 801 (vw), 723 (vw), 641 (w), 560 (vw), 523 (s) cm^{-1}.

4-(THP–OCH_2CH_2O)phthalodinitrile (**2a**, $C_{15}H_{16}N_2O_3$)

4-Nitrophthalodinitrile (5.00 g, 28.9 mmol) and K_2CO_3 (7.98 g, 57.8 mmol) were dissolved in *DMF* (50 cm^3) and heated to 50°C. The protected alcohol *THP*–OCH_2CH_2OH (8.44 g, 57.8 mmol) was added over a period of 30 min, the reaction mixture stirred at 50°C for another 20 h and then cooled to room temperature. After the addition of water (100 cm^3) the mixture was extracted with toluene and the reaction product obtained as a colourless solid after removal of the solvent in vacuo. Yield 6.45 g (23.6 mmol, 82%); mp 75°C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 1.76$–1.50 (m, 6H, e-H, f-H, g-H), 3.48 (m, 1H, d-H_{axial}), 3.78 (m, 2H, b-H), 4.04 (m, 1H, d-H_{equat}), 4.23 (m, 2H, a-H), 4.63 (m, 1H, c-H), 7.21 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.6$ Hz, 1H, 5-H), 7.31 (d, $^4J_{HH} = 2.6$ Hz, 1H, 3-H), 7.67 (d, $^3J_{HH} = 8.7$ Hz, 1H, 6-H) ppm; {^{1}H}^{13}C NMR (50.3 MHz, $CDCl_3$, 295 K): $\delta = 19.3$ (C-f), 25.2 (C-e), 30.4 (C-d), 62.4 (C-g), 65.4 (C-b), 68.6 (C-a), 99.2 (C-c), 107.3 (C-1), 115.2 (C-7), 115.6 (C-7), 117.3 (C-2), 119.6 (C-3), 119.8 (C-5), 135.1 (C-6), 162.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 3082$ (w), 2936 (m), 2872 (w), 2230 (s), 1601 (s), 1562 (m), 1490 (m), 1452 (vw), 1431 (vw), 1353 (vw), 1312 (s), 1288 (w), 1256 (s), 1200(w), 1180 (w), 1144 (m), 1123 (m), 1089 (m), 1082 (m), 1046 (m), 1023 (m), 985 (s), 873 (w), 835 (m), 816 (w) cm^{-1}.

4-($HOCH_2CH_2O$)phthalodinitrile (**2b**, $C_{10}H_8N_2O_2$)

The *THP*-protected phthalodinitrile **2a** was suspended in 50 cm^3 of methanol and subsequently treated with 10 cm^3 of HCl/Et_2O. After stirring at ambient temperature for 12 h the volatiles were removed in vacuo and the residue dissolved in water. By slow addition of an aqueous solution of K_2CO_3 a *pH* of 7 was obtained and the aqueous phase extracted several times with CH_2Cl_2. The combined organic extracts were dried over $MgSO_4$ and upon removal of the solvents in vacuo compound **2b** was obtained as an analytically pure colourless crystalline (needles) solid. Yield 4.31 g (22.9 mmol, 97%); mp 97°C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 2.31$ (s, br, 1H, –OH), 3.96 (t, $^3J_{HH} = 4.6$ Hz, 2H, b-H), 4.13 (t, $^3J_{HH} = 4.6$ Hz, 2H, a-H), 7.20 (dd, $^3J_{HH} = 8.7$ Hz, $^4J_{HH} = 2.6$ Hz, 1H, 5-H), 7.26 (d, $^4J_{HH} = 2.6$ Hz, 1H, 3-H), 7.68 (d, $^3J_{HH} = 8.7$ Hz, 1H, 6-H) ppm; {^{1}H}^{13}C NMR (50.3 MHz, $CDCl_3$, 295 K): $\delta = 60.5$ (C-b), 70.3 (C-a), 107.2 (C-1), 115.2 (C-7), 115.6 (C-7), 117.1 (C-2), 119.4 (C-3), 119.6 (C-5), 135.2 (C-6), 161.8 (C-4) ppm; IR (KBr): $\bar{\nu} = 3307$ (m, br), 3082 (w), 2962 (m), 2235 (s), 1599 (s), 1564 (s), 1496 (s), 1452 (w), 1427 (vw), 1313 (s), 1293 (m), 1260 (s), 1100 (m), 1070 (m), 1044 (m), 961 (w), 898 (m), 854 (m), 727 (w) cm^{-1}.

4-Me-10-^{t}BuBPI (**3**, $C_{27}H_{31}N_5$)

4-Methylphthalodinitrile (1.50 g, 10.6 mmol), 2-amino-4-^{t}butylpyridine (3.96 g, 26.1 mmol), and $CaCl_2$ (0.16 g, 1.36 mmol) were suspended in 1-hexanol (50 cm^3) and heated at reflux for 18 h. After cooling to room temperature the reaction product was isolated as a yellow solid (yellow needles) washed with water and dried over P_4O_{10}. Yield 2.53 g (5.94 mmol, 56%); mp 204°C; ^{1}H NMR (400.16 MHz, C_6D_6, 298 K): $\delta = 1.1$, 1.2 (2s, 2 × 9H, 10-^{t}Bu), 2.05 (s, 3H, 4-CH_3), 6.84 (m, 2H, 11-H), 6.94 (d, br, $^3J_{HH} = 7.9$ Hz, 1H, 5-H), 7.72 (m, 2H, 9-H), 8.02 (s, br, 1H, 3-H), 8.12 (d, $^3J_{HH} = 7.9$ Hz, 1H, 6-H), 8.60 (d, $^3J_{HH} = 5.3$ Hz, 2H, 12-H), 11.91 (s, br, 1H, N–H) ppm; {^{1}H}^{13}C NMR (100.6 MHz, C_6D_6):

$\delta = 21.6$ (4-$\underline{C}H_3$), 30.4 (10-C($\underline{C}H_3)_3$), 34.5 (10-$\underline{C}(CH_3)_3$), 117.7 (C-11), 121.1 (C-9), 122.9 (C-5), 123.6 (C-6), 132.8 (C-3), 137.2 (C-1, C-2), 141.9 (C-4), 148.1 (C-12), 154.1 (C-7), 161.8 (C-8, C-10) ppm; IR (KBr): $\bar{\nu} = 3237$ (m, br), 2962 (m), 2867 (w), 1633 (m), 1590 (s), 1534 (w), 1477 (w), 1401 (w), 1365 (w), 1354 (w), 1310 (vw), 1285 (w), 1265 (w), 1219 (w), 1201 (vw), 1180 (vw), 1108 (vw), 1037 (vw), 928 (m), 890 (m), 826 (m), 716 (m) cm^{-1}.

4-(3-Butenoxy)-10-MeBPI (**4**, $C_{24}H_{23}N_5O$)

4-(3-Butenoxy)phthalodinitrile (**1**, 1.00 g, 5.05 mmol), 2-amino-4-methylpyridine (1.37 g, 12.6 mmol), and $CaCl_2$ (0.16 g, 1.36 mmol) were suspended in 1-hexanol (80 cm^3) and heated at reflux for 72 h. After cooling to room temperature the reaction product was isolated as a yellow solid (yellow needles) washed with water and dried over P_4O_{10}. Yield 1.04 g (2.62 mmol, 52%); mp 127°C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 2.36$ (s, 6H, 10-CH_3), 2.58 (m, 2H, $OCH_2C\underline{H}_2$), 4.15 (t, $^3J_{HH} = 6.9$ Hz, 2H, –OCH_2–), 5.14 (m, 2H, =CH_2), 5.90 (m, 1H, =C(H)–), 6.89 (m, 2H, 11-H), 7.12 (dd, $^3J_{HH} = 8.3$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, 5-H), 7.24 (s, br, 2H, 9-H), 7.52 (d, $^4J_{HH} = 2.2$ Hz, 1H, 3-H), 7.98 (d, $^3J_{HH} = 8.3$ Hz, 1H, 6-H), 8.43 (m, 2H, 12-H), 10.90 (s, br, 1H, NH) ppm; {^{1}H}^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 20.9$ (10-CH_3), 33.4 ($OCH_2\underline{C}H_2$–), 67.7 (OCH_2), 106.4 (C-3), 117.2 (=CH_2), 119.6 (C-5), 121.0/121.2 (C-9), 123.4/123.5 (C-11), 123.7 (C-6), 128.0 (C-1), 134.0 (=C(H)–), 137.9 (C-2), 147.3/147.4 (C-12) 149.1 (C-10), 153.6 (C-7), 160.3/160.5 (C-8), 162.2 (C-4) ppm; IR (KBr): $\bar{\nu} = 3219$ (vw), 3042 (vw), 2923 (vw), 2863 (vw), 1630 (s), 1584 (s), 1541 (m), 1488 (m), 1463 (m), 1352 (w), 1328 (m), 1276 (w), 1235 (s), 1195 (vw), 1162 (w), 1100 (m), 1033 (s), 918 (vw), 836 (vw), 813 (w), 714 (vw), 456 (w) cm^{-1}.

4-(2-Hydroxyethanoxy)-10-MeBPI (**5**, $C_{22}H_{21}N_5O_2$)

4-(2-Hydroxyethanoxy)phthalodinitrile (**2a**, 1.00 g, 5.34 mmol), 2-amino-4-methylpyridine (1.44 g, 13.4 mmol), and $CaCl_2$ (0.16 g, 1.36 mmol) were suspended in 1-hexanol (50 cm^3) and heated at reflux for 72 h. After cooling to room temperature the reaction product was isolated as a yellow solid (needle-shaped crystals), washed with water, and dried over P_4O_{10}. Yield 1.26 g (3.36 mmol, 61%); mp 202°C; ^{1}H NMR (300.17 MHz, d_6-*DMSO*, 298 K): $\delta = 2.35$, 2.36 (2s, 2×3H, 10-CH_3), 3.78 (m, 2H, $OCH_2C\underline{H}_2$), 4.18 (t, $^3J_{HH} = 4.7$ Hz, 2H, –OCH_2–), 4.96 (t, $^3J_{HH} = 5.6$ Hz, 1H, –OH), 7.07 (m, 2H, 11-H), 7.24 (m, 3H, 5-H, 9-H), 7.43 (d, $^4J_{HH} = 2.3$ Hz, 1H, 3-H), 7.86 (d, $^3J_{HH} = 8.5$ Hz, 1H, 6-H), 8.50 (m, 2H, 12-H), 8.99 (s, br, 1H, NH) ppm; {^{1}H}^{13}C NMR (100.6 MHz, d_6-*DMSO*, 298 K): $\delta = 20.3$ (10-CH_3), 59.4 ($HOCH_2$–), 70.3 (–CH_2O–), 106.4 (C-3), 119.5 (C-5), 121.4/121.6 (C-9), 123.1/123.3 (C-11), 123.7 (C-6), 127.1 (C-1), 137.2 (C-2), 147.5/147.6 (C-12), 149.3 (C-10), 152.3 (C-7), 159.5/159.7 (C-8), 162.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 3208$ (vw), 2920 (vw), 1634 (s), 1596 (s), 1543 (m), 1485 (m), 1467 (m), 1365 (m), 1327 (vw), 1295 (w), 1286 (w), 1245 (m), 1230 (m), 1195 (vw), 1169 (m), 1119 (w), 1057 (vw), 1032 (vw), 927 (m), 813 (m), 720 (w) cm^{-1}.

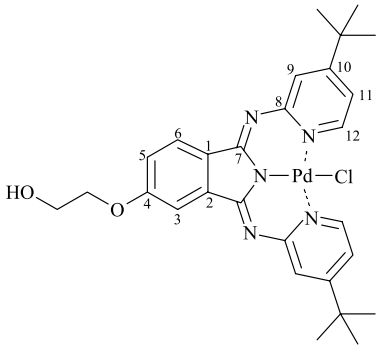
4-(2-Hydroxyethanoxy)-10-^{t}BuBPI (**6**, $C_{28}H_{33}N_5O_2$)

4-(2-Hydroxyethanoxy)phthalodinitrile (**2b**, 0.59 g, 3.14 mmol), 2-amino-4-^{t}butylpyridine (1.18 g, 7.85 mmol), and $CaCl_2$ (0.07 g, 0.68 mmol) were suspended in 1-hexanol (50 cm^3) and heated at reflux for 18 h. After cooling to room temperature the reaction product was isolated as a yellow solid (needles) washed with water and dried over P_4O_{10}. Yield 0.67 g (1.41 mmol, 45%); mp 210°C; ^{1}H NMR (400.16 MHz, CD_2Cl_2, 298 K): $\delta = 1.36$ (s, 18H, 10-C($CH_3)_3$), 4.00 (t, $^3J_{HH} = 4.2$ Hz, 2H, $HOC\underline{H}_2$–), 4.24 (t, $^3J_{HH} = 4.2$ Hz, 2H, –OCH_2–), 7.15 (m, 3H, 5-H, 11-H), 7.42 (m, 2H, 9-H), 7.53 (s, br, 1H, 3-H), 7.90 (d, $^3J_{HH} = 8.5$ Hz, 1H, 6-H), 8.21 (s, br, 1H, NH), 8.51 (m, 2H, 12-H) ppm; {^{1}H}^{13}C NMR (100.6 MHz, CD_2Cl_2, 298 K): $\delta = 30.4$ (10-C($\underline{C}H_3)_3$), 34.8 (10-$\underline{C}(CH_3)_3$), 61.2 ($HOCH_2$–), 70.2 (–CH_2O–), 106.4 (C-3), 117.6/117.8 (C-9), 119.4 (C-5), 119.9/120.0 (C-11), 123.7 (C-6), 128.5 (C-1), 138.2 (C-2), 147.6/147.7 (C-12), 153.2 (C-7), 160.6/160.7 (C-8), 162.1 (C-4), 162.5/162.6 (C-10) ppm; IR (KBr): $\bar{\nu} = 3244$ (w, br), 2962 (m), 2869 (w), 1633 (s), 1590 (s), 1536 (m), 1488 (m), 1477 (m), 1401 (w), 1366 (m), 1355 (w), 1327 (m), 1295 (w), 1286 (w), 1245 (m), 1225 (m), 1113 (w), 1085 (vw), 1051 (w), 915 (w), 834 (w), 720 (w) cm^{-1}.

[G-0]$_{4\text{-}exo}$-4-[O(CH$_2$)$_2$O]-10-MeBPI (**7**, $C_{108}H_{128}N_{20}O_8Si_5$)
To a solution of tetraallylsilane (38.5 mg, 0.20 mmol) in 1 cm^3 of benzene were added 1 cm^3 of dimethylchlorosilane and a few drops of a solution of *Karsted*'s catalyst, and the reaction mixture was subsequently stirred at 50°C for 12 h. After removal of the volatiles the zeroth generation [G-0]$_{4\text{-}exo}$-Cl was obtained as a light brown oil which was used without further purification. In a separate reaction vessel 0.31 g (0.80 mmol) of Si{(CH$_2$)$_3$Si*Me*$_2$Cl}$_4$ were dissolved in 80 cm^3 of *THF* and then cooled to −80°C. After the dropwise addition of 0.4 cm^3 of a *2 M* solution of *LDA* in *THF*, the reaction mixture was warmed to −40°C and stirred for 30 min. After recooling to −80°C a solution of [G-0]$_{4\text{-}exo}$-Cl in benzene was added, the reaction mixture subsequently warmed to ambient temperature and stirred for another 16 h. After removal of the volatiles in vacuo and redissolution in benzene, the insoluble components were removed by centrifugation and the solvents removed in vacuo. The clear yellow oil was washed several times with *n*-pentane and then dried in vacuo to give **7** as an amorphous yellow solid. Yield 0.36 g (0.18 mmol, 91%); mp 61°C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 0.14$ (s, 24H, c-H), 0.68 (m, 8H, f-H), 0.71 (m, 8H, d-H), 1.41 (m, 8H, e-H), 2.34 (s, 24H, 10-CH_3), 3.95 (t, $^3J_{HH} = 5.0$ Hz, 8H, b-H), 4.15 (t, $^3J_{HH} = 5.0$ Hz, 8H, a-H), 6.89 (m, 8H, 11-H), 7.11 (m, 4H, 5-H), 7.22 (m, 8H, 9-H), 7.47 (d, $^4J_{HH} = 2.2$ Hz, 4H, 3-H), 7.88 (d, $^3J_{HH} = 8.1$ Hz, 4H, 6-H), 8.41 (m, 8H, 12-H), 13.81 (s, br, 4H, NH) ppm; {^{1}H}^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = -1.8$ (C-c), 17.2/17.9 (C-d, C-f), 20.9 (10-CH_3), 21.2 (C-e), 61.3 (C-b), 69.9 (C-a), 106.5 (C-3), 119.6 (C-5), 121.0/121.2 (C-9), 123.4/123.6 (C-11), 123.7 (C-6), 128.2 (C-1), 138.0 (C-2), 147.4/147.5 (C-12), 149.1 (C-10), 153.6 (C-7), 160.5/160.6 (C-8), 162.2 (C-4) ppm; {^{1}H}^{29}Si NMR (79.5 MHz, $CDCl_3$, 298 K): $\delta = 0.4$ (Si(CH_2)–), 18.8 (Si–O) ppm; IR (KBr): $\bar{\nu} = 3420$ (m, br), 2948 (w), 2914 (w), 2862 (w), 1631 (s), 1591 (s), 1543 (m), 1486 (m), 1466 (m), 1400 (vw), 1359 (w), 1328 (w), 1280 (w), 1243 (m), 1191 (vw), 1163 (w), 1100 (m), 924 (vw), 822 (m), 717 (vw), 457 (m) cm^{-1}; MS (FAB): $m/z = 1974.9$ [M].

(4-(HOCH$_2$CH$_2$–)-10-MeBPI)PdCl (**8**, $C_{22}H_{20}ClN_5O_2Pd$)
4-(2-Hydroxyethanoxy)-10-*MeBPI* (**5**, 0.12 g, 0.30 mmol) and (*Ph*CN)$_2$PdCl$_2$ (0.13 g, 0.33 mmol) were dissolved in benzene (10 cm^3) and N*Et*$_3$ (33.0 mg, 0.33 mmol) was then added to this solution which was subsequently stirred at room temperature for 15 h. The crude palladium complex and N*Et*$_3$HCl were isolated by filtration, the ammonium salt was removed by extraction with water, and the reaction product was recrystallized from CH_2Cl_2/*n*-hexane, giving **8** as a yellow microcrystalline solid. Yield 0.11 g (0.21 mmol, 69%); mp 151°C; ^{1}H NMR (300.17 MHz, d_6-*DMSO*, 298 K): $\delta = 2.32$, 2.33 (s, 3×3H, 10-CH_3), 3.78 (m, 2H, –OCH$_2$C*H*$_2$), 4.06 (t, $^3J_{HH} = 4.7$ Hz, 2H, –OCH$_2$–), 4.97 (t, $^3J_{HH} = 5.5$ Hz, 1H, –OH), 6.94 (m, 3H, 5-H, 11-H), 7.12 (m, 3H, 3-H, 9-H), 7.53 (d, $^3J_{HH} = 8.0$ Hz, 1H, 6-H), 9.29 (m, 2H, 12-H) ppm; {^{1}H}^{13}C NMR (75.5 MHz, d_6-*DMSO*, 298 K): $\delta = 19.9$ (10-CH_3), 59.4 (HOCH$_2$–), 69.9 (–CH$_2$O–), 106.0 (C-3), 118.3 (C-5), 120.8/121.0 (C-9), 123.0 (C-6), 126.1/126.2 (C-11), 128.9 (C-1), 138.2 (C-2), 150.2/150.4/151.1 (C-7/C-8/C-10), 152.0 (C-12), 161.5 (C-4) ppm; IR (KBr): $\bar{\nu} = 3214$ (w, br), 2922 (w), 2850 (w), 1634 (m), 1579 (s), 1515 (m), 1470 (m), 1366 (w), 1331 (w), 1292 (w), 1233 (w), 1078 (w, br), 1027 (vw), 819 (m), 748 (vw), 716 (vw), 669 (vw) cm^{-1}.

(4-(HOCH$_2$CH$_2$–)-10-^{t}BuBPI)PdCl (**9**, $C_{28}H_{32}ClN_5O_2Pd$)
4-(2-Hydroxyethanoxy)-10-^{t}*BuBPI* (**6**, 0.20 g, 0.50 mmol) and (*Ph*CN)$_2$PdCl$_2$ (0.21 g, 0.55 mmol) were dissolved in benzene (10 cm^3) and N*Et*$_3$ (56.0 mg, 0.55 mmol) was then added to this solution which was subsequently stirred at room temperature for 15 h. The crude palladium complex and N*Et*$_3$HCl were isolated by filtration, the ammonium salt was removed by extraction with water, and the reaction product was recrystallized from CH_2Cl_2/*n*-hexane, giving **9** as a yellow microcrystalline solid. Yield 0.13 g (0.21 mmol, 88%); mp 165°C; ^{1}H NMR (400.16 MHz, CD_2Cl_2, 298 K): $\delta = 1.39$ (s, 18H, 10-^{t}Bu), 2.53 (s, br, 1H, –OH), 3.99 (t, $^3J_{HH} = 4.4$ Hz, 2H, HOC*H*$_2$–), 4.22 (t, $^3J_{HH} = 4.4$ Hz, 2H, –OCH$_2$–), 7.05 (m, 3H, 5-H, 11-H), 7.39 (d, $^4J_{HH} = 2.1$ Hz, 1H, 3-H), 7.45/7.48 (2d, 2× $^4J_{HH} = 2.1$ Hz, 2×1H, 9-H), 7.72 (d, $^3J_{HH} = 8.2$ Hz, 1H, 6-H), 9.62 (d, $^3J_{HH} = 6.7$ Hz, 2H,



12-H) ppm; {^{1}H}^{13}C NMR (100.6 MHz, CD_2Cl_2, 298 K): $\delta = 31.5$ (10-C($\underline{C}H_3)_3$), 36.4 (10-$\underline{C}(CH_3)_3$), 62.7 ($HOCH_2$–), 71.7 (–CH_2O–), 108.4 (C-3), 119.1/119.3 (C-9), 120.1 (C-5), 124.4/124.5 (C-11), 124.9 (C-6), 131.9 (C-1), 141.6 (C-2), 153.3/153.4 (C-7), 154.1/154.2 (C-12), 154.7/154.8 (C-8), 163.5 (C-4), 165.3/165.4 (C-10) ppm; IR (KBr): $\bar{\nu} = 3244$ (w, br), 2961 (m), 2904 (w), 2868 (w), 1602 (s), 1579 (s), 1520 (m), 1505 (m), 1480 (s), 1403 (m), 1367 (s), 1330 (m), 1269 (m), 1251 (w), 1230 (m), 1187 (m), 1145 (m), 1105 (s), 1078 (m), 925 (m) cm^{-1}.

(4-(3-Butenoxy)-10-MeBPI)PdCl (**10**, $C_{24}H_{22}ClN_5OPd$)

4-(3-Butenoxy)-10-*MeBPI* (**12**, 0.20 g, 0.50 mmol) and (*Ph*CN)$_2$PdCl$_2$ (0.21 g, 0.55 mmol) were dissolved in benzene (10 cm^3) and N*Et*$_3$ (56.0 mg, 0.55 mmol) was then added to this solution. After stirring for 15 h the volatiles were removed in vacuo, the residue was extracted with benzene, and the N*Et*$_3$HCl formed in the reaction was removed by filtration through Celite. The solvent of the filtrate was evaporated in vacuo, the yellow solid residue extracted with water and *n*-hexane, and then recrystallized from CH_2Cl_2/*n*-hexane to give the pure palladium complex **10**. Yield 0.22 g (0.41 mmol, 81%); mp 166°C; ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 2.37$ (s, 6H, 10-CH_3), 2.59 (m, 2H, $OCH_2C\underline{H}_2$), 4.12 (t, $^3J_{HH} = 6.6$ Hz, 2H, –OCH_2–), 5.20 (m, 2H, =CH_2), 5.92 (m, 1H, =C(H)–), 6.78 (m, 2H, 11-H), 6.97 (d, br, $^3J_{HH} = 8.1$ Hz, 1H, 5-H), 7.26 (s, br, 2H, 9-H), 7.35 (s, br, 1H, 3-H), 7.74 (d, $^3J_{HH} = 8.1$ Hz, 1H, 6-H), 9.57 (m, 2H, 12-H) ppm; {^{1}H}^{13}C-NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 20.6$ (10-CH_3), 33.5 ($OCH_2C\underline{H}_2$–), 67.7 (OCH_2), 106.7 (C-3), 117.3 (=CH_2), 118.8 (C-5), 120.9/121.0 (C-9), 123.6 (C-6), 126.3/126.4 (C-11), 129.8 (C-1), 134.1 (=C(H)–), 139.7 (C-2), 150.9 (C-10), 151.3 (C-7/C-8), 152.5/152.6 (C-12), 153.3/153.5 (C-7/C-8), 162.1 (C-4) ppm; IR (KBr): $\bar{\nu} = 3124$ (vw), 3078 (vw), 2924 (vw), 2873 (vw), 1582 (s), 1518 (m), 1468 (s), 1364 (m), 1332 (m), 1292 (m), 1231 (m), 1190 (m), 1175 (w), 1109 (m), 1082 (m), 1027 (w), 929 (vw), 877 (vw), 860 (vw), 820 (w), 751 (vw), 712 (vw), 670 (vw) cm^{-1}.

(BPI)PtCl (**11**, $C_{18}H_{12}ClN_5Pt$)

BPI (0.14 g, 0.48 mmol) and [(*COD*)$PtCl_2$] (0.20 g, 0.52 mmol) were suspended in *Me*OH (10 cm^3). To this suspension N*Et*$_3$ (53.0 mg, 0.52 mmol) was added and the reaction mixture was subsequently stirred at 50°C for 24 h. The crude platinum complex and N*Et*$_3$HCl were isolated by filtration and the ammonium salt was removed by extraction with water. The orange reaction product was purified by recrystallization from CH_2Cl_2/*n*-hexane (1:1). Yield 0.19 g (0.36 mmol, 75%); mp 303°C. ^{1}H NMR (300.17 MHz, $CDCl_3$/d_6-*DMSO*, 298 K): $\delta = 6.81$ (m, 2H, 11-H), 7.39 (m, 4H, 4-H, 5-H, 9-H), 7.72 (m, 2H, 10-H), 7.82 (m, 2H, 3-H, 6-H), 10.01 (d, $^3J_{HH} = 6.7$ Hz, 2H, 12-H) ppm; IR (KBr): $\bar{\nu} = 2939$ (vw), 1586 (s), 1531 (s), 1465 (s), 1432 (m), 1386 (m), 1299 (w), 1189 (w), 1119 (m), 1109 (m), 914 (w), 765 (m), 698 (m) cm^{-1}; MS (FAB): $m/z = 528.7$ [M]$^+$.

(4-MeBPI)PtCl (**12**, $C_{19}H_{14}ClN_5Pt \cdot C_5H_{12}$)

4-*MeBPI* (0.13 g, 0.40 mmol) and [(*COD*)$PtCl_2$] (0.16 g, 0.44 mmol) were suspended in *Me*OH (10 cm^3). To this suspension N*Et*$_3$ (45.0 mg, 0.44 mmol) was added and the reaction mixture was

subsequently stirred at 50°C for 24 h. The crude platinum complex and N*Et*$_3$HCl were isolated by filtration and the ammonium salt was removed by extraction with water. The orange reaction product was purified by recrystallization from CH_2Cl_2/*n*-hexane (1:1). Yield 0.18 g (0.30 mmol, 75%); mp 226°C; ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K): $\delta = 2.48$ (s, 3H, 4-CH_3), 6.94 (m, 2H, 11-H), 7.36 (d, $^3J_{HH} = 7.3$ Hz, 1H, 5-H), 7.51 (dd, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 1.8$ Hz, 2H, 9-H), 7.78 (s, br, 1H, 3-H), 7.84 (m, 3H, 6-H, 10-H), 10.22 (d, $^3J_{HH} = 6.6$ Hz, $^3J_{PtH} = 19.7$ Hz, 2H, 12-H) ppm; {^{1}H}^{13}C NMR (100.6 MHz, $CDCl_3$, 298 K): $\delta = 21.9$ (4-$\underline{C}H_3$), 119.5 (C-11), 122.1 (C-5), 122.8 (C-6), 127.4 (C-9), 132.1 (C-3), 134.8 (C-1), 137.7 (C-2), 137.9 (C-10), 142.2 (C-4), 149.9/151.1 (C-7/C-8), 152.4 (C-12) ppm; IR (KBr): $\bar{\nu} = 2920$ (m), 2849 (w), 1653 (vw), 1585 (s), 1527 (m), 1465 (s), 1424 (vw), 1375 (m), 1287 (w), 1263 (vw), 1188 (w), 1133 (m), 1088 (w), 1020 (w), 829 (vw), 790 (vw), 780 (w) cm^{-1}.

(4-Me-10-^{t}BuBPI)PtCl (**13**, $C_{27}H_{30}ClN_5Pt$)
4-*Me*-10-*^{t}BuBPI* (**11**, 80.0 mg, 0.19 mmol) and [(*COD*)$PtCl_2$] (78.0 g, 0.21 mmol) were suspended in *Me*OH (10 cm^3). To this suspension N*Et*$_3$ (22.0 mg, 0.21 mmol) was added and the reaction mixture was subsequently stirred at 50°C for 24 h. After removal of the volatiles in vacuo, the orange-red residue was extracted first with water and then with diethyl ether and *n*-hexane. The crude solid was recrystallized from CH_2Cl_2/*n*-hexane (1:1) to give the pure compound **13**. Yield 92.0 mg (0.14 mmol, 74%); mp 76°C; ^{1}H NMR (400.16 MHz, CD_2Cl_2, 298 K): $\delta = 1.28$ (s, 18H, 10-^{t}Bu), 2.42 (s, 3H, 4-CH_3), 6.90 (dd, $^3J_{HH} = 6.3$ Hz, $^4J_{HH} = 2.2$ Hz, 2H, 11-H), 7.32 (d, $^3J_{HH} = 7.6$ Hz, 1H, 5-H), 7.39 (m, 2H, 9-H), 7.69 (s, br, 1H, 3-H), 7.74 (d, $^3J_{HH} = 7.6$ Hz, 1H, 6-H), 9.96 (d, $^3J_{HH} = 6.3$ Hz, $^3J_{PtH} = 19.9$ Hz, 2H, 12-H) ppm; {^{1}H}^{13}C NMR (100.6 MHz, CD_2Cl_2, 298 K): $\delta = 20.3$ (4-$\underline{C}H_3$), 28.4 (10-$\underline{C}(CH_3)_3$), 33.4 (10-$\underline{C}(CH_3)_3$), 116.3 (C-11), 120.4 (C-5), 121.1 (C-6), 122.4 (C-9), 130.6 (C-3), 133.5 (C-1), 136.5 (C-2), 140.8 (C-4), 148.3/149.5 (C-7/C-8), 150.0 (C-12), 161.3 (C-10) ppm; IR (KBr): $\bar{\nu} = 2958$ (m), 2868 (w), 1653 (w), 1612.5 (m), 1582 (s), 1502 (s), 1478 (s), 1404 (m), 1373 (m), 1321 (w), 1295 (m), 1184 (m), 1116 (m), 1087 (m), 1023 (w), 949 (w), 888 (w), 822 (w), 713 (w) cm^{-1}.

(4-(3-Butenoxy)-10-MeBPI)PtCl (**14**, $C_{24}H_{22}ClN_5OPt$)
4-(3-Butenoxy)-10-*MeBPI* (**12**, 0.15 g, 0.39 mmol) and [(*COD*)$PtCl_2$] (0.16 g, 0.42 mmol) were suspended in *Me*OH (15 cm^3). To this suspension N*Et*$_3$ (43.0 mg, 0.42 mmol) was added and the reaction mixture was subsequently stirred at 50°C for 24 h. After removal of the volatiles in vacuo, the orange-red residue was extracted first with water and then with diethyl ether and *n*-hexane. The crude solid was recrystallised from CH_2Cl_2/*n*-hexane (1:1) to give the pure compound **14**. Yield 0.18 g (0.29 mmol, 74%); mp 154°C (dec); ^{1}H NMR (300.17 MHz, $CDCl_3$, 298 K): $\delta = 2.35$ (s, 6H, 10-CH_3), 2.62 (m, 2H, $OCH_2C\underline{H}_2$), 4.18 (t, $^3J_{HH} = 6.6$ Hz, 2H, –OCH_2–), 5.19 (m, 2H, =CH_2), 5.94 (m, 1H, =C(H)–), 6.81 (m, 2H, 11-H), 7.11 (dd, $^3J_{HH} = 8.4$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, 5-H), 7.37 (s, br, 2H, 9-H), 7.51 (d, $^4J_{HH} = 2.2$ Hz, 1H, 3-H), 7.90 (d, $^3J_{HH} = 8.4$ Hz, 1H, 6-H), 10.08 (m, 2H, 12-H) ppm; {^{1}H}^{13}C NMR (75.5 MHz, $CDCl_3$, 298 K): $\delta = 20.7$ (10-CH_3), 33.5 ($OCH_2C\underline{H}_2$–), 67.8 (OCH_2), 106.7 (C-3), 117.3 (=CH_2), 118.5 (C-5), 120.9/121.1 (C-9), 123.4 (C-6), 127.3 (C-11), 129.6 (C-1), 134.1 (=C(H)–), 139.6 (C-2), 149.5/149.6/149.7/149.8/150.7/150.9 (C-7/C-8/C-10), 151.4 (C-12), 162.2 (C-4) ppm; IR (KBr): $\bar{\nu} = 2918$ (w), 1582 (s), 1515 (m), 1470 (m), 1372 (m), 1333 (w), 1290 (w, br), 1229 (w), 1191 (m), 1109 (m), 1026 (w), 813 (w, br) cm^{-1}.

*X-Ray Crystallographic Study of **8** and **13***
Suitable crystals of the complexes **8** and **13** were obtained by layering concentrated solutions of the compounds in dichloromethane or chloroform with hexanes and allowing slow diffusion at room temperature. The crystal data for **8** were collected on a Nonius Kappa CCD diffractometer at −100°C and transfered to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used [22]. The data for **13** were collected on a CAD4 (Enraf-Nonius) four circle diffractometer at −80°C and the structure solution was carried out using the SHELX-97 structure solution packages.

All structures were solved using direct methods with absorption corrections being part of the scaling procedure of the data reductions. After refinement of the heavy atoms, difference *Fourier* maps revealed the maxima of residual electron density close to the positions expected for the hydrogen atoms; they were introduced as fixed contributors in the structure factor calculations with fixed coordinates (C–H: 0.95 Å) and isotropic temperature factors ($B(H) = 1.3\ B_{eqv}(C)$ Å^2) but not refined. The hydrogen atoms of the solvents were not refined. Full least-square refinements on F^2. A final difference map revealed no significant maxima of electron density. The scattering factor coefficients and the anomalous dispersion coefficients were taken from Ref. [23]. Crystal data and experimental details for the crystals of **8** and **13** are given in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication

Table 1. X-Ray experimental data of compounds **8** and **13**

	8	**13**
Formula	$C_{24}H_{22}ClN_5Opd$	$C_{27}H_{30}ClN_5Pt$
Molecular weight	538.33	655.10
Crystal system	monoclinic	triclinic
Space group	$P\text{-}2_1/c$	$P\text{-}1$
a/Å	10.8058(2)	10.4591(16)
b/Å	25.8236(6)	10.698(2)
c/Å	8.2113(4)	11.585(2)
α/°	–	90.084(12)
β/°	103.923(5)	103.972(10)
γ/°	–	98.553(10)
V/Å^3	2224.0(1)	1243.0(4)
Z	4	2
Color	yellow	yellow
Crystal dim (mm)	$0.16 \times 0.06 \times 0.04$	$0.30 \times 0.30 \times 0.30$
D_{calc}/gcm^{-3}	1.61	1.75
F000	1088	644
μ/mm^{-1}	0.982	5.777
Trans. min and max	0.8131/1.0000	0.9981/0.6483
Temperature/K	173	193
Wavelength/Å	0.71073	0.71073
Radiation	MoKα	MoKα
Scan mode	ϕ-scans	ω/θ-scan
hkl limits	−8/8, −31/33, −13/13	−13/13, −13/13, −14/14
θ-limits/°	2.5/27.46	2.03/27.01
Number of data meas.	7937	5424
Number of data with $I > 3\sigma(I)$	2694 $I > 2\sigma(I)$	4844
Number of variables	289	388
R	0.058	
Rw	0.072	
R_1	–	0.0301
wR_2	–	0.0701
GOF	1.217	1.044
Largest peak in final difference/eÅ^{-3}	1.076	1.282

nos. CCDC 265747 and 265748. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +(44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

References

[1] a) Gates BC (1982) Catalytic Chemistry, Wiley, New York; b) Lecuyer C, Quignard F, Choplin A, Olivier D, Basset J-M (1991) Angew Chem Int Ed Engl **30**: 1660; c) Budzichowski TA, Chacon ST, Chisholm MH, Feher FJ, Streib W (1991) J Am Chem Soc **113**: 689

[2] a) Hartley FR (1989) Supported Metal Complexes – A New Generation of Catalysts. Reidel, Dordrecht; b) Yermakov YI, Kuznetsov BN, Zakharov VA (1981) Catalysis by Supported Complexes. Elsevier, Amsterdam; c) Herrmann WA, Kohlpaintner CW (1993) Angew Chem Int Ed Engl **32**: 1524

[3] a) Bacchi A, Carcelli M, Costa M, Leporati A, Leporati E, Pelagatt P, Pelizzi C, Pelizzi G (1997) J Organomet Chem **535**: 107; b) Pelagatti P, Bacchi A, Carcelli M, Costa M, Fochi A, Ghiaini P, Leporati E, Masi M, Pelizzi C, Pelizzi G (1999) J Organomet Chem **583**: 94; c) Pelagatti P, Venturini A, Leporati A, Carcelli M, Costa M, Bacchi A, Pelizzi G, Pelizzi C (1998) J Chem Soc Dalton Trans 2715; d) Costa M, Pelagatti P, Pellizi C, Rogolino D (2002) J Mol Catal A: Chemical **178**: 21

[4] a) Siggelkow B, Meder MB, Galka CH, Gade LH (2004) Eur J Inorg Chem 3424; b) Meder MB, Haller I, Gade LH (2005) Dalton Trans 1403; c) Siggelkow B, Gade LH (2005) Z Anorg Allg Chem (in press)

[5] a) Siegl WO (1977) J Org Chem **42**: 1872; b) Siegl WO (1974) Inorg Nucl Chem Letters **10**: 825; c) Siegl WO, Ferris FC, Mucci PA (1977) J Org Chem **42**: 3442; d) Siegl WO (1981) J Heterocyclic Chem **18**: 1613

[6] a) Gagné RR, Marritt WA, Marks DN, Siegl WO (1981) Inorg Chem **20**: 3260; b) Gagné RR, Gall RS, Lisensky GC, Marsh RE, Speltz LM (1979) Inorg Chem **18**: 771; c) Marks DN, Siegl WO, Gagné RP (1982) Inorg Chem **21**: 3140

[7] Addison AW, Burke PJ, Henrick K (1982) Inorg Chem **21**: 60

[8] a) Balogh-Hergovich E, Kaiser J, Speier G, Huttner G, Jacobi A (2000) Inorg Chem **39**: 4224; b) Balogh-Hergovich E, Speier G, Réglier M, Giorgi M, Kuzmann E, Vértes A (2003) Eur J Inorg Chem, 1735; c) Anderson OP, La Cour A, Dodd A, Garrett AD, Wicholas M (2003) Inorg Chem **42**: 4513

[9] a) Bereman RD, Shields GD, Dorfman JR, Bordner J (1983) J Inorg Biochem **19**: 75; b) Baird DM, Maehlmann WP, Bereman RD, Singh P (1997) J Coord Chem **42**: 107

[10] a) Tolman CA, Druliner JD, Krusic PJ, Nappa MJ, Seidel WC, Williams ID, Ittel SD (1988) J Mol Catal **48**: 129; b) Domaille PJ, Harlow RL, Ittel SD, Peet WG (1983) Inorg Chem **22**: 3944

[11] a) Saussine L, Brazi E, Robine A, Mimoun H, Fischer J, Weiss R (1985) J Am Chem Soc **107**: 3534; b) Farinas ET, Nguyen CV, Mascharak PK (1997) Inorg Chim Acta **263**: 17; c) Chavez FA, Mascharak PK (2000) Acc Chem Res **33**: 539

[12] Meder MB, Gade LH (2004) Eur J Inorg Chem 2716

[13] Meder MB, Siggelkow BA, Gade LH (2004) Z Anorg Allg Chem **630**: 1962

[14] Brewis M, Clarkson GJ, Holder AM, McKeown NB (1998) Chem Commun 969

[15] a) van der Made AW, van Leeuwen PWNM (1992) J Chem Soc Chem Commun 1400; b) van der Made AW, van Leeuwen PWNM, de Wilde JC, Brandes RAC (1993) Adv Mater **5**: 466; c) Zhan L-L, Roovers J (1993) Macromolecules **26**: 963; d) Roovers J, Toporowski PM, Zhan L-L (1992) Polym Prepr (Am Chem Sci Div Polym Chem) **23**: 182; e) Muzafarov AM, Gorbatsevich OB, Rebrov EA, Ignat'eva GM, Myakushev TB, Bulkin AF, Papkov VS (1993) Polym Sci Ser A **35**: 1575; f) Seyferth D, Son DY, Rheingold AL, Ostrander RL (1994) Organometallics **13**: 2682

[16] Findeis R, Gade LH (2003) Eur J Inorg Chem 99

[17] Griffith WP, Swars K (1989) Gmelin Handbook of Inorganic Chemistry. Springer, Berlin
[18] Cárdenas DJ, Echavarren AM, Ramírez de Arellano MC (1999) Organometallics **18**: 3337
[19] a) Hartley FR (1960) Organomet Chem Rev **6**: 119; b) Kharasch MS, Seyler RC, Mayo FR (1938) J Am Chem Soc **60**: 882; c) Doyle JR, Slade PE, Jonassen HB (1960) Inorg Synth **6**: 218; d) Kuljian E, Frye E (1964) Z Naturforsch (B) **19**: 651
[20] McDermott JX, White JF, Whitesides GM (1976) J Am Chem Soc **98**: 6521
[21] de Vries EFJ, Steenwinkel P, Brussee J, Kruse CG, van den Gen A (1993) J Org Chem **58**: 4315
[22] Nonius OpenMoleN, Interactive Structure Solution. Delft, 1997
[23] Cromer DT, Waber JT (1974) International Tables for X-ray Crystallography. The Kynoch Press, Birmingham