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Porphyrin-Based Switchable Molecular Turnstiles

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Abstract: The design, synthesis and structural characterisation, in solution, of two new molecular turnstiles based on Sn–porphyrin derivatives are described. The system is composed of a stator (5-(4-pyridyl)-10,15,20-triphenylporphyrin), a hinge (Sn^{IV}) and a rotor (handle equipped with 2,6-pyridinedicarboxamide as a tridentate coordinating site or its Pd^{II} complex). The presence of interaction sites, both on the stator and the rotor, offers the possibility of switching between an open state (free rotation of the handle around the porphyrin) and a closed state (blockage of the rotation) by either establishment of hydrogen bonds between the stator and the rotor or by the simultaneous binding of Pd by both coordinating groups.

Keywords: molecular motion · molecular turnstiles · palladium · porphyrinoids · synthesis design

Introduction

In living organisms, the control of molecular motion is essential for many biological processes.[1] Translational motors based on myosine[2,3] or kinesine[4,5] and rotational motors, such as adenosine triphosphate (ATP) synthase,[6,7] have been discovered and studied. The complexity of these machineries is beyond synthetic chemistry. However, molecular chemists have proposed elegant design principles of molecular motors and machines that are considerably less sophisticated than the natural ones.[8] In particular, the two pioneering strategies developed by the groups of Stoddart and Balzani and by Sauvage paved the way to an active research topic that is still of intense interest.[9,10] The design principles followed by the two groups are based on rotaxanes and catenanes; two peculiar classes of preorganised architectures. Whereas Stoddart and co-workers exploited the supramolecular approach by designing translational motors based on specific interactions between organic moieties in rotaxane-type assemblies,[9] Sauvage and co-workers, using catenane-type molecules, exploited the coordination strategy for the design of both rotational and translational systems based on geometric and binding-propensity differences for metal cations in two different oxidation states.[10] Based on the same type of strategy, the same group has also reported a movable system described as an artificial molecular muscle.[11] Based on other molecular platforms, Kelly et al.[12] and Feringa et al.[13] described two other elegant molecular motors based on thermal or photochemical processes. Examples of molecular cars,[14] wheelbarrows[15] and turnstiles[16] have also been reported. The design and synthesis of molecular motors and machines still remain a challenge.[17–26]

Herein, we report on two new molecular turnstiles, **2** and **3**, based on a Sn–porphyrin (stator) combining a peripheral monodentate coordinating site on the porphyrin core and a tridentate chelate on the handle (rotor) (Scheme 1).

Results and Discussion

Design of the system: Recently, we have described the design and synthesis of a series of new molecular turnstiles based on a Sn–porphyrin backbone.[27,28] These systems are composed of a stator, a hinge and a handle (Figure 1). The stator is a porphyrin backbone with a 4-pyridyl unit at one of the *meso* positions acting as a monodentate coordinating site. The connection of the latter to the porphyrin imposes the outward orientation (Figure 1a). The hinge is a Sn^{IV} atom—a strong oxophilic Lewis acid adopting an octahedral coordination geometry—complexed by the tetraaza core of the porphyrin and thus offering two free axial positions (Figure 1b). The handle is a rather flexible fragment possessing a pyridyl central coordination site oriented towards the porphyrin backbone and two terminal resorcinol moieties connected to the pyridine unit by two oligoethyleneglycol spacers. The connection of the handle to the stator is ensured through Sn–O bonds between the two terminal resorcinol groups and the two free apical positions of the Sn^{IV} centre located at the centre of the porphyrin (Figure 1c).

The behaviour of turnstile **1** (Scheme 1) was investigated in solution by ^1H NMR spectroscopy in the absence and in the presence of Ag^+ cation acting as an effector. As expected, whereas in the absence of the cation, the handle freely rotates around the stator (open state, Figure 1c), in the pres-

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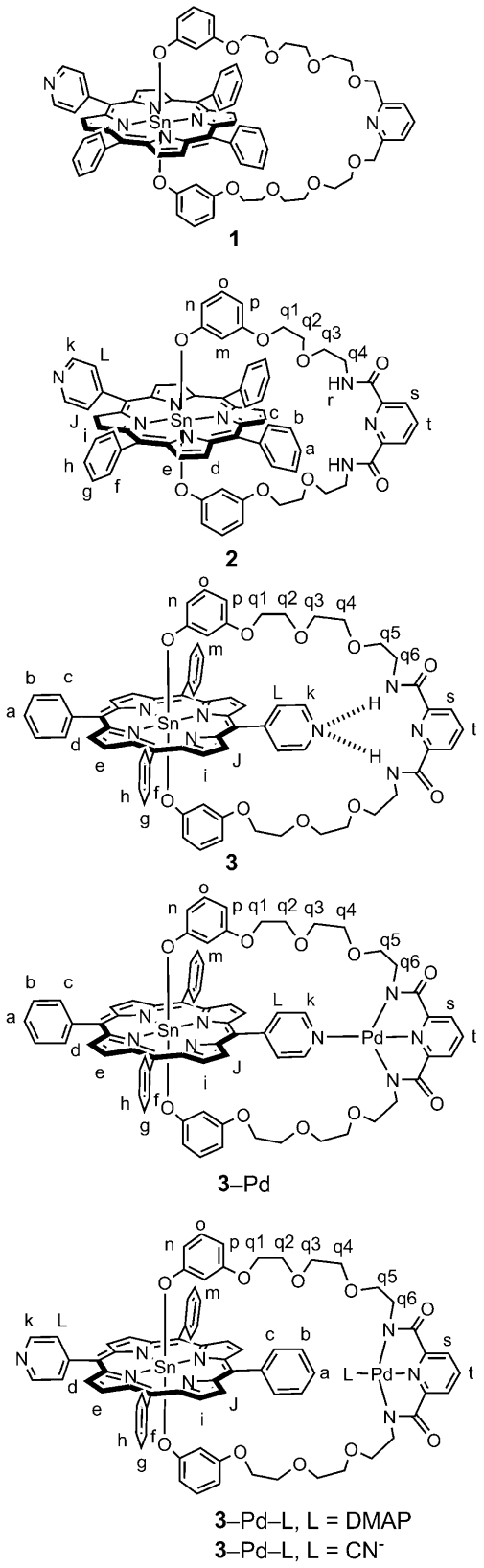


Scheme 1. Structures of compounds **1**–**3**, **3**–Pd and **3**–Pd–L complexes and labelling of hydrogen atoms.

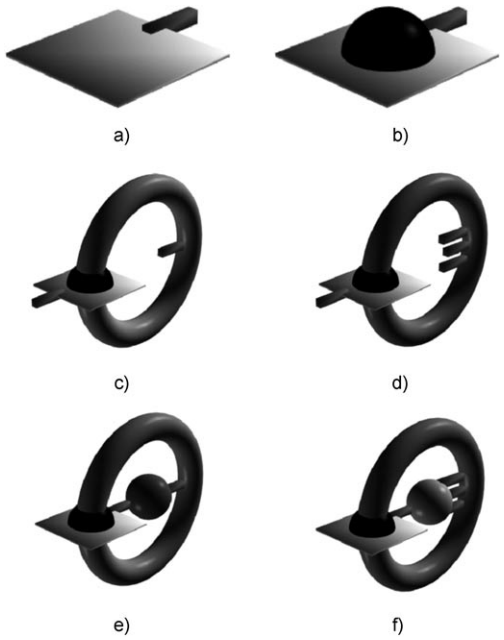
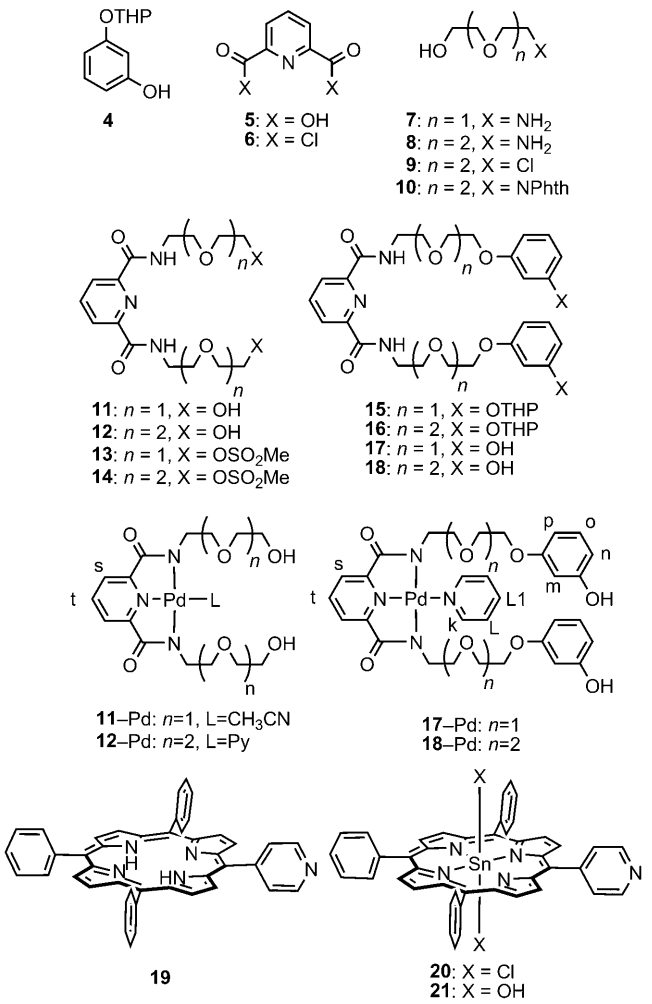


Figure 1. Schematic representation of a stator, a porphyrin derivative with a monodentate coordinating site at one of the *meso* positions (a); a hinge, an Sn^{IV} centre complexed by the tetraaza macrocyclic core of the porphyrin (b); a turnstile resulting from the interconnection of a handle with a monodentate (c) or a tridentate coordinating moiety (d) in the open (c and d) and closed (e and f) states, resulting from the simultaneous binding of a metal centre.

ence of the effector, the rotation is blocked by the simultaneous binding of a Ag^+ cation by both pyridine units located on the porphyrin backbone and on the handle (closed state, Figure 1e). However, the stability constant, K_s, of only 5700 $mol\,L^{-1}$ (ΔG of ca. $-21.4\,kJ\,mol^{-1}$) appeared to be rather low. To strengthen the interaction between the handle and the metal centre, it appeared judicious to substitute the monodentate pyridine moiety on the handle by the 2,6-pyridinedicarboxamide group, which is a dianionic tridentate chelating unit (Figure 1d). The choice of the chelating group was based on previously reported rotaxanes[29–33] or catenanes[34] and a turnstile[35] leading to rather stable complexes. As the effector, instead of Ag^+ cation, Pd^{II} was chosen because the latter adopts a square-planar coordination geometry, and furthermore, owing to the dianionic nature of the chelating site on the handle, should lead to a neutral turnstile (Figure 1f).

To explore the above-mentioned design principle, compounds **2** and **3** (Scheme 1) were synthesised. These two turnstiles are structural analogues and differ only by the length of the oligoethyleneglycol spacer connecting the chelating unit to the resorcinol moieties ($(CH_2)_2O(CH_2)_2$ for **2** and $(CH_2)_2O(CH_2)_2O(CH_2)_2$ for **3**).

Synthesis of the two turnstiles: The synthetic strategy for the preparation of compounds **2** and **3** (Scheme 1) was based on the condensation of the dihydroxy porphyrin **21** with the handles **17** and **18**, respectively (Scheme 2).



Scheme 2. THP = tetrahydropyranyl, Phth = phthalimidoyl, Py = pyridine.

The synthesis of handle **17** was achieved in about 75% yield upon condensation of monoprotected resorcinol **4** with dimesylate **13** in the presence of Cs_2CO_3 in acetonitrile at reflux, followed by deprotection at room temperature in about 80% yield by using a solution of methanol/aqueous HCl. Dimesylate **13** was prepared in two steps. The reaction[34a] of diacylchloride derivative **6**[36] with the commercially available aminoglycol **7** at room temperature and in the presence of Et_3N afforded in about 72% yield the diol **11**, which was subsequently transformed into the dimesylate **13** in about 72% yield upon treatment with methanesulfonyl chloride in the presence of triethylamine in dry THF at room temperature.

The syntheses of handle **18**[35] and porphyrin **21**[28] were reported earlier.

Turnstile **2** was prepared in 70% yield upon condensation of **21** with a small excess of **17** in dry $CHCl_3$ for 7 days at room temperature. By using a similar procedure, compound **3** was prepared in 91% yield upon condensation of handle **18** with porphyrin **21** in $CHCl_3$ at room temperature for 4 days. In both cases, the completion of the reaction was monitored by ^{1}H NMR spectroscopy.

Solution behaviour of compound 2: In solution, as expected, owing to the magnetic anisotropy of the porphyrin core, the ^{1}H NMR spectrum of compound **2** showed significant upfield shifts of the proton signals belonging to the resorcinol moieties of the handle.

In CD_2Cl_2, the signals corresponding to the β-pyrrolic protons consist of a singlet and two doublets, as observed for the parent porphyrin **21**, indicating that, on the NMR timescale, the average local environment of the porphyrin **2** is similar to that of **21** and implies free rotation of the handle around the stator. This was further confirmed by a comparison of the ^{1}H NMR spectra of free handle **17** and compound **2**; this showed the absence of interaction between the handle and the porphyrin moiety (Table 1). Indeed, in CD_2Cl_2, the resonance corresponding to the amide protons H_r (for signal assignment see Scheme 1) is only slightly upfield shifted ($\Delta\delta = 0.31$ ppm) upon formation of compound **2**. The free rotation of the handle was further evidenced by 2D ROESY NMR spectroscopy experiments, which showed no through-space correlations between protons belonging to the handle and protons located on the stator (Figure 2). Finally, a similar behaviour is observed in [D$_6$]DMSO ($\Delta\delta = 0.08$ ppm for the H_r protons when comparing the free handle **17** and compound **2**).

Table 1. ^{1}H NMR (300 MHz, 298 K) chemical shifts of protons H_r (see Scheme 1 for proton labelling) for compounds **2**, **3**, **17** and **18** in CD_2Cl_2 and [D$_6$]DMSO.

	δ [ppm]	
	CD_2Cl_2	[D$_6$]DMSO
2	≈8.20[a]	9.48
17	8.51	9.40
3	9.33	9.52
18	8.84	9.42

[a] Multiplet.

Solution behaviour of compound 3: In solution, the structure and dynamics of compound **3** were studied by ^{1}H NMR spectroscopy at 298 K in [D$_6$]DMSO and CD_2Cl_2 (Figure 3) and by 2D NMR spectroscopic techniques both in [D$_6$]DMSO at 298 K and in CD_2Cl_2 at 273 K (Figure 4).

In [D$_6$]DMSO, compound **3** behaves in a similar fashion to compound **2**. In particular, a rather small upfield shift of 0.1 ppm of the amide protons H_r is observed (Table 1). Again, owing to the magnetic anisotropy of the porphyrin, upon attachment of the handle to the Sn–porphyrin, protons belonging to the resorcinol moieties undergo significant shielding. Furthermore, couplings between the two ^{117}Sn and ^{119}Sn isotopes and the β-pyrrolic protons enabled the assignment of their signals. The signals corresponding to the β-pyrrolic protons appear as a sharp multiplet at $\delta = 9.12$ ppm. Finally, the ROESY experiment at 298 K shows only the ex-

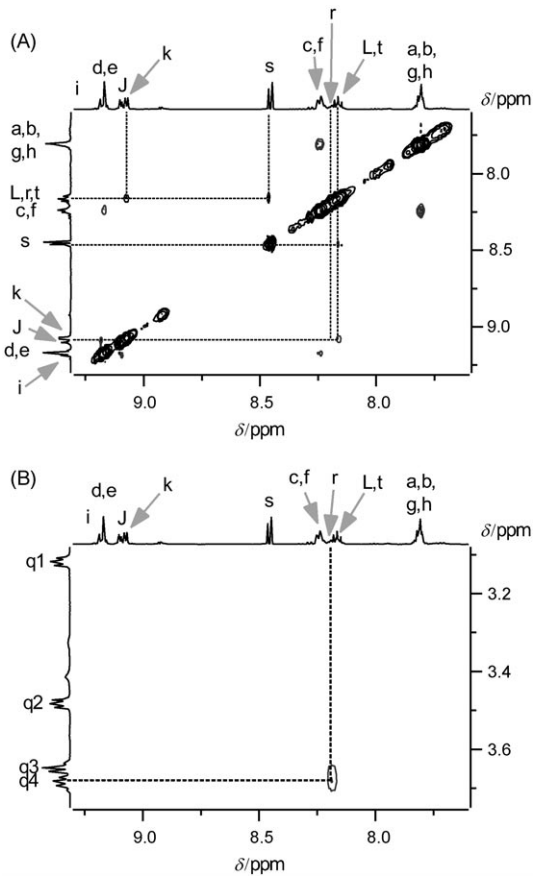


Figure 2. Portions of the 2D ROESY correlation (^{1}H–^{1}H NMR, 500 MHz, CD_2Cl_2, 298 K) of compound **2** and assignment of signals between $\delta =$ 7.60 and 9.30 ppm (A) and 3.00 and 3.75 ppm (B). For assignment of the protons, see Scheme 1.

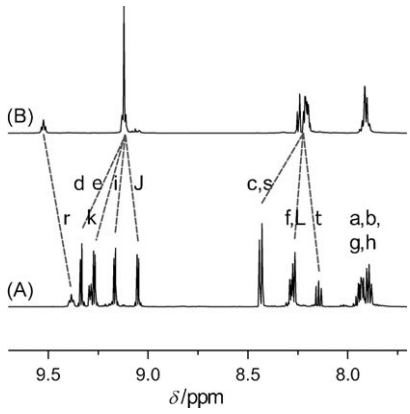


Figure 3. Portions of the ^{1}H NMR spectra (600 MHz, 298 K) in CD_2Cl_2 (A) and in [D_6]DMSO (B) and assignment of signals between $\delta = 7.5$–9.6 ppm for compound **3**. For assignment of the protons, see Scheme 1.

pected correlations between chemically linked protons (Figure 4 A). These observations clearly show that in [D_6]DMSO, as in the case of **2**, the handle freely rotates around the O-Sn-O axis.

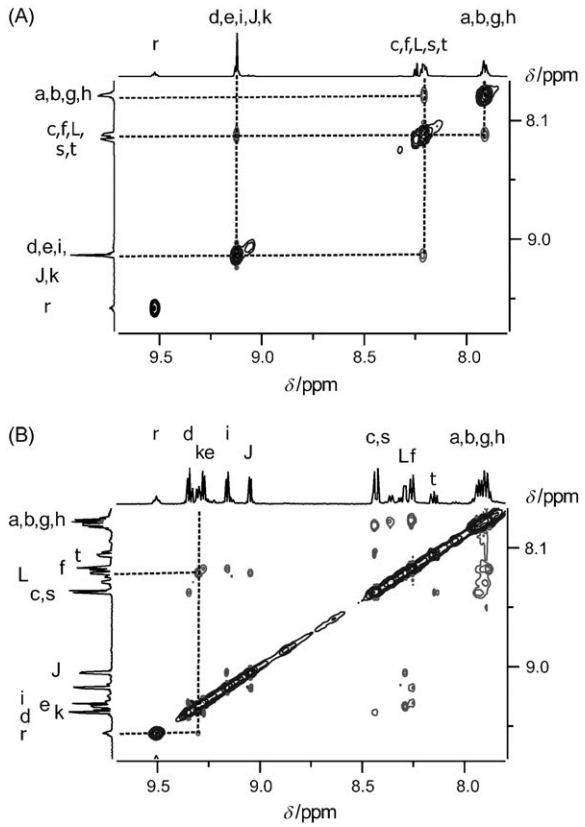


Figure 4. Portions of the 2D ROESY correlation (^{1}H–^{1}H NMR) of compound **3** in [D_6]DMSO (A) (600 MHz, 298 K) and in CD_2Cl_2 (B) (500 MHz, 273 K). For assignment of the protons, see Scheme 1.

In marked contrast, in CD_2Cl_2, compound **3** shows rather different behaviour and a lower symmetry (Figure 3). The amide protons H_r are shifted upfield in CD_2Cl_2 ($\delta =$ 9.33 ppm in CD_2Cl_2 versus $\delta = 9.52$ ppm in [D_6]DMSO). Protons *s* and *t* (Scheme 1), belonging to the pyridine moiety located on the handle, are deshielded by 0.20 ppm and slightly shielded by 0.07 ppm, respectively. Signals assigned to the β-pyrrolic protons appear as four doublets ($\delta = 9.05$, 9.17, 9.27, 9.33 ppm), implying a change in the environment of the porphyrin (a sharp multiplet in [D_6]DMSO). Furthermore, the signal corresponding to proton *k* located on the pyridine moiety of the stator is shifted downfield by 0.17 ppm. Similar behaviour was observed previously for the closed state of turnstile **1** upon binding of Ag^+ cations.[26,27] Here, the only possibility that affords the closed state is the formation of hydrogen bonds between the two acidic amide protons H_r of the handle and the pyridine moiety of the stator. This hypothesis is supported by a comparison of the ^{1}H NMR spectra of the free handle **18** and compound **3** in CD_2Cl_2. Indeed, contrary to what observed for compounds **2** and **17**, the establishment of hydrogen bonds between the pyridine unit of the stator and the amide protons H_r leads to a deshielding of the amide protons resonances by about 0.5 ppm. Further evidence for the existence of such interactions between the handle and the stator arises from 2D ROESY NMR spectroscopy experiments performed in CD_2Cl_2. At

298 K, although a correlation peak between the amide protons *r* and protons *k* belonging to the pyridine of the stator is observed, one might argue that the observation is ambiguous because of an overlap of signals. To get a clear-cut measurement, the same experiment was carried out at lower temperature (273 K), which caused a slight downfield shift of the triplet corresponding to the H_r protons. The above-mentioned experiment unambiguously confirmed the presence of the postulated hydrogen bonds (Figure 4B). Finally, as expected, the ROESY experiment showed a correlation between proton *L* located on the porphyrin and those of the ethyleneglycol chain *q1*, *q3* and *q4*, indicating their spatial proximity. The different behaviour observed for compound **3** upon switching from CD_2Cl_2 to [D_6]DMSO, which is a much more polar solvent, is in agreement with the formation of intramolecular hydrogen bonds. Indeed, it is expected that CD_2Cl_2 would promote the formation of such an interaction, whereas [D_6]DMSO would disrupt it. It is also worth noting that similar hydrogen bonds between amide protons and pyridine groups have been previously reported by Leigh et al. for [2]rotaxane-type architectures.[30,31,38]

Structural investigations of 3 in the solid state: The presence of hydrogen bonds between the handle and the hinge was further confirmed in the crystalline phase by X-ray diffraction on a single crystal obtained upon vapour diffusion of pentane into a solution of **3** in CH_2Cl_2 (Figure 5).

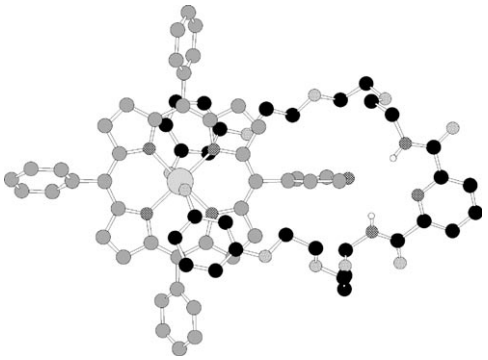


Figure 5. Solid-state structure of **3**. A fragment of the triethyleneglycol units was found to be disordered. Hydrogen atoms and solvent molecules are omitted for the sake of clarity. The C atoms of the stator (grey) and the handle (black) are shown in different colours for clarity. For bond lengths and angles, see Table 2.

Compound **3** crystallises in the triclinic system (space group $P\bar{1}$) with four dichloromethane molecules. One of the ethyleneglycol units was found to be disordered. The structural features (Table 2) are similar to those already reported for similar complexes[28] and other tin phenolate porphyrins.[38] The porphyrin plane is slightly distorted and the Sn atom is located almost at the centre of the four pyrrolic units. The Sn^{IV} cation is hexacoordinated and adopts an almost octahedral coordination geometry. Its coordination sphere is composed of four N atoms belonging to the porphyrin and two O atoms of the resorcinol groups occupying the two apical positions. The three phenyl groups are tilted with respect to the porphyrin plane (C-C-C-C dihedral angles: +57.1, +116.35 and +118.16°). The pyridine located on the fourth *meso* position of the porphyrin is also tilted (C-C-C-C dihedral angle: +101.59°).

Table 2. Selected bond lengths [Å] and angles [°] for **3**.

Sn–O	2.040(7), 2.059(6)
Sn–N	2.102(7), 2.103(7), 2.114(6), 2.117(6)
O-Sn-O	173.9(3)
N-Sn-O	86.5(3), 88.6(3), 87.0(3), 89.5(3), 91.4(3), 92.3(3), 92.5(3), 92.5(3)
N-Sn-N *trans*	178.6(3), 178.9(3)
N-Sn-N *cis*	89.3(3), 89.5(3), 90.1(3), 91.1(3)

Interestingly, hydrogen bonds between the pyridine unit of the stator and the amide protons are also present in the solid state (see Table 3 for bond lengths). Indeed, the N_{amide}–$N_{porphyrin}$ distance is about 3.12 Å. Following the classification proposed by Jeffrey,[39a,b] the hydrogen bonds observed may be considered as "moderate".

Table 3. X···A and H···A distances [Å] and the N–H···N angles [°] for **3** in the crystalline phase.

N_{amide}–$N_{porphyrin}$	3.053, 3.197
N_{amide}–N_{handle}	2.685, 2.690
H–$N_{porphyrin}$	2.264, 2.377
H–N_{handle}	2.291, 2.312
N_{amide}-H-$N_{porphyrin}$	149.29, 155.29

In the light of structural features observed for **3**, the absence of hydrogen bonding for compound **2** mentioned above, even in a rather apolar solvent such as CD_2Cl_2, is probably due to the length of the spacers connecting the tridentate unit to the resorcinol moieties ($(CH_2)_2O(CH_2)_2$).

In summary, the molecular turnstile **3** displays solvent-dependent behaviour. Whereas in [D_6]DMSO, which is a hydrogen-bond-disrupting solvent, the handle rotates freely around the stator (open state), in a relatively apolar solvent, such as CD_2Cl_2, owing to the formation of hydrogen bonds between the pyridyl moiety located on the stator and the amide protons belonging to the handle, the rotation of the latter is blocked (closed state).

Coordination of palladium(II) by precursors: Both compounds **2** and **3**, with a tridentate moiety on the handle, were designed to strongly bind square-planar metal centres such as Pd^{II}. As mentioned above, since for compound **2**, the handle was found to be too short to allow the formation of intramolecular hydrogen bonds, we thought that the same would apply to the binding of Pd^{II}, and thus, only the behaviour of compound **3** was explored. To investigate the structural features of **3**–Pd by ^{1}H NMR spectroscopy, reference complexes **11**–Pd, **12**–Pd, **17**–Pd and **18**–Pd (Scheme 2) were prepared. Their synthesis was based on reported procedures by Hirao et al.[40] and Leigh et al.[34a] for similar complexes.

At room temperature, the reaction of precursors **11**, **12**, **17** and **18** with a small excess of palladium acetate in acetonitrile afforded the desired complexes in 31 to 52% yield. Complexes with pyridine as the fourth ligand appeared to be more stable than those with acetonitrile.

While for the free ligands **11**, **12**, **17** and **18**, the triplet corresponding to the proton *t* located on the pyridine is systematically more shielded than protons *s* (doublet), the reverse situation, that is, an upfield shift of the doublet, is observed for the Pd complexes (Table 4 and Figure 6 for **18** and **18**–Pd). As expected, the three signals of the pyridine acting as the fourth ligand in complexes **12**–Pd, **17**–Pd and **18**–Pd are shifted downfield when compared with free pyridine.

Table 4. Selected ^{1}H NMR (300 MHz, 298 K) chemical shifts (δ) for compounds **11**, **12**, **17**, **18**, **11**–Pd, **12**–Pd, **17**–Pd and **18**–Pd.

	H_t [ppm]	H_s [ppm]
11[a]	8.07	8.24
11–Pd[a]	8.11	7.59
12[b]	8.01	8.28
12–Pd[b]	8.01	7.68
17[c]	8.15	8.20
17–Pd[c]	8.20	7.65
18[b]	7.99	8.27
18–Pd[b]	8.04	7.75

[a] Recorded in CD_3CN. [b] Recorded in CD_2Cl_2. [c] Recorded in [D_6]DMSO.

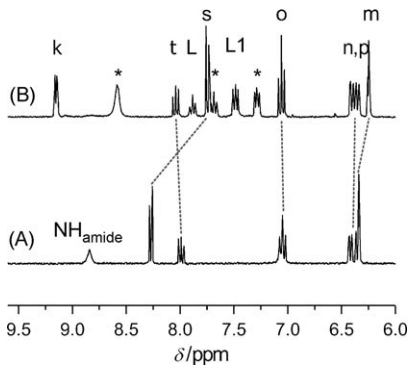


Figure 6. Portions of the ^{1}H NMR spectra (300 MHz, CD_2Cl_2, 298 K) and assignment of signals for compounds **18** (A) and **18–Pd** (B). For labelling of the protons, see Scheme 2. * indicates residual free pyridine.

Synthesis and solution behaviour of 3–Pd: It should be noted that the synthetic method followed for the preparation of reference Pd complexes mentioned above could not be used for the synthesis of **3**–Pd. Indeed, this procedure leads to the formation of acetic acid, which dissociates the handle through the replacement of the two resorcinate moieties by acetate anions.[27] To overcome this difficulty, two different strategies were developed for the synthesis of **3**–Pd. The first one (method A) was based on the complexation of the metal centre by the handle **18** prior to its condensation with tin porphyrin **21**. A further advantage of this strategy could be a template effect of the palladium(II) cation[29–31,41] previously employed for the synthesis of catenanes and rotaxanes.[42,43] Thus, at room temperature, the reaction of **21** with **18**–Pd for 4 days afforded the desired heterobimetallic porphyrin **3**–Pd in 90% yield. The second method (method B) was based on the direct condensation of compound **3** with $[Pd(CH_3CN)_4](PF_6)_2$. At room temperature, the condensation in the presence of triethylamine in a mixture of CH_2Cl_2 and CH_3CN for 3 h afforded **3**–Pd in 85% yield. Compound **3**–Pd was characterised both by ^{1}H NMR spectroscopy and mass spectrometry. Independent of the method used, the MALDI-TOF spectra showed, in addition to the molecular ion signal at 1449.3 for $[\mathbf{3}-Pd+H]^+$, two other signals at *m*/*z* 958.2 and 768.1 corresponding to an adduct formed with the matrix used (dithranol) and to the hydrolysed porphyrin **21**, respectively. A comparison of the ^{1}H NMR spectra of **3** and **3**–Pd clearly indicates the simultaneous coordination of palladium to the tridentate site on the handle and the monodentate site located at the *meso* position of the porphyrin. As mentioned above for **18**–Pd, protons *s* are shifted upfield by about 0.63 ppm (Figure 7), whereas proton *t* is barely affected ($\Delta\delta$ $\approx$0.01 ppm). Possibly, owing to the rigidification of the system induced by the coordination of Pd^{II}, signals corresponding to the oligoethyleneglycol chain (*q1*, *q2*, *q3*, *q4*, *q5* and *q6*) are broadened. No significant change is observed for signals corresponding to the β-pyrrolic protons (four doublets, the same as for **3** in CD_2Cl_2), indicating that compounds **3** and **3**–Pd display the same symmetry. As expected, protons *k* and *L*, belonging to the pyridine attached to the stator, experience deshielding upon coordination to Pd^{II}.

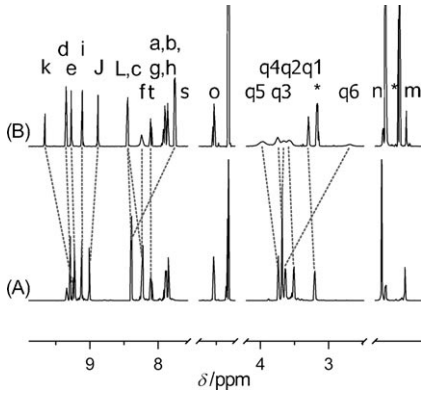


Figure 7. Portions of the ^{1}H NMR spectra (600 MHz, CD_2Cl_2, 298 K) for compound **3** (A) and its palladium complex **3**–Pd (B). For labelling of the protons, see Scheme 1. * indicates the triethylammonium salt.

Decoordination of palladium: As stated above, compound **3**–Pd corresponds to the closed state of the turnstile (Figure 1 f). To switch to the open state, two demetallation strategies have been explored. The first one aimed at generating the partially decoordinated state **3**–Pd–L (Scheme 1), corre-

sponding to the displacement of the pyridyl unit belonging to the stator. The second strategy was based on the complete removal of Pd^{II} and the generation of **3**. For the partial decoordination, *p*-dimethylaminopyridine (DMAP), which is a more strongly coordinating ligand than pyridine, was used.[32a,e,35,44] Unfortunately, even in large excess (10 equiv) and after six days, no decoordination of the palladium was observed, as evidenced by the absence of shift of the signal related to protons *k*. A possible reason might be steric hindrance preventing DMAP from accessing the Pd centre. To overcome this, CN^- anions, which are less sterically demanding and stronger ligands, were used. The decoordination process was monitored by ^{1}H NMR spectroscopy. Different amounts of Bu_4NCN were added to aliquots of a solution of **3**–Pd in CD_2Cl_2 at room temperature and ^{1}H NMR spectra were recorded at different times until an equilibrium state was reached (Figure 8).

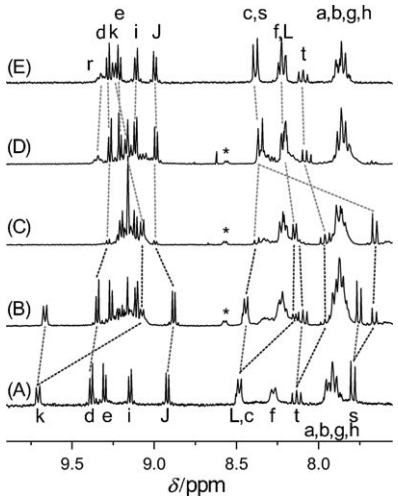


Figure 8. Portions of the ^{1}H NMR spectra (300 MHz, CD_2Cl_2, 298 K) and assignment of signals of **3**–Pd in the presence of 0 (A), 1 (B), 2 (C) and 10 equivalents (D) of Bu_4NCN and of complex **3** (E). For labelling of the protons, see Scheme 1. * indicates an impurity.

As expected, depending on the number of equivalents of cyanide anions added, the presence of different species in solution was observed. Upon the addition of one equivalent of CN^-, compounds **3**–Pd and **3**–Pd–CN coexist. Indeed, two sets of resonances for protons *k*, *L*, *s* and *t* corresponding to **3**–Pd ($\delta = 9.66$ (*k*), 8.44 (*L*), 8.10 (*t*), 7.75 ppm (*s*)) and to **3**–Pd–CN ($\delta = 9.07$ (*k*), 8.15 (*L*), 7.96 (*t*), 7.66 ppm (*s*)) were observed in a ratio of 2:1 (Figure 8B). With respect to the last set of resonances, the signals corresponding to the protons located on the tridentate site are shifted upfield. Furthermore, protons *s*—more shielded than proton *t*, which remains almost unaffected—are shifted upfield relative to **3**–Pd, indicating that Pd is still coordinated to the tridentate site and the fourth coordination site on the metal is occupied by the cyanide anion. Electrospray mass spectrometry in positive and negative modes performed on the NMR sample confirmed the presence of **3**–Pd (*m*/*z* 1449.3 $[M+H]^+$; 1690.6 $[M+TBA]^+$ TBA = tetrabutylammonium and **3**–Pd–CN (*m*/*z* 1474.26 $[M]^-$). However, compound **3**–Pd is the major component of the mixture. Upon the addition of two equivalents of cyanide anions, the pyridyl unit is displaced, thus leading to **3**–Pd–CN as the major species. Indeed, signals assigned to compound **3**–Pd disappear and the intensity of those corresponding to **3**–Pd–CN increase (Figure 8C). It is interesting to note that signals corresponding to the β-pyrrolic protons appear as a singlet and two doublets. This pattern is similar to that observed for compound **3** in [D_6]DMSO, indicating free rotation of the handle. The above-mentioned observations are further substantiated by mass spectrometry, which shows the presence of **3**–Pd–CN (*m*/*z* 1474.41 $[M]^-$) and the absence of a signal at *m*/*z* 1449.3 (in positive mode) corresponding to **3**–Pd. However, while **3**–Pd–CN is the dominant complex in solution, traces of the fully decoordinated species **3** are seen ($\delta = 9.29$ (*d*), 9.00 (*J*), 8.10 ppm (*t*)). Upon the addition of 10 equivalents of Bu_4NCN, complete demetallation of **3**–Pd to afford **3** occurs. Indeed, as expected, a triplet corresponding to proton *r* ($\delta = 9.35$ ppm) and a downfield shift of the signals corresponding to proton *s* are observed (Figure 8D). Moreover, β-pyrrolic protons appear as four doublets ($\delta =$ 9.28 (*d*), 9.22 (*c*), 9.12 (*i*), 9.00 ppm (*J*)). The small differences in chemical shifts observed between signals observed for pure compound **3** and **3**–Pd in the presence of 10 equivalents of Bu_4NCN are probably due to differences in ionic strength. Again, assumptions made on the basis of the ^{1}H NMR spectroscopic studies are confirmed by mass spectrometry, which reveals the presence of signals at *m*/*z* 1345.3 $[M+H]^+$ and 1586.6 $[M+TBA]^+$ corresponding to **3**.

In summary, compound **3**–Pd may be partially or completely demetallated upon addition of tetrabutylammonium cyanide. Although substitution of the monodentate pyridyl unit, leading to **3**–Pd–CN, by a cyanide ligand is feasible, the reaction is not quantitative because traces of **3**–Pd or **3** are also present.

Conclusion

Two new molecular turnstiles have been designed and prepared. The two systems, based on a porphyrin backbone with a pyridyl unit at one *meso* position (stator), connected through a Sn^{IV} atom complexed by the tetraaza core of the porphyrin (hinge) to a handle composed of two terminal resorcinol units connected to a 2,6-pyridinedicarboxamide tridentate coordinating site or its Pd^{II} complex by oligoethyleneglycol spacers (rotor), differ only by the length of the spacer. In an apolar solvent, such as CD_2Cl_2, owing to the presence of the tridentate unit on the handle and the pyridyl moiety on the stator acting as hydrogen-bond donor and acceptor sites, respectively, the formation of hydrogen bonds between the two units leads to the closed state of turnstile **3**. This may be opened (free rotation of the handle around the porphyrin) upon addition of a hydrogen-bond disrupting solvent, such as DMSO. The same compound **3**, upon treat-

ment with a Pd^{II} salt, leads to the formation of the neutral palladium complex **3**–Pd. The formation of the latter, resulting from the simultaneous binding of the cation by both the deprotonated tridentate unit and the pyridyl group, generates the closed state of the turnstile. Again, the system may be opened upon addition of CN^- anions as competitive ligands.

Work on analogous systems with several coordinating sites located at the *meso* positions of the porphyrin backbone is currently under progress.

Experimental Section

General: Compounds **5**, **7** and **9** were commercially available and used without further purification. Compounds **4**,[28] **6**, **8**, **10**, **12**, **14**, **16**, **18**,[35] and **19**–**21**[28] were synthesised according to published procedures. The syntheses of compounds **11**, **11**–Pd, **12**–Pd, **13**, **15**, **17**, **17**–Pd and **18**–Pd are described in the Supporting Information. CH_3CN and $CHCl_3$ were dried over molecular sieves; THF and CH_2Cl_2 were dried and distilled over sodium and CaH_2. Triethylamine was dried and distilled over KOH. Analytical EtOH and MeOH were used without further purification. ^1H and ^{13}C NMR spectra were recorded at 25 °C, unless stated otherwise, on either Bruker AV300 (300 MHz), Bruker AV400 (400 MHz), Bruker AV500 (500 MHz) or Bruker AV600 (600 MHz) spectrometers, with the deuterated solvent as the lock and residual solvent as the internal reference. Absorption spectra were recorded by using a Uvikon XL spectrophotometer. Melting points were measured by using a Stuart Scientific Melting Point SMP-1 apparatus without further correction. MALDI-TOF spectra were recorded on a Bruker autoflex II TOF TOF (equipped with a nitrogen laser and used in reflectron mode) instrument with dithranol (1,8,9-trihydroxyanthracene) as the matrix. A microTOF LC (Bruker Daltonics, Bremen) spectrometer equipped with an electrospray source was used for the electrospray mass spectrometry measurements.

X-ray crystal-structure analyses: Data were collected on a Bruker SMART CCD diffractometer with $Mo_{K\alpha}$ radiation. The structures were solved by using the SHELXS-97 program and refined by full-matrix least squares on F^2 using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were introduced at calculated positions and not refined (riding model). CCDC-803619 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 2: Compound **21** (70 mg, 0.091 mmol, 1 equiv) was added as a solid to a solution of **17** (51 mg, 0.097 mmol, 1.1 equiv) in CH_2Cl_2 (160 mL). The resulting solution was stirred at room temperature for 7 days. After removal of the solvent, the residue was recrystallised from CH_2Cl_2/pentane (7 mL/50 mL) to afford a deep red powder (80 mg, 70 %). ^1H NMR (500 MHz, CD_2Cl_2) (assignments according to COSY and ROESY 2D ^1H–^1H NMR experiments): $\delta = 1.17$ (t, $^3J(H,H) = 2.3$ Hz, 2H; H_m), 1.52 (ddd, $^3J(H,H) = 8.0$, $^4J(H,H) = 2.1$, $^4J(H,H) = 0.9$ Hz, 2H; H_n), 3.09–3.15 (m, 4H; H_{q1}), 3.46–3.51 (m, 4H; H_{q2}), 3.62–3.66 (m, 4H; H_{q3}), 3.67–3.73 (m, 4H; H_{q4}), 5.36 (ddd, $^3J(H,H) = 8.0$, $^4J(H,H) = 2.5$, $^4J(H,H) = 0.9$ Hz, 2H; H_p), 5.53 (t, $^3J(H,H) = 8.0$ Hz, 2H; H_o), 7.77–7.85 (m, 9H; H_a, H_b, H_g, H_h), 8.13–8.21 (m, 3H; H_L, H_r, H_t), 8.21–8.27 (m, 3H; H_c and H_f), 8.45 (d, $^3J(H,H) = 7.9$ Hz, 2H; H_s), 9.07 (dd, $^3J(H,H) = 4.2$, $^4J(H,H) = 1.6$ Hz, 2H; H_k), 9.10 (d, $^3J(H,H) = 4.7$ Hz, 2H; H_J), 9.17 (s, 4H; H_e, H_d), 9.18 ppm (d, $^3J(H,H) = 4.8$ Hz, 2H; H_l); ^{13}C NMR (125 MHz, CD_2Cl_2) (assignments according to HSQC and HMBC 2D ^1H–^{13}C NMR experiments): $\delta = 39.8$ (C_{q4}), 65.9 (C_{q1}), 69.6 (C_{q2}), 69.8 (C_{q3}), 102.8 (C_m), 103.7 (C_p), 110.2 (C_n), 125.2 (C_s), 126.6 (C_o), 127.0 (C_a, C_h), 128.6 (C_b, C_g), 129.8 (C_L), 131.7 (C_J), 132.8 (C_d, C_e), 139.1 (C_t), 140.3 (C_{c1}, C_{e3}), 146.2 (C_{J1}), 148.3 (C_{J3}), 148.7 (C_k), 155.6 (C_{m1}), 156.5 (C_{m2}), 163.4 ppm (C_{s2}) (labelling of the hydrogen and carbon atoms is given in the Supporting Information); UV/VIS (CH_2Cl_2): λ_{max} (ε) = 425 (330000), 561 (25000), 600 nm (14000 $mol^{-1}m^3cm^{-1}$); MALDI-TOF: *m*/*z* (%): 1257.29 (44) $[M-H]^+$, 958.13 (46) $[\mathbf{19}-Sn-C_{14}H_{10}O_3]^+$, 733.14 (10) $[\mathbf{19}-Sn]^+$.

Synthesis of 3: Under argon, a solution of **12** (35.3 mg, 0.057 mmol, 1.1 equiv) in dry $CHCl_3$ (40 mL) was added dropwise, by using a cannula, to a solution of **21** (40.1 mg, 0.052 mmol, 1 equiv) in dry $CHCl_3$ (30 mL). The resulting mixture was stirred at room temperature for 4 days. Evolution of the reaction was monitored by ^1H NMR spectroscopy. After removal of the solvent, the residue was recrystallised from toluene/pentane (12 mL/60 mL) to afford a deep red–purple powder (63.9 mg, 91 %). Single crystals suitable for X-ray analysis were obtained by slow diffusion of pentane into a solution of **3** in dichloromethane. ^1H NMR (400 MHz, CD_2Cl_2) (assignments according to COSY and ROESY 2D ^1H–^1H NMR experiments): $\delta = 1.26$ (t, $^4J(H,H) = 2.3$ Hz, 2H; H_m), 1.55 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 2.1$ Hz, 2H; H_n), 3.20 (t, $^3J(H,H) = 4.5$ Hz, 4H; H_{q1}), 3.51 (t, $^3J(H,H) = 4.6$ Hz, 4H; H_{q2}), 3.56 (m, 4H; H_{q6}), 3.67–3.71 (m, 12H; H_{q3}, H_{q4}, H_{q5}), 5.35 (dd, $^3J(H,H) = 7.9$, $^4J(H,H) = 2.4$ Hz, 2H; H_p), 5.54 (t, $^3J(H,H) = 8.0$ Hz, 2H; H_o), 7.83–7.92 (m, 9H; H_a, H_b, H_g, H_h), 8.09 (t, $^3J(H,H) = 7.8$ Hz, 1H; H_t), 8.22–8.25 (m, 6H; H_f, H_L), 8.37–8.41 (m, 4H; H_s, H_c), 9.00 (d, $^3J(H,H) = 4.7$, $^4J(Sn,H) = 16.7$ Hz, 2H; H_J), 9.13 (d, $^3J(H,H) = 4.7$, $^4J(Sn,H) = 16.7$ Hz, 2H; H_l), 9.16 (dd, $^3J(H,H) = 4.3$, $^4J(H,H) = 1.3$ Hz, 2H; H_k), 9.23 (m, 4H; H_e, H_w), 9.30 ppm (d, $^3J(H,H) = 4.8$, $^4J(Sn\text{-}H) = 17.3$ Hz, 2H; H_d); ^{13}C NMR (100 MHz, CD_2Cl_2): δ = (assignments according to HSQC and HMBC 2D ^1H–^{13}C NMR experiments): 40.0 (C_{q6}), 66.9 (C_{q1}), 69.9 (C_{q2}), 70.4 (C_{q5}), 70.9 (C_{q4}, C_{q3}), 103.4 (C_p), 103.8 (C_m), 110.8 (C_n), 118.6 (C_{j3}), 122.4 (C_{e2}), 122.8 (C_{c2}, C_{j2}), 125.1 (C_s), 127.1 (C_o), 127.4 (C_a, C_h), 128.9 (C_b, C_g), 130.1 (C_L), 132.0 (C_J), 133.3 (C_e), 133.4 (C_d, C_i), 135.1 (C_{c1}), 135.4 (C_f), 135.5 (C_c), 139.3 (C_t), 140.8 (C_{e3}), 146.5 (C_{j1}), 147.2 (C_{c3}), 147.5 (C_{i1}), 147.9 (C_{e1}), 149.4 (C_{s1}), 149.6 (C_k), 164.2 ppm (C_{s2}) (labelling of the hydrogen and carbon atoms is given in the Supporting Information); UV/VIS (CH_2Cl_2): λ_{max} (ε) = 427 (390000), 561 (15000), 600 nm (6000 $mol^{-1}m^3cm^{-1}$); MALDI-TOF: *m*/*z* (%): 1345.61 (33) $[M-H]^+$, 958.32 (53) $[\mathbf{19}-Sn-C_{14}H_{10}O_3]^+$, 733.24 (14) $[\mathbf{19}-Sn]^+$.

Crystal data for 3: $C_{78}H_{72}Cl_8N_8O_{10}Sn$; $M_r = 1683.73$; purple crystal; $0.05 \times 0.05 \times 0.02$ mm; triclinic; space group $P\bar{1}$; $a = 9.8866(5)$, $b = 14.8757(8)$, $c = 27.7531(14)$ Å; $\alpha = 90.905(3)$, $\beta = 95.079(3)$, $\gamma = 108.221(3)°$; $V = 3857.7(3)$ Å^3; $T = 173(2)$ K; $Z = 2$; $\rho_{calcd} = 1.450$ g cm^{-3}; $\mu = 0.672$ mm^{-1}; 28114 collected reflections, 15911 independent (R(int) = 0.0453), GooF = 1.167, $R1 = 0.1073$, $wR2 = 0.2685$ for $I > 2\sigma(I)$ and $R1 = 0.1458$, $wR2 = 0.2918$ for all data.

Synthesis of 3–Pd

Method A: Under argon, a solution of **18**–Pd (10.5 mg, 0.013 mmol, 1.1 equiv) in distilled CH_2Cl_2 (25 mL) was added dropwise, by using a cannula, to a solution of **21** (9.3 mg, 0.012 mmol, 1 equiv) in distilled CH_2Cl_2 (10 mL). The resulting solution was stirred at room temperature for 4 days. Evolution of the reaction was monitored by ^1H NMR spectroscopy. After removal of the solvent, a purple powder was obtained (16.0 mg, 90 %).

Method B: Et_3N (25 μL, 0.182 mmol, 25 equiv) was added to a solution of **3** (10 mg, 7.44×10^{-3} mmol, 1 equiv) in distilled CH_2Cl_2 (10 mL). A solution of $[Pd(CH_3CN)_4](PF_6)_2$ (4.2 mg, 7.44×10^{-3} mmol, 1 equiv) in dry CH_3CN (10 mL) was added dropwise to the mixture. The resulting mixture was stirred at room temperature for 3 h. No colour change was observed. The solvent was evaporated and the crude product was dissolved in CH_2Cl_2 (2 mL) and precipitated upon addition of pentane (10 mL). The violet powder was further recrystallised from CH_2Cl_2/pentane (3 mL/15 mL) to afford the desired compound **3**–Pd as a purple powder (9.2 mg, 85 %). ^1H NMR (500 MHz, CD_2Cl_2) (assignments according to COSY and ROESY 2D ^1H-^1H NMR experiments): $\delta = 1.15$ (t, $^4J(H,H) = 2.5$ Hz, 2H; H_m), 1.48 (dd, $^3J(H,H) = 7.7$, $^4J(H,H) = 1.7$ Hz, 2H; H_n), 2.66 (m, 4H; H_{q6}), 3.28 (m, 4H; H_{q1}), 3.61 (m, 4H; H_{q2}), 3.68 (m, 4H; H_{q3}), 3.76 (m, 4H; H_{q4}), 3.97 (m, 4H; H_{q5}), 5.31 (m, 2H; H_p), 5.53 (t, $^3J(H,H) = 8.0$ Hz, 2H; H_o), 7.68 (d, $^3J(H,H) = 7.5$ Hz, 2H; H_s), 7.80–7.89 (m, 9H; H_a, H_b, H_g, H_h), 8.02 (t, $^3J(H,H) = 7.7$ Hz, 1H; H_t), 8.24 (m, 4H; H_f), 8.40–8.43 (m, 4H; H_L, H_c), 8.89 (d, $^3J(H,H) = 5.0$, $^4J(Sn,H) = 17.0$ Hz, 2H; H_J), 9.12 (d, $^3J(H,H) = 4.5$, $^4J(Sn,H) = 16.5$ Hz, 2H; H_l), 9.28 (d, $^3J(H,H) = 4.5$, $^4J(Sn,H) = 17.5$ Hz, 2H; H_e), 9.32 (d, $^3J(H,H) = 5.0$, $^4J(Sn,H) = 17.0$ Hz, 2H; H_d), 9.65 ppm (dd, $^3J(H,H) = 5.0$, $^4J(H,H) =$

1.5 Hz, 2H; H_k); ^{13}C NMR (125 MHz, CD_2Cl_2) (assignments according to HSQC and HMBC 2D ^1H-^{13}C NMR experiments): $\delta = 47.3$ (C_{q6}), 66.5 (C_{q1}), 69.6 (C_{q4}), 70.0 (C_{q2}), 70.8 (C_{q3}), 70.9 (C_{q5}), 101.9 (C_p), 103.9 (C_m), 110.7 (C_n), 117.0 (C_{c2}), 123.9 (C_s), 126.4 (C_o), 127.1 (C_a, C_h), 127.5 (C_{e2}), 128.5 (C_b, C_g), 128.9 (C_{c1}), 130.9 (C_J), 131.2 (C_L), 132.9 (C_e), 133.3 (C_d), 133.4 (C_i), 133.6 (C_{J2}), 134.9 (C_f), 135.2 (C_c), 140.6 (C_t), 140.7 (C_{e3}), 146.4 (C_{J1}), 147.2 (C_{c3}), 147.3 (C_{i1}), 148.0 (C_{e1}), 151.9 (C_{J3}), 152.2 (C_k), 153.1 (C_{s1}), 156.0 (C_{m1}), 157.2 ppm (C_{m2}) (labelling of the hydrogen and carbon atoms is given in the Supporting Information); UV/VIS (CH_2Cl_2): λ_{max} (ε) = 426 (290000), 561 (19000), 601 nm (12000 $mol^{-1}m^3cm^{-1}$); MALDI-TOF: m/z (%): 1449.26 (38) $[M-H]^+$, 958.17 (40) $[\mathbf{19}-Sn-C_{14}H_{10}O_3]^+$, 768.08 (22) $[\mathbf{21}-H]^+$.

Addition of cyanide salts: Different amounts of solid Bu_4NCN (1, 2 or 10 equiv) were added to a solution of **3**–Pd (5 mg, 3.45×10^{-3} mmol, 1 equiv) in CD_2Cl_2 (0.6 mL). The resulting mixture was stirred for a few minutes at room temperature and transferred into an NMR tube. ^1H NMR spectra were recorded at different reaction times to ensure that the reaction was complete.

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