Synthesis, Structures and Catalytic Properties of Bis(2-pyridylimino)-isoindolatopalladium Complexes

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Reaction of the bis(2-pyridylimino)isoindole derivatives (10-Me)-BPI (**1a**), (11-Me)-BPI (**1b**), (11-Br)-BPI (**1c**), (4-Me)-BPI (**1d**) and 4-Me-10-*t*BuBPI (**1e**) with $[PdCl_2(PhCN)_2]$ and triethylamine in benzene gave the square-planar palladium(II) complexes [PdCl{(10-Me)-BPI}] (**2a**), [PdCl{(11-Me)-BPI}] (**2b**), [PdCl{(11-Br)-BPI}] (**2c**), [PdCl(4-MeBPI)] (**2d**) and [PdCl(4-Me-10-*t*BuBPI)] (**2e**), respectively. Extraction of the crude product **2b** with aqueous sodium carbonate solution led to the formation of the dinuclear carbonato-bridged complex $[\{(11\text{-Me-BPI})Pd\}_2(\mu\text{-}CO_3)]$ (**3**) which was characterized by an X-ray structure analysis. Reaction of 11-Br-BPI (**1c**) with a large excess (6 equiv.) of the acetylenes Me_3SiCCH, Ph_3SiCCH and PhCCH under Sonogashira conditions gave the alkynylated derivatives 11-(Me_3SiCC)-BPI (**4a**), 11-(Ph_3SiCC)-BPI (**4b**) and 11-(PhCC)-BPI (**4c**), which were metallated with bis(benzonitrile)dichloropalladium(II) to yield the Pd^{II} complexes [PdCl{11-(Me_3SiCC)-BPI}] (**5a**), [PdCl{11-(Ph_3SiCC)-BPI}] (**5b**) and [PdCl{11-(PhCC)-BPI}] (**5c**), respectively. The activity of **2b** in the catalytic hydrogenation of C=C double bonds was tested for the reaction with styrene, 1-octene and cyclohexene. The stability of the palladium complex, the reproducibility of the reaction kinetics, the different behaviour towards the three olefins chosen as substrates, as well as the possibility of isolating the non-decomposed catalyst after several catalytic runs, provides circumstantial evidence for molecular catalysis with the BPI-palladium complexes.

Introduction

Polydentate ligands have been widely used in the development of homogeneous hydrogenation catalysts.[1] In most cases phosphane or phosphane-heterodonor ligands have been chosen due to the well-established capacity of the soft phosphane ligators to stabilize the low-valent intermediates in the catalytic cycle.[2] A practical disadvantage in the use of phosphorus-based ligands is their propensity to be oxidized if exposed to air over extended periods of time. This has encouraged research into non-phosphorus-containing hydrogenation catalysts which combine molecular stability with sufficient activity to allow the catalytic hydrogenation of alkenes at atmospheric dihydrogen pressure.[3]

Costa, Pelagatti et al. have recently studied the hydrogenation activity of palladium(II) complexes stabilized by polydentate P∩N∩O,[4,5] N∩N∩S,[6] and N∩N∩N ligands.[7] 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 is subsequently involved in the elimination of the saturated reaction product.

In view of this work on palladium-catalyzed homogeneous hydrogenations we have studied the catalytic activity of Pd complexes containing derivatives of the well-established bis(2-pyridylimino)isoindolate (BPI) ligands (**A**).[8–10] These ligands have been extensively studied in oxidation catalysis;[11] however, there is as yet no report of their application to other catalytic reactions. This class of formally anionic ligands appeared to be promising for the development of new palladium-based hydrogenation catalysts due to their tendency to tautomerise and act as neutral ligands **A′**, as has been recently established for the free ligand in solution and for the Cd complex **B** by X-ray diffraction.[12] Given the work by Costa, Pelagatti and coworkers,[4–7] this capacity of the BPI ligands was thought to favour homogeneous hydrogenation activity of their palladium(II) complexes.

There are only two previous reports in the literature of the coordination of BPI ligands to divalent palladium,[13,14] although with no further investigation of their reactivity. In this work we report the synthesis and structural characterization of several new BPI-Pd complexes, the first results of the integration of the BPI-ligand unit into more elaborate molecular architectures and, finally, a first study of the hydrogenation activity of a BPI-Pd derivative towards several alkenes.

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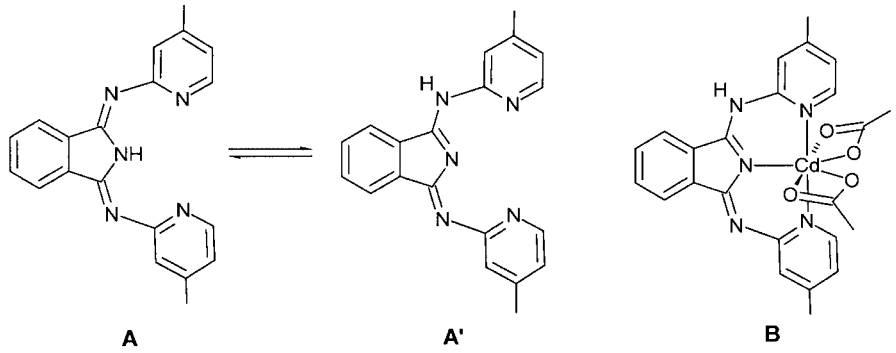


Results and Discussion

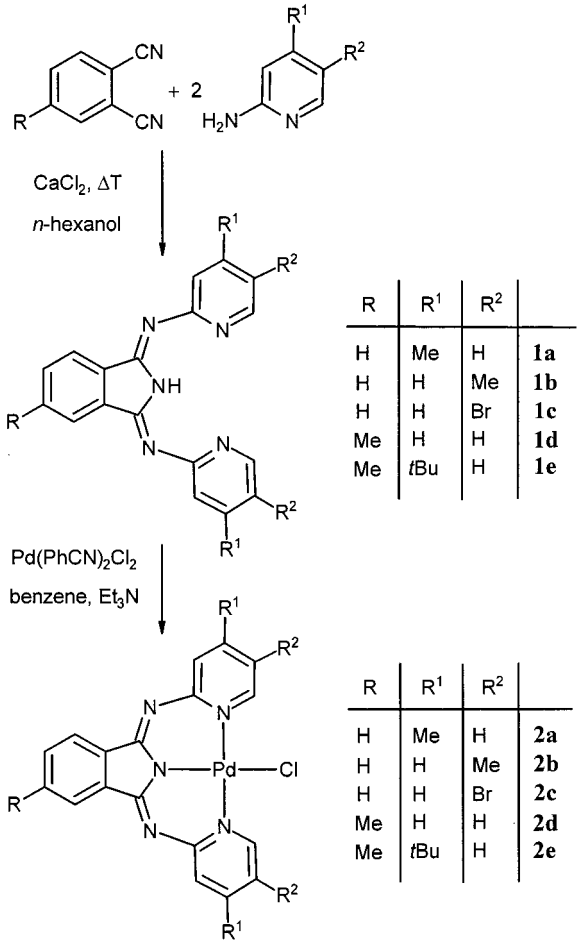
Synthesis and Structural Characterization of the BPI-Palladium Complexes

The bis(2-pyridylimino)isoindole derivatives **1a**−**1e** were prepared according to the synthetic route first described by Siegl et al. by reaction of a 2-aminopyridine derivative with an *ortho*-phthalodinitrile (Scheme 1).[9] A slight modification of the reaction conditions — the replacement of *n*-butanol by *n*-hexanol as the solvent — gave significantly better yields of the ligand precursors than those reported in the literature.

The preparation of the corresponding square-planar palladium(II) complexes **2a**−**2e** was carried out in benzene using $[PdCl_2(PhCN)_2]$ as the Pd^{II} precursor and triethylamine as auxiliary base (Scheme 1). The coordination of the BPI ligands to palladium(II) can be conveniently monitored by ^1H NMR spectroscopy. The most characteristic change in the NMR spectra is the coordination shift of the 6-pyridyl protons from ca. $\delta = 8.4$ ppm in the free ligand to ca. $\delta = 9.5$ ppm in the palladium complexes, and the disappearance of the NH resonance of the isoindole unit.

Since there is no previous example of an X-ray structure analysis of a BPI-Pd complex, and in order to establish the structural details of these compounds, single-crystal X-ray diffraction studies of compounds [PdCl(11-Br-BPI)] (**2c**) and [PdCl(4-Me-10-*t*Bu-BPI)] (**2e**) were carried out. Their molecular structures are displayed in Figure 1 and 2, respectively, and their principal bond lengths and angles are compared in Table 1.

Both complexes are mononuclear and possess the expected square-planar coordination geometry. The central palladium atom is coordinated to the three ligating nitrogen atoms of the BPI ligand (N1, N3 and N5) as well as to the chloro ligand. The chloropalladium units are slightly displaced from the molecular plane defined by the three N atoms, as is evident from the N1−Pd−N5 angles of 172.0(1)° and 171.0(2)° for **2c** and **2e**, respectively. This distortion is reflected in an even more pronounced way by the N3−Pd−Cl angles [**2c**: 167.75(9)°; **2e**: 166.3(2)°] and may be due to the repulsive interaction of the chloro ligand with the *ortho*-hydrogen atoms of the pyridyl groups. The Pd−N bond lengths to the pyridyl units are in the range of 2.053−2.071 Å, whereas the amide-type central Pd−N3 bond length is contracted to 1.962(3) Å for **2c** and 1.957 Å for **2e**. This pattern is consistent with the previously reported structural data of BPI-transition metal complexes.[9,10] The Pd−Cl bond lengths of 2.333(1) Å (**2c**) and 2.332(3) Å (**2e**) are similar to those found for other chloropalladium complexes bearing tridentate ligands.[15]



R	R¹	R²	
H	Me	H	**1a**
H	H	Me	**1b**
H	H	Br	**1c**
Me	H	H	**1d**
Me	*t*Bu	H	**1e**

R	R¹	R²	
H	Me	H	**2a**
H	H	Me	**2b**
H	H	Br	**2c**
Me	H	H	**2d**
Me	*t*Bu	H	**2e**

Scheme 1. Synthesis of the BPI-ligands **1a**−**1e** and their palladation to give the Pd^{II} complexes **2a**−**2e**

In the metallation of the BPI ligand-precursors stoichiometric amounts of triethylammonium chloride are formed, which are usually extracted with water after the complete conversion into the complexes. In the synthesis of **2b** the

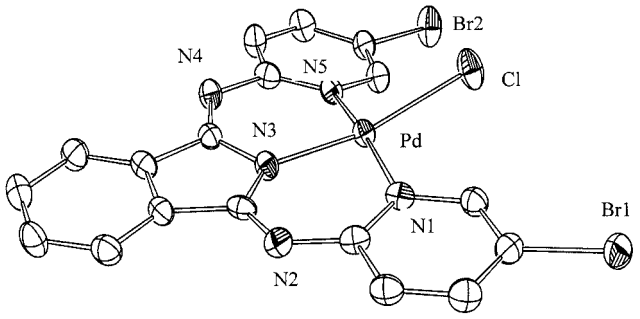


Figure 1. Molecular structure of complex **2c**; selected bond lengths and angles are listed in Table 1

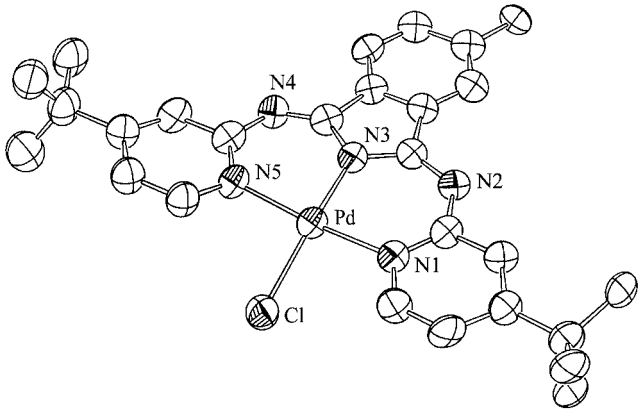


Figure 2. Molecular structure of complex **2e**; selected bond lengths and angles are listed in Table 1

Table 1. Selected bond lengths (Å) and angles (°) of complexes **2c** and **2e**

	2c	**2e**
Pd−N1	2.068(3)	2.071(7)
Pd−Cl	2.333(1)	2.332(3)
Pd−N5:	2.053(3)	2.058(7)
C2−Br1	1.895(4)	–
Pd−N3	1.962(3)	1.957(6)
C16−Br2	1.884(4)	–
Cl−Pd−N1	92.85(9)	92.2(2)
Cl−Pd−N3	167.75(9)	166.31(19)
Cl−Pd−N5	89.95(8)	91.1(2)
N1−Pd−N5	172.0(1)	171.0(2)

crude product was extracted with an aqueous sodium carbonate solution on one occasion, which led to a partial exchange of the chloro ligand by the carbonate dianion. From this mixture the dinuclear carbonato-bridged complex [{(11-Me-BPI)Pd}$_2$(μ-CO_3)] crystallized and its structure was established by a single-crystal X-ray structure analysis. Its molecular structure is displayed in Figure 3 along with the principal bond lengths and angles.

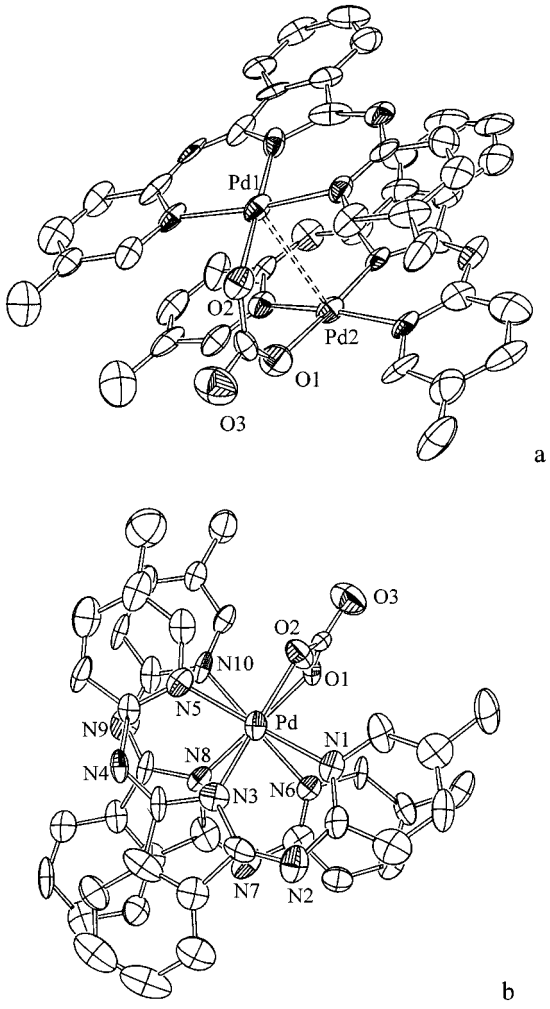


Figure 3. a) Molecular structure of complex **3**; selected bond lengths (Å) and angles (°): Pd1−N1 2.05(1), Pd2−N6 2.07(1), C41−O1 1.23(2), Pd1−N3 1.93(2), Pd2−N8 1.94(1), C41−O2 1.34(2), Pd1−N5 2.05(1), Pd2−N10 2.06(2), C41−O3 1.22(2), Pd1−O2 2.04(1), Pd2−O1 2.03(1); N1−Pd1−N5 172.5(5), N1−Pd1−O2 89.7(6), N6−Pd2−O1 90.4(7), N6−Pd2−N10 73.4(5), N3−Pd1−O2 178.3(5), N8−Pd2−O1 175.7(6); b) view along the Pd−Pd axis

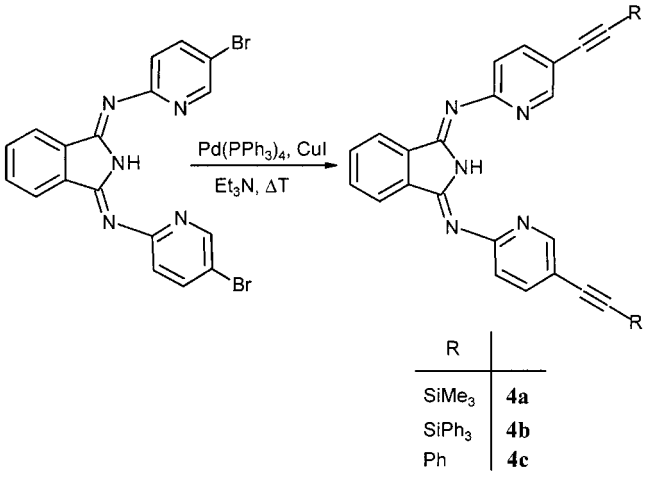
As is evident from the structure represented in Figure 3, the exchange of the chloro ligands in two of the Pd complexes by a bridging carbonato ligand gives a dinuclear complex with a stacked arrangement of the two complex fragments. The relative disposition of the two molecular halves and their parallel orientation may be due to the combination of a weakly attractive Pd−Pd contact and π-stacking interactions between the aromatic rings in the ligands. The Pd−Pd distance of 3.031 Å is in the range of previously established d^8-metal-metal contacts.[16] The view along the Pd−Pd axis in Figure 3b reveals the slight twist in the orientation of the two planar metal-ligand units (N5−Pd1−Pd2−N10 = 16.5°).

We note that Gagné et al. have reported the crystal structure of a dinuclear BPI-copper complex containing a bridging carbonato ligand.[9c] In contrast to the Pd complex presented in this work, the CO_3^{2-} ligand in their Cu complex

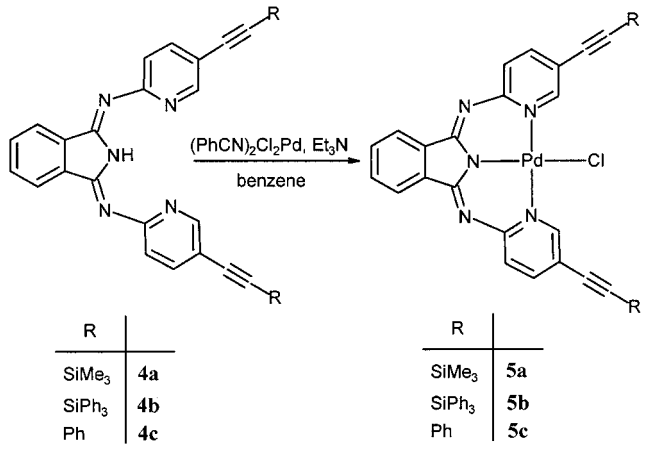
connects two orthogonally oriented BPI-metal units. Both Pd atoms in compound **3** possess an almost ideal square-planar coordination geometry and the two halves of the molecule are structurally almost identical and very similar to **2c** and **2e**. The carbonato ligand is almost planar, with similar metric parameters to the copper complex mentioned above. It is interesting to note the difference in the C−O bond lengths [C41−O1 1.23(2), C41−O3 1.22(2) Å, C41−O2 1.34(2) Å] in the bridging ligand.

Synthesis of Alkynyl-Substituted BPI Ligands

The bis(2-pyridylimino)isoindole ligands give well-defined complex structures and may thus be used as building blocks in more complex molecular architectures. In order to test whether the ligand periphery of the BPI ligands may be modified a posteriori, we studied the alkynylation of the ligand **1c** by the Sonogashira method.[17] The reaction of 11-Br-BPI (**1c**) with a large excess (6 equiv.) of the acetylenes Me_3SiCCH, Ph_3SiCCH and PhCCH in Et_3N using 10 mol % of $[Pd(PPh_3)_4]$/CuI gave the alkynylated derivatives 11-(Me_3SiCC)-BPI (**4a**), 11-(Ph_3SiCC)-BPI (**4b**) and 11-(PhCC)-BPI (**4c**) as yellow solids in good yields (Scheme 2).



Scheme 2. Synthesis of the alkynyl-substituted BPI ligands **4a**−**4c**



Scheme 3. Synthesis of the alkynyl-substituted BPI-palladium(II) complexes **5a**−**5c**

Synthesis and Structural Characterization of the Alkynyl-Substituted BPI-Palladium Complexes

The synthesis of the corresponding palladium(II) complexes was carried out as described above for complexes **2a**−**2e**, by reaction of the ligands **4a**−**4c** with bis(benzonitrile)dichloropalladium(II) and triethylamine in benzene. After workup, the orange complexes [PdCl{11-(Me_3SiCC)-BPI}] (**5a**) and [PdCl{11-(Ph_3SiCC)-BPI}] (**5b**) as well as the dark-red compound [{11-(PhCC)-BPI}PdCl] (**5c**), respectively, were isolated in good yields (Scheme 3).

The metallation of the BPI ligands **4a** and **4b** may be conveniently monitored by ^{29}Si NMR spectroscopy. The resonances of the Me_3Si-substituted ligand are shifted from $\delta = -17.4$ ppm in **4a** to $\delta = -22.0$ ppm in [PdCl{11-(Me_3SiCC)-BPI}] (**5a**) and from $\delta = -28.5$ ppm in **4b** to $\delta = -22.1$ ppm in [PdCl{11-(Ph_3SiCC)-BPI}] (**5b**). The formation of the alkynyl-substituted complexes **5a**−**5c** was confirmed by their FAB mass spectra, in which the $[M - Cl]^+$ cation was found as the principal fragment.

Single crystals of **5a** and **5b** which were suitable for X-ray diffraction were obtained from solutions of the compounds in CH_2Cl_2 (**5a**) and CH_2Cl_2/pentane (**5b**) at ambient temperature. In order to establish the details of the influence that the alkynyl substitution exerts upon the molecular structures of the BPI-palladium complexes, X-ray structure analyses of both complexes **5a** and **5b** were carried out. Their molecular structures are displayed in Figure 4 and 5, respectively, and their principal bond lengths and angles are compared in Table 2.

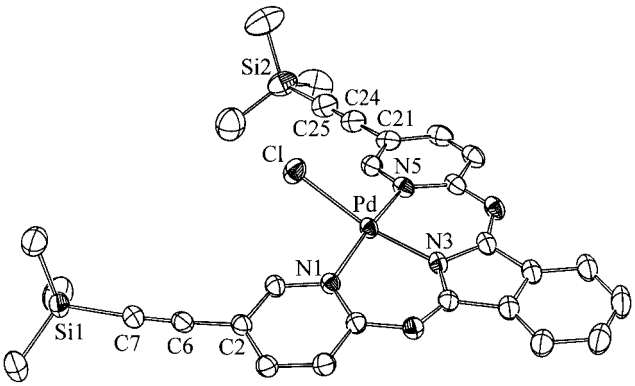


Figure 4. Molecular structure of complex **5a**; selected bond lengths and angles are listed in Table 2

The general features of the metal complex structures of **5a** and **5b** are similar to those of **2c** and **2e**. As in the case of the latter, the palladium atom is slightly displaced from the plane defined by the N-donors, as can be inferred from the N5−Pd−N1 angles [**5a**: 168.41(6)°; **5b**: 167.4(1)°]. The "bending" of the chloro ligands out of the plane of the BPI-Pd unit is even more pronounced than in **2c** and **2e** [N3−Pd−Cl = 165.30(5)° (**5a**) and 163.75(8)°(**5b**)]. This decrease of the N3−Pd−Cl angle may be attributed to increased steric crowding at the 11-position in the series Br < Me_3Si < Ph_3Si, along with the *ortho*-H···Cl repulsion, thus

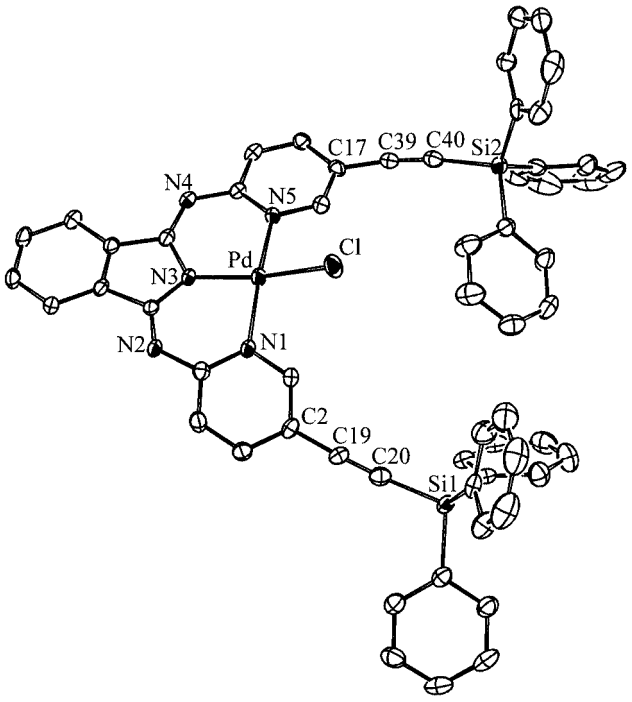


Figure 5. Molecular structure of complex **5b**; selected bond lengths and angles are listed in Table 2

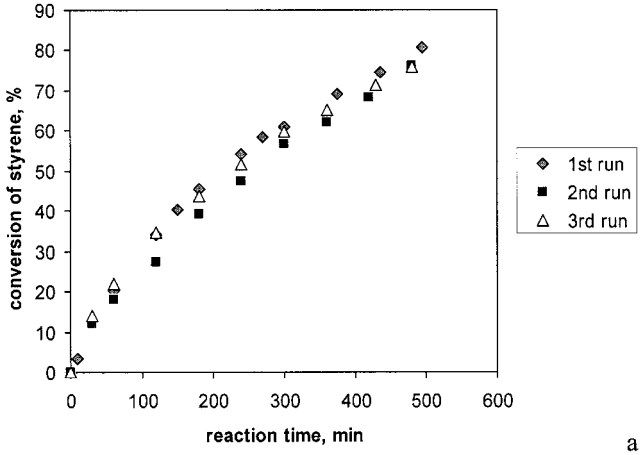
Table 2. Selected bond lengths (Å) and angles (°) of complexes **5a** and **5b**

	5a	5b
Pd−N1	2.052(2)	2.034(3)
Pd−N3	1.958(2)	1.952(2)
Pd−N5	2.046(2)	2.027(2)
Pd−Cl	2.3350(6)	2.3353(8)
C6−C7	1.203(3)	
C24−C25	1.203(4)	
C19−C20		1.190(4)
C39−C40		1.192(4)
N1−Pd−N5	168.41(6)	167.4(1)
Cl−Pd−N3	165.30(5)	163.75(8)
C2−C6−C7	176.8(2)	
C17−C39−C40		171.1(3)
C6−C7−Si1	176.6(2)	
C39−C40−Si2		175.3(3)
C21−C24−C25	179.9(2)	
C2−C19−C20		177.2(3)
C24−C25−Si2	178.7(2)	
C19−C20−Si1		164.2(3)

pushing the Cl ligands out of the plane. The Pd−N bond-length pattern is again similar to that observed in **2c** and **2e**, with greater Pd−N distances for the pyridyl groups [Pd−N5 = 2.046(2) Å (**5a**), 2.027(2) Å (**5b**) and Pd−N1 = 2.052(2) Å (**5a**), 2.034(3) Å (**5b**)] and contracted bond lengths for the central formally anionic donor [Pd−N3 = 1.958(2) Å (**5a**) 1.952(2) Å (**5b**)].

Catalytic Hydrogenation of Olefins with [PdCl(4-Me-BPI)] (2b)

As indicated in the introduction, there is a substantial interest in the development of molecular non-phosphane-containing palladium catalysts for homogeneous hydrogenations. A limiting factor is the propensity of many palladium complexes of that type to undergo degradation under the conditions of the catalytic reaction. Given the stability of the BPI-Pd complexes and the capacity of the imino units in the ligand framework to act as sites of intermediate protonation, we hoped that they might hydrogenate alkenes without decomposition. As a first test system we chose the complex [PdCl(4-Me-BPI)] (**2b**) which is significantly more soluble in polar organic solvents than the unsubstituted parent complex. In order to test its activity towards hydrogenation of C=C double bonds in different chemical environments, the hydrogenation of three substrates — styrene, 1-octene and cyclohexene — was investigated.



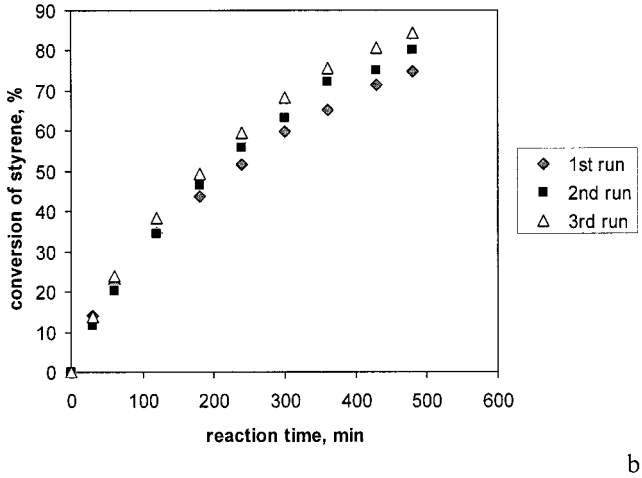


Figure 6. Hydrogenation of styrene at 25 ± 1 °C in THF at a hydrogen pressure of 1 bar using 2 mol % of the catalyst **2b**: a) the conversion curves for three independent catalytic runs; b) isolation of the catalyst that had been used in the third run and re-used in two further catalytic runs

All reactions were carried out at 25 ± 1 °C in THF at a hydrogen pressure of 1 bar using 2 mol % of the catalyst **2b**. We first studied the hydrogenation of styrene to ethylbenzene. The conversion curves for three independent catalytic runs are displayed in part a of Figure 6 which were carried out under the specified standard conditions and the same substrate and catalyst concentrations; in all three cases the catalyst **2b** was isolated without detectible decomposition after the conversion. In view of this apparent stability of the catalyst, the sample which had been used in the third run and had subsequently been isolated, was employed in two further catalytic runs, again under identical conditions. As can be seen in part b of Figure 6, this procedure also did not lead to a significant change in the catalytic activity of **2b**. After each of the three catalytic runs, the solvent and reaction product were removed in vacuo, the solid residue characterized by ^{1}H NMR spectroscopy and then used in the subsequent catalytic conversion. It is evident from the absence of a signal at δ = 8.5 ppm, which would be due to the demetallated BPI ligand, that there was no decomposition even after three cycles. The stability of the system is shown by comparison of the ^{1}H NMR spectra of **2b** before the catalysis (Figure 7, top) with that recorded after the three cycles of catalysis, isolation of the catalyst and re-use of the catalyst (Figure 7, bottom). We were not able to detect hydridopalladium intermediates by ^{1}H NMR spectroscopy during the course of the catalytic reaction.

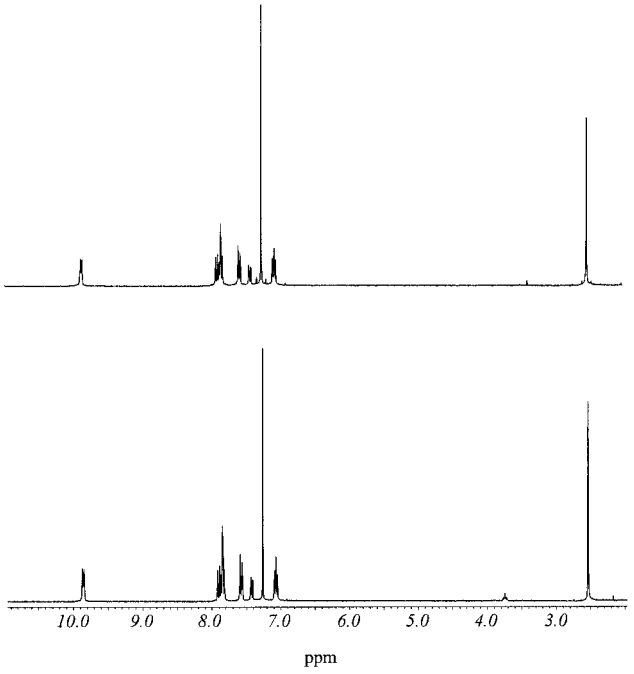


Figure 7. Top: ^{1}H NMR spectrum of **2b** before the catalysis; bottom: ^{1}H NMR spectrum of the catalyst recorded after three cycles of catalysis, isolation of the catalyst, and re-use of the catalyst

We found that if the hydrogenation is carried out in methanol instead of THF as solvent, the palladium complex decomposes during the course of the reaction leading to the precipitation of palladium black, which is inactive under the reaction conditions. This catalyst degradation is evidenced by ^{1}H NMR spectroscopy and the observation of the proton signal of the free ligand at δ = 8.5 ppm.

As a second substrate, and as an example of a long-chain terminal alkene, the hydrogenation of 1-octene catalyzed by **2b** was investigated. Of particular interest was the competing reaction in this transformation, the isomerization of the alkene to a mixture of *E*- and *Z*-2-octene. The course of this reaction, as followed by GC-MS, is represented in Figure 8.

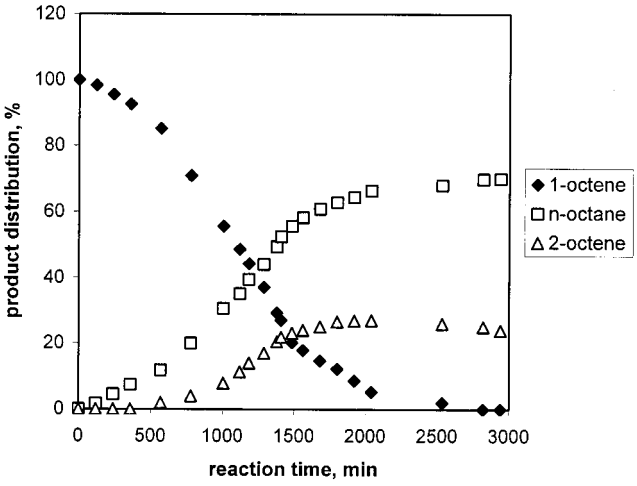


Figure 8. Hydrogenation of 1-octene catalyzed by **2b** and the concomitant isomerization of the alkene to a mixture of *E*- and *Z*-2-octene, as followed by GC-MS

After a short induction period, during which the catalytically active species is generated, the conversion of 1-octene sets in, giving n-octane and a mixture of *Z*-2-octene and *E*-2-octene. After the complete consumption of 1-octene, the conversion into n-octane was around 70%, while 27% of the starting material were converted into the mixture of 2-octenes. The hydrogenation of the latter is extremely slow and practically insignificant within the timeframe represented in Figure 8.

The lack of activity in the hydrogenation of internal C=C double bonds was also apparent from the reaction with cyclohexene. Whereas this substrate is readily hydrogenated by colloidal or heterogeneous Pd catalysts, it is known to be converted only very slowly by molecular Pd catalysts.[18] After 1500 minutes only 5% of the alkene had been converted and even after 9000 minutes the conversion was only at about 12%. A comparison of the conversion curves for the hydrogenation of the three alkenes investigated in this study is given in Figure 9.

As previously noted by Elsevier et al. for N-ligand Pd catalysts, the "mercury test"[19] for potential colloidal metal catalysis is not applicable to palladium compounds such as **2b**.[3d,18] However, the stability of complex **2b** that we observed in the catalytic hydrogenations, the reproducibility of the reaction kinetics, the different behaviour towards the three olefins chosen as substrates and, finally, the possibility of isolating the non-decomposed catalyst after several cata-

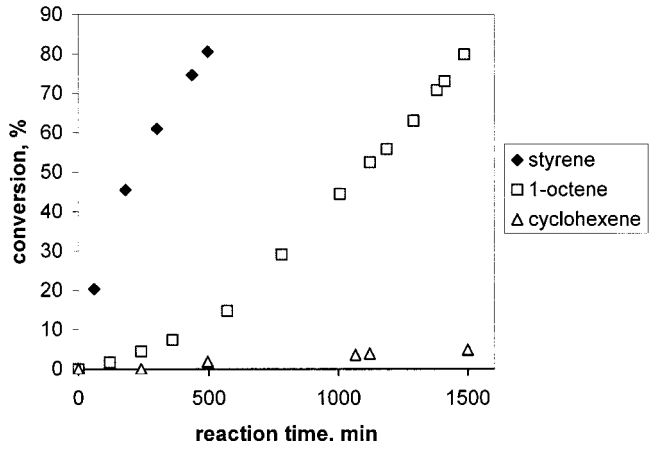


Figure 9. A comparison of the conversion curves for the hydrogenation of styrene, 1-octene and cyclohexene

lytic runs, provides strong circumstantial evidence for molecular catalysis with the BPI-palladium complex.

Although the mechanistic details of the catalytic cycle remain to be established, and no reaction intermediates could be detected to date, a reaction sequence based on the mechanistic proposal by Costa, Pelagatti and co-workers,[4−7] is put forward in Scheme 4. It takes the previously observed possibility of imino-N protonation in the ligand framework into account.[12] Preliminary studies with the other BPI derivatives reported in this work indicate an essentially similar behaviour.

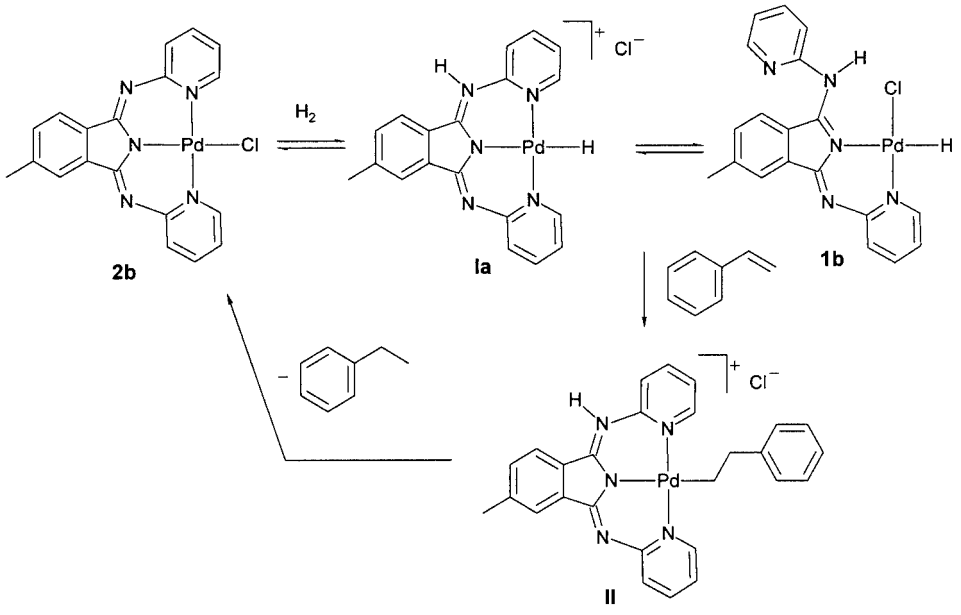
Conclusion

In this paper we have reported the first detailed synthetic and structural study of bis(2-pyridylimino)isoindolatopalladium(II) complexes. The possibility of modifying the peripheral ligand structure after the assembly of the BPI unit has been demonstrated by the Sonogashira alkynylation of a bromopyridyl derivative. This provides the first example of a possible modular variation of these ligands which is of particular interest in catalyst design based on these systems. A detailed study into the hydrogenation activity of one of the Pd complexes has established a novel active molecular catalyst for alkene hydrogenation. Current and future work is aimed towards the elucidation of the mechanism of this catalytic reaction.

Experimental Section

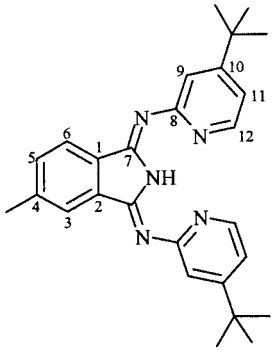
All manipulations were performed under nitrogen. Solvents were dried according to standard methods and saturated with nitrogen. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze-pump-thaw" cycles and stored over 4 Å molecular sieves. Solids 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, respectively [reference: tetramethylsilane, using the residual protonated solvent peak (^{1}H) or the carbon resonance (^{13}C)]. Infrared spectra were recorded on a Nicolet Magna IRTM 750 spectrometer. Elemental analyses were carried out by the microanalytical service at the Chemistry Department of the University of Strasbourg. (10-Me)-BPI (**1a**), (11-Me)-BPI (**1b**), (11-Br)-BPI (**1c**), (4-Me)-BPI (**1d**)[9] and $[PdCl_2(PhCN)_2]$[20] were prepared according to published procedures. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of 4-Me-10-*t*BuBPI (1e): 4-Methylphthalodinitrile (1.50 g, 10.6 mmol) and 2-amino-4-(*tert*-butyl)pyridine (3.96 *g* = 26.1 mmol) were heated unter reflux in hexanol in the presence of a catalytic amount of $CaCl_2$ (0.16 g, 1.36 mmol) for 18 h. After



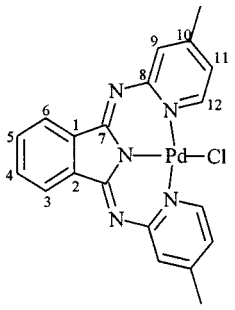
Scheme 4. Proposed mechanism of the Pd-catalyzed hydrogenation

cooling to room temperature, the solid reaction product was isolated by filtration washed three times with 50 mL of water and then dried in a dessiccator over P_4O_{10} to give compound **1e** as a crystalline yellow solid. Yield: 2.53 g (5.94 mmol, 56%). M.p. 204 °C. ^{1}H NMR (400.16 MHz, C_6D_6): δ = 1.1, 1.2 (each s, each 9 H, 10-*t*Bu), 2.05 (s, 3 H, 4-CH_3), 6.84 (m, 2 H, 11-H), 6.94 (br. d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 5-H), 7.72 (m, 2 H, 9-H), 8.02 (br. s, 1 H, 3-H), 8.12 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, 6-H), 8.60 (d, $^3J_{H,H}$ = 5.3 Hz, 2 H, 12-H), 11.91 (br. s, 1 H, N−H) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): δ = 21.6 (4-*C*H_3), 30.4 [10-C(*C*H_3)$_3$], 34.5 [10-*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): $\tilde{\nu}$ = 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}. $C_{27}H_{31}N_5$ (425.57): calcd. C 76.20, H 7.34, N 16.46; found C 76.48, H 7.36, N 16.25.

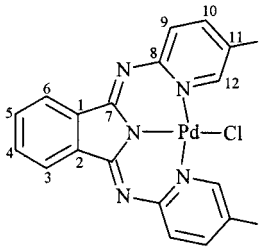


General Procedure for the Preparation of the Palladium(II) Complexes 2a−2e: The bis(2-pyridyl)isoindole (BPI) derivative (in general 0.3 mmol) together with 1.1 molar equivalents of $[PdCl_2(PhCN)_2]$ and 1.1 molar equivalents of NEt_3 were dissolved in benzene and stirred at room temperature for two days. Depending on the substitution pattern of the ligand, the palladium complex either precipitated directly from the reaction mixture or remained in solution. For compounds **2a−2d** direct precipitation of the reaction product was observed and the resulting solid was separated by filtration. The co-product NEt_3HCl was extracted from the solid by extraction three times with 50 mL of water and the crude product thus obtained was recrystallized from CH_2Cl_2/*n*-hexane. In the case of complex **2e** 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 three times with 50 mL of water and 10 mL of hexane, the crude product thus obtained was recrystallized from CH_2Cl_2/*n*-hexane. Compounds **2a−2e** are deep yellow-ochre crystalline solids.

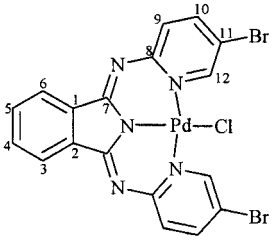
[PdCl{(10-Me)-BPI}] (2a): Yield: 45%. M.p. 287 °C (dec.). ^{1}H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 2.41 (s, 6 H, CH_3), 6.88 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, H-11), 7.40 (s, 2 H, H-9), 7.60 (m, 2 H, H-5), 8.01 (m, 2 H, H-6), 9.67 (d, $^3J_{H,H}$ = 6.6 Hz, 2 H, H-12) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 20.6 (CH_3), 121.3 (C-11), 122.2 (C-9), 126.6 (C-5), 131.3 (C-6), 137.9 (C-1,2), 149.9 (C-7/8/10/12), 151.2 (C-7/8/10/12), 152.7 (C-7/8/10/12), 153.8 (C-7/8/10/12) ppm. IR (KBr): $\tilde{\nu}$ = 1581 (vs), 1517 (s), 1466 (s), 1402 (vw), 1376 (w), 1295 (s), 1315 (w), 1180 (s), 1098 (vs), 944 (w) cm^{-1}. $C_{20}H_{16}ClN_5Pd$ (468.25): calcd. C 51.30, H 3.44, N 14.96; found C 50.97, H 2.89, N 15.38.



[PdCl{(11-Me)-BPI}] (2b): Yield: 98%. M.p.: 280 °C. ^{1}H NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 2.38 (s, 6 H, CH_3), 7.43 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H-9), 7.61 (dd, $^3J_{H,H}$ = 5.5, $^4J_{H,H}$ = 2.9 Hz, 2 H, H-5), 7.68 (dd, $^3J_{H,H}$ = 8.2, $^4J_{H,H}$ = 2.2 Hz, 2 H, H-10), 7.95 (dd, $^3J_{H,H}$ = 5.5, $^4J_{H,H}$ = 2.9 Hz, 2 H, H-6), 9.64 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, H-12) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, CD_2Cl_2, 295 K): δ = 18.1 (CH_3), 122.0 (C-5), 125.8 (C-9), 129.8 (C-11), 131.2 (C-6), 137.9 (C-1,2), 140.5 (C-10), 150.2 (C-12), 152.7 (C-7/8), 152.9 (C-7/8) ppm. IR (KBr): $\tilde{\nu}$ = 2920 (br), 1620 (w), 1587 (s), 1576 (s), 1482 (w), 1473 (s), 1375 (s), 1302 (w), 1243 (w), 1189 (w), 1143 (vw), 1100 (s), 912 (w), 832 (w), 692 (s) cm^{-1}. $C_{20}H_{16}ClN_5Pd$ (468.25): calcd. C 51.30, H 3.44, N 14.96; found C 51.75, H 3.30, N 14.46.

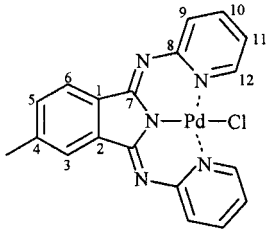


[PdCl{(11-Br)-BPI}] (2c): Yield: 34%. M.p.: 202 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$, 295 K): δ = 7.47 (d, $^3J_{H,H}$ = 8.7 Hz, 2 H, H-9), 7.64 (dd, $^3J_{H,H}$ = 8.7, $^4J_{H,H}$ = 2.2 Hz, 2 H, H-10), 8.06−8.09 (m, 4 H, H-5,6), 10.07 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, H-12) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, 295 K): δ = 114.9 (C-11), 122.7 (C-5), 127.4 (C-9), 131.6 (C-6), 137.4 (C-1,2), 141.9 (C-10), 148.6 (C-12), 150.7 (C-8), 153.7 (C-7) ppm. FAB-MS: *m*/*z* = 562 [M − Cl]$^+$. IR (KBr): $\tilde{\nu}$ = 3450 (br), 3110 (vw), 2962 (w), 2924 (vw), 2361 (vw), 1640 (w), 1598 (w), 1563 (s), 1518 (s), 1454 (s), 1361 (m), 1320 (vw), 1290 (vw), 1261 (m), 1232 (vw), 1185 (s), 1098 (s), 1020 (s), 915 (w), 860 (w), 839 (w), 801 (s), 702 (w), 684 (w) cm^{-1}. $C_{18}H_{10}Br_2ClN_5Pd$ (597.99): calcd. C 36.15, H 1.68, N 11.71; found C 36.74, H 2.01, N 11.60.

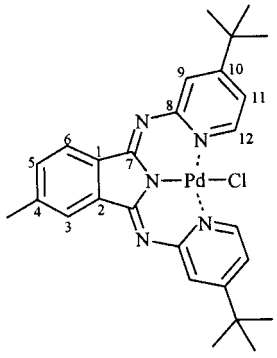


[PdCl(4-MeBPI)] (2d): Yield: 63%. M.p.: >165 °C (dec.). ^{1}H NMR (200.14 MHz, CD_2Cl_2, 298 K): δ = 2.37 (s, 3 H, 4-CH_3), 6.92 (m,

2 H, 11-H), 7.25 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, 5-H), 7.36 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, 9-H), 7.60 (br. s, 1 H, 3-H), 7.65 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, 6-H), 7.71 (m, 2 H, 10-H), 9.63 (d, $^3J_{H,H}$ = 6.2 Hz, 2 H, 12-H) ppm. $^{13}C\{^1H\}$ NMR (75.5 MHz, [D$_6$]DMSO, 353 K): δ = 21.3 (4-CH_3), 121.2 (C-11), 123.5 (C-9), 124.2 (C-5), 128.0 (C-6), 133.8 (C-3), 136.8 (C-1), 139.6 (C-2), 140.9 (C-10), 144.0 (C-4), 153.6 (C-8), 155.4 (C-7 u. C-12) ppm. IR (KBr): $\tilde{\nu}$ = 2917 (w), 1644 (w), 1579 (s), 1530 (s), 1487 (vw), 1461 (s), 1427 (m), 1367 (m), 1320 (w), 1289 (m), 1215 (vw), 1182 (w), 1135 (m), 1079 (w), 1016 (w), 873 (vw), 826 (vw), 770 (m), 708 (vw) cm^{-1}. $C_{19}H_{14}ClN_5Pd$ (454.04): calcd. 50.22, H 3.11, N 15.42; found C 49.84, H 3.21, N 15.23.

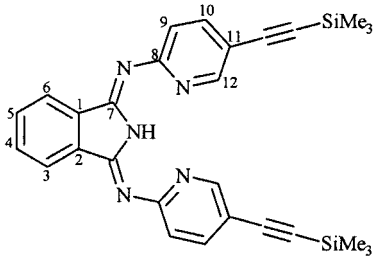


[PdCl(4-Me-10-*t*BuBPI)] (2e): Yield: 73%. M.p.: 192 °C (dec.). ^1H NMR (400.16 MHz, CD_2Cl_2, 298 K): δ = 1.27 (s, 18 H, 10-*tBu*), 2.39 (s, 3 H, 4-CH_3), 6.93 (m, 2 H, 11-H), 7.25 (br. d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 5-H), 7.35 (m, 2 H, 9-H), 7.57 (br. s, 1 H, 3-H), 7.61 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, 6-H), 9.51 (m, 2 H, 12-H) ppm. $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, 298 K): δ = 22.3 (4-*C*H$_3$), 30.5 [10-C(*C*H$_3$)$_3$], 35.4 [10-*C*(CH$_3$)$_3$], 118.2 (C-11), 122.4 (C-5), 123.0 (C-6), 123.6 (C-9), 132.6 (C-3), 135.9 (C-1), 138.7 (C-2), 142.6 (C-4), 152.4 (C-7/C-8), 153.5 (C-12), 154.1 (C-7/C-8), 164.4 (C-10) ppm. IR (KBr): $\tilde{\nu}$ = 2962 (m), 2867 (w), 1577 (s), 1559 (w), 1521 (w), 1507 (m), 1477 (m), 1402 (w), 1368 (w), 1319 (vw), 1296 (w), 1262 (w), 1214 (vw), 1181 (m), 1145 (w), 1114 (m), 1048 (m), 1022 (w), 949 (vw), 920 (vw), 890 (vw), 797 (w), 714 (w) cm^{-1}. $C_{27}H_{30}ClN_5Pd$ (566.44): calcd. C 57.25, H 5.34, N 12.36; found C 57.08, H 5.50, N 12.16.

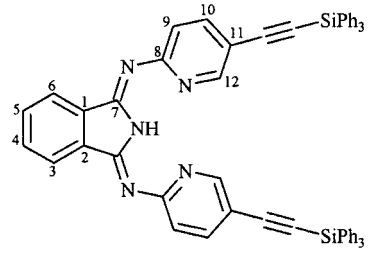


General Procedure for the Preparation of the Alkynyl-Substituted Ligands 4a−4c: The BPI derivative **1c** (0.7 mmol), six molar equivalents of the substituted acetylene, 0.2 molar equivalents of CuI and 0.2 molar equivalents of tetrakis(triphenylphosphane)palladium(0) were stirred in 10 mL of triethylamine at 60 °C. The reaction time was 6 d for **4a**, 4 d for **4b** and 24 h for **4c**. 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 microcrystalline solids.

(11-TMS-ethynyl)-BPI (4a): Yield: 50%. M.p.: 168 °C. ^1H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 0.29 (s, 18 H, CH_3), 7.32 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, H-9), 7.58 (s, 2 H, H-5), 7.77 (dd, $^3J_{H,H}$ = 7.4, $^4J_{H,H}$ = 3.6 Hz, 2 H, H-10), 7.97 (s, 2 H, H-6), 8.66 (d, $^3J_{H,H}$ = 3.6 Hz, 2 H, H-12), 13.72 (s, 1 H, N−H) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 0.9 (CH_3), 98.2 (C-Si), 102.2 (*C*-C$_{aryle}$), 116.3 (C-11), 122.6 (C-9), 128.3 (C-5), 131.7 (C-6), 135.5 (C-1,2), 140.8 (C-10), 150.9 (C-12), 153.8 (C-7), 159.2 (C-8) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 295 K): δ = −17.4 ppm. IR (KBr): $\tilde{\nu}$ = 2959 (s), 2155 (s), 1624 (s), 1566 (s), 1465 (s), 1360 (w), 1307 (vw), 1251 (w), 1220 (s), 1096 (w), 1036 (w), 925 (vw), 872 (s), 843 (s), 758 (w), 695 (w) cm^{-1}. $C_{28}H_{29}N_5Si_2$ (491.74): calcd. C 68.39, H 5.94, N 14.24; found C 68.52, H 6.51, N 13.63.

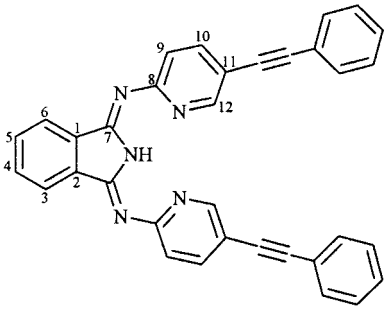


(11-Ph$_3$Si-ethynyl)-BPI (4b): Yield: 69%. M.p.: 198 °C. ^1H NMR (300.17 MHz, $CDCl_3$, 295 K): δ = 7.37−7.72 (m, 34 H, Ph−H, H-5, H-9), 7.91 (d, $^3J_{H,H}$ = 7.0 Hz, 2 H, H-10), 8.07 (s, 2 H, H-6), 8.82 (s, 2 H, H-12), 13.77 (s, 1 H, N−H) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 295 K): δ = 82.0 (C≡*C*Si), 91.7 (*C*≡CSi), 106.0 (C-Ph), 116.1 (C-11), 122.5 (C-5/9), 123.0 (C-5/9), 127.9 (C-Ph), 129.8 (C-Ph), 130.1 (C-Ph), 131.9 (C-6), 135.5 (C-1,2), 141.1 (C-10), 151.0 (C-12), 153.7 (C-7), 158.4 (C-8) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 295 K): δ = −28.5 ppm. FAB-MS: *m*/*z* = 864 [M + H]$^+$. IR (KBr): $\tilde{\nu}$ = 3304 (br), 2935 (w), 2676 (s), 2070 (s), 1623 (vs), 1565 (vs), 1459 (s), 1428 (vs), 1185 (w), 1113 (vs), 1035 (w) cm^{-1}. $C_{58}H_{41}N_5Si_2$ (864.17): calcd. C 80.61, H 4.78, N 8.10; found C 80.36, H 4.33, N 7.72.



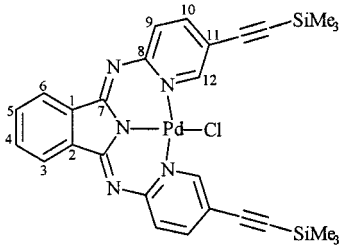
(11-Ph-ethynyl)-BPI (4c): Yield: 77%. M.p.: 246 °C. ^1H NMR (300.17 MHz, CD_2Cl_2, 295 K): δ = 7.39−7.45 (m, 10 H, Ph−H), 7.60 (d, $^3J_{H,H}$ = 7.9 Hz, 2 H, H-9), 7.68−7.70 (dd, $^3J_{H,H}$ = 5.5, $^4J_{H,H}$ = 3.0 Hz, 2 H, H-5), 7.89−7.93 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 2.2 Hz, 2 H, H-10), 8.05 (dd, $^3J_{H,H}$ = 5.5, $^4J_{H,H}$ = 2.9 Hz, 2 H, H-6), 8.84 (d, $^4J_{H,H}$ = 2.2 Hz, 2 H, H-12), 14.07 (s, 1 H, N−H) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): δ = 86.5 (C≡C), 92.8 (C≡C), 107.2 (C-Ph), 116.6 (C-11), 122.6 (C-9), 127.6 (C-5), 128.4 (C-Ph), 128.6 (C-Ph), 129.5 (C-Ph), 131.6 (C-6), 135.3 (C-1,2), 140.4 (C-10), 150.5 (C-12), 153.8 (C-7), 158.9 (C-8) ppm. IR (KBr): $\tilde{\nu}$ = 3278 (br), 2962 (s), 2145 (vw), 1638 (s), 1571 (s), 1492 (w), 1463 (w), 1457 (vw), 1261 (s), 1220 (vw), 1095 (s), 1019 (s), 800 (s),

693 (vw) cm^{-1}. $C_{34}H_{21}N_5$ (499.57): calcd. C 81.74, H 4.23, N 14.02; found C 82.33, H 4.87, N 14.59.

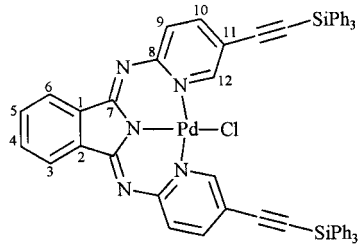


Preparation of Complexes 5a−5c: The preparation of complexes **5a** and **5c** was carried out using 0.3 mmol of the ligand precursors **4a** and **4c** following the procedure described for **2e**. Complex **5b** was prepared on the same scale as described above for **2a−2d**. The alkynyl-substituted complexes were obtained as orange or orange-red crystalline solids.

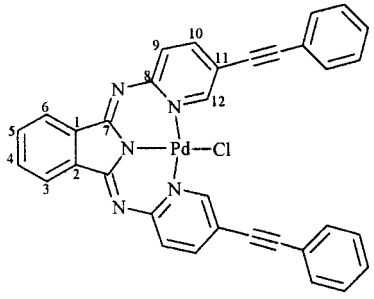
[PdCl{(11-TMS-ethynyl)-BPI}](5a): Yield: 49%. M.p.: 197 °C (dec.). ^1H NMR (300.17 MHz, $CDCl_3$, 295 K): $\delta = -0.26$ (s, 18 H, CH_3), 7.45 (d, $^3J_{H,H} = 9.0$ Hz,, 2 H H-9), 7.58 (m, 2 H, H-5), 7.82 (dd, $^3J_{H,H} = 9.0$, $^4J_{H,H} = 2.2$ Hz, 2 H, H-10), 7.96 (m, 2 H, H-6), 9.91 (d, $^4J_{H,H} = 2.2$ Hz, 2 H, H-12) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 295 K): $\delta = 99.9$ (*C*≡CSi), 100.2 (C≡*C*Si), 116.4 (C-11), 122.4 (C-9), 125.9 (C-5), 131.5 (C-6), 137.5 (C-1,2), 141.4 (C-10), 150.7 (C-12), 153.9 (C-7), 156.6 (C-8) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 295 K): $\delta = -22.0$ ppm. FAB-MS: $m/z = 596$ $[M - Cl]^+$. IR (KBr): $\tilde{\nu} = 2959$ (w), 2145 (w), 1560 (s), 1474 (s), 1459 (vs), 1364 (w), 1288 (w), 1248 (w), 1185 (w), 1099 (s) cm^{-1}. $C_{28}H_{28}ClN_5PdSi_2$ (632.61): calcd. C 53.16, H 4.46, N 11.07; found C 53.02, H 4.18, N 10.89.



[PdCl{(11-Ph_3Si-ethynyl)-BPI}] (5b): Yield: 42%. M.p.: 202 °C. ^1H NMR (300.18 MHz, $CDCl_3$, 295 K): $\delta = 7.37-7.71$ (m, 34 H, H−Ph, H-5,9), 7.92 (d, $^3J_{H,H} = 8.8$ Hz, 2 H, H-10), 8.04 (m, 2 H, H-6), 10.11 (s, 2 H, H-12) ppm. $^{13}C\{^1H\}$ NMR (75.48 MHz, $CDCl_3$, 295 K): $\delta = 82.2$ (C≡C), 95.1 (C≡C), 104.5 (C-Ph), 115.9 (C-11), 122.6 (C-9), 126.1 (C-5), 128.1 (C-Ph), 130.1 (C-Ph), 131.8 (C−Ph, C-6), 132.2 (C−Ph, C-8), 132.8 (C-Ph), 137.6 (C-1,2), 141.6 (C-10), 151.2 (C-12), 154.3 (C-7), 157.1 (C-8) ppm. ^{29}Si NMR (79.5 MHz, $CDCl_3$, 295 K): $\delta = -22.1$ ppm. FAB-MS: $m/z = 968$ $[M - Cl]^+$. IR (KBr): $\tilde{\nu} = 3065$ (s), 2155 (s), 2070 (s), 1624 (s), 1566 (vs), 1483 (w), 1459 (s), 1425 (s), 1359 (vw), 1304 (vw), 1262 (vw), 1218 (w), 1185 (w), 1113 (s), 1028 (w), 997 (w), 846 (vw), 818 (w) cm^{-1}. $C_{58}H_{40}ClN_5PdSi_2$ (1003.0): calcd. C 69.31, H 4.01, N 6.97; found C 69.83, H 4.55, N 6.35.



[PdCl{(11-Ph-ethynyl)-BPI}] (5c): Yield: 136 mg (212 μmol, 53%). M.p.: 150 °C. ^1H NMR (300.17 MHz, $CDCl_3$, 295 K): $\delta = 7.35$ (m, 8 H, Ph−H), 7.46 (d, $^3J_{H,H} = 7.0$ Hz, 2 H, H-9), 7.54 (m, 4 H, Ph−H, H-5), 7.85 (d, $^3J_{H,H} = 7.0$ Hz, 2 H, H-10), 7.92 (s, 2 H, H-6), 10.07 (s, 2 H, H-12) ppm. $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 295 K): $\delta = 85.2$ (C≡C), 94.0 (C≡C), 116.6 (C-11), 122.4 (C-5), 126.0 (C-9), 128.4 (C-Ph), 128.9 (C-Ph), 131.4 (C-Ph), 131.8 (C-Ph), 132.1 (C-6), 137.4 (C-1,2), 140.9 (C-10), 150.4 (C-12), 153.7 (C-7), 156.2 (C-8) ppm. FAB: $m/z = 604$ $[M - Cl]^+$. IR (KBr): $\tilde{\nu} = 2963$ (s), 2217 (w), 1560 (s), 1491 (w), 1459 (s), 1364 (w), 1261 (s), 1185 (w), 1097 (vs), 1022 (vs) cm^{-1}. $C_{34}H_{20}ClN_5Pd$ (640.44). calcd.: calcd. C 63.76, H 3.15, N 10.94; found C 63.32, H 2.99, N 10.63.



Catalyst Testing: 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 performed with a Shimadzu GC-17A/GCMS-QP5050A. Column: SGE BPX5, 5% phenyl, polysilylphenylene-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.

GC/MS Parameters for 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, 80 °C; 20 °C/min, 250 °C; retention times: t_R (ethylbenzene) = 7.84 min, t_R (styrene) = 9.12 min,

GC/MS Parameters for 1-Octene Hydrogenation: T (start) = 35 °C, T (injector) = 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, 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.

GC/MS Parameters for Cyclohexene Hydrogenation: T (start) = 35 °C, T (injector) = 250 °C, T (interface) = 280 °C, 30.0 m (0.22 mm), 1.5 mL/min He (flow rate), 133.2 kPa (column press-

Table 3. X-ray experimental data of compounds **2c**, **2e**, **3**, **5a**, and **5b**

	2c	**2e**	**3**	**5a**	**5b**
Formula	$C_{39}H_{26}Br_4Cl_8N_{10}Pd_2$	$C_{31.5}H_{40}Cl_5N_5Pd$	$C_{87}H_{82}Cl_{10}N_{20}O_{10}Pd_4$	$C_{29}H_{30}Cl_3N_5PdSi_2$	$C_{58}H_{40}ClN_5PdSi_2$
Formula mass	1450.77	772.34	2347.88	717.53	1005.02
Crystal system	monoclinic	triclinic	orthorhombic	triclinic	triclinic
Space group	*C*2/*c*	$P\bar{1}$	*Pbcn*	$P\bar{1}$	$P\bar{1}$
a (Å)	12.8115(3)	7.6784(15)	27.7458(5)	8.3844(1)	9.0527(2)
b (Å)	13.4458(3)	14.752(3)	14.4426(6)	12.8717(3)	14.2176(2)
c (Å)	26.3815(7)	15.751(3)	23.158(1)	15.9248(4)	19.3151(4)
α (°)	–	74.79(3)	–	77.111(5)	74.634(5)
β (°)	91.723(5)	85.90(3)	–	84.970(5)	88.341(5)
γ (°)	–	88.83(3)	–	80.587(5)	82.949(5)
V (Å^3)	4542.4(2)	1717.2(6)	9279.9(6)	1650.42(6)	2378.99(8)
Z	4	2	4	2	2
$\rho_{calcd.}$ (g·cm^{-3})	2.12	1.49	1.68	1.44	1.40
*F*000	2792	790	4712	728	1028
μ (mm^{-1})	4.826	0.959	1.120	0.905	0.542
Temperature (K)	173	193	173	173	173
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Radiation		Mo-K_α graphite monochromated			
Number of data meas.	8979	5053	19840	10278	16796
Number of data with $I > 3\sigma(I)$	3684	3435 ($I > 2\ \sigma(I)$]	3886	5878	7055
Number of variables	285	494	589	361	604
R	0.029	0.072	0.081	0.027	0.036
Rw	0.039	–	0.100	0.034	0.046
wR_2	–	0.186	–	–	–
GOF	1.006	1.081	1.006	1.030	1.039
Largest peak in final difference (e·Å^{-3})	0.301	1.204	1.450	0.308	0.669

ure), temperature program: 8.0 min, 35 °C; 30 °C/min, 250 °C; t_R (cyclohexane) = 2.49 min, t_R (cyclohexene) = 2.74 min.

X-ray Crystallographic Study of 2c, 2e, 3, 5a and 5b: Suitable crystals of the complexes **2c**, **2e**, **3**, **5a** and **5b** 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 **2c**, **3**, **5a** and **5b** were collected on a Nonius Kappa CCD diffractometer at −100 °C and transferred to a DEC Alpha workstation; for all subsequent calculations the Nonius OpenMoleN package was used.[21] The data for **2e** 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 package.

All structures were solved by 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 temerature 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 the literature.[22] Crystal data and experimental details for the crystals of **2c**, **2e**, **3**, **5a** and **5b** are given in Table 3.

CCDC-232252 to -232256 (for **2c**, **2e**, **3**, **5a** and **5b**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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