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Synthesis and molecular structure of chiral metallo-based sterically overcrowded alkenes

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Abstract—A four step synthesis of pyridyl-2-yl-thioxanthen-9-ylidene-isoquinolines is described. The corresponding palladium complexes are the first examples of a novel class of chiral, metallo-based, sterically overcrowded alkenes. The crystal and molecular structure of the palladium dichloride complex shows an anti-folded helical configuration with significant distortion of the central olefinic bond.

1. Introduction

The development of organic materials for optical data storage and molecular optical devices whose properties can be modulated by light has attracted considerable interest in recent years.[1] The efforts in our group were focused on the synthesis of helically shaped-sterically overcrowded alkenes. The intriguing thermochromic, photochromic and stereochemical properties associated with these chiral compounds have resulted in chiroptical molecular switches[2,3] and the first light-driven molecular motor.[4,5] The properties of molecules to be used in optical memory devices should meet three basic requirements: (a) thermal stability of both isomers, (b) a repeatable switching cycle without loss of activity, (c) ready detectability of both forms.

The photochemical process in chiroptical molecular switches, based on sterically overcrowded alkenes, pertains to the bistability of the *cis*- and *trans*-'pseudo-enantiomeric' forms[6] of such helical compounds. Stereospecific interconversion between 'pseudo-enantiomers' with M-helicity and P-helicity can be achieved by irradiation with light of different wavelengths. Selectivity in the switching process is accomplished by incorporation of electron donating and withdrawing substituents within the molecule.[3]

Essential for the thermal stability of both stereoisomers, and as a consequence the possibility to repeat the switching cycle, is the presence of a high racemization barrier. It was shown that a remarkable correlation exists between racemization barriers and both the aryl-X and aryl-Y bond lengths in symmetric[7] and non-symmetric inherently[5] dissymmetric alkenes (Fig. 1).[5,7]

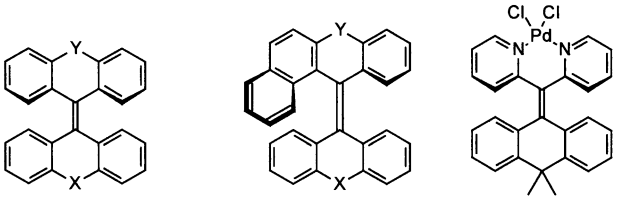

Figure 1. Structures of symmetrically and inherently dissymmetric overcrowded alkenes.

Recently we reported the first metallo-based overcrowded alkene[8] and it was shown that the isomerization barrier increased considerably when the aryl-Y covalent bond in **1** was replaced by a metal ion coordinated to two pyridine moieties as in complex **3**.

In order to combine the advantage of the larger racemization barrier expected for the metallo-based overcrowded alkenes and the possibility to tune the wavelength of the photoisomerization process and the selectivity in the chiroptical switches, a novel class of metallo-based molecular switches was envisioned. Towards this goal we report here the synthesis and structural analysis of a chiral-helical shaped-metallo-based overcrowded alkene.

2. Results and discussion

The palladium complexes **4** were chosen as the target structures (Fig. 2). Compared to structure **2** the upper

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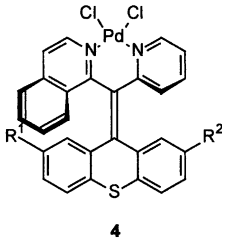

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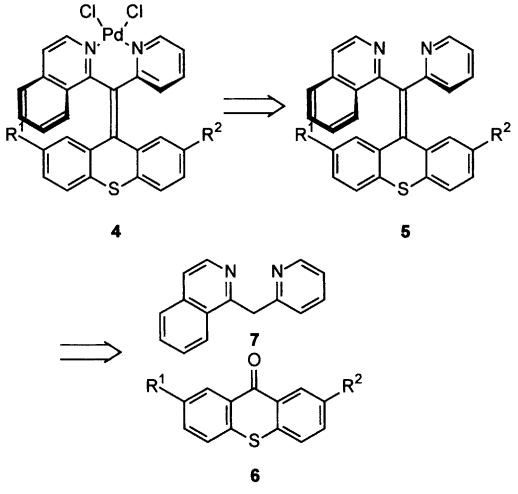
Figure 2. The chiral metallo-based overcrowded alkenes.

benzo[*a*]thioxanthene moiety is replaced by a pyridine and isoquinoline moiety, connected by a methylene group, and $PdCl_2$, the bridging Y group. The structural features of this system show that by incorporation of metal binding sites control can be achieved of the conformation and the dynamic processes by metal binding. It is anticipated that by adding a metal to the ligand, the otherwise free rotation of the ligating pyridine and isoquinoline moieties is constrained and the position of these moieties is locked. As a consequence, due to steric hindrance around the central olefinic bond, the whole complex is forced to adopt a helical architecture.

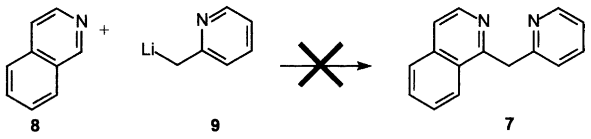
The key step in the synthesis of overcrowded alkenes is the formation of the central sterically hindered double bond connecting upper and lower halves. The retrosynthetic scheme below shows that the ligands **4**, necessary for the formation of Pd-complexes **4**, are to be obtained by coupling of a thioxanthene lower half and an upper half bearing the coordinating heterocycles (Scheme 1).



Scheme 1. Retrosynthetic scheme for **4** based on the *gem*-dichloride approach.

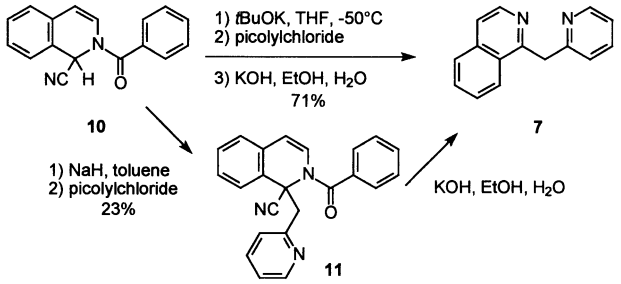
There are several methods for the synthesis of a sterically hindered olefinic bond: the McMurry coupling,[9] the Barton–Kellogg reaction,[10,11] Peterson olefination,[12] and *gem*-dichloride coupling.[13] When the first of these are to be employed, one would eventually need a ketone moiety at the position at which double bond is to be formed both in upper and lower halves leading to several coupling products. The latter two methods require a methylene and ketone moiety at these positions. Based upon our experience with the total synthesis of other overcrowded alkenes[14] the method of choice is a *gem*-dichloride coupling reaction which requires lower half thioxanthones **6** and for the upper half **7** (Scheme 1).

Initially the synthesis of **7** was attempted by addition of isoquinoline **8** to (2-pyridinylmethyl)lithium **9**. However, this coupling reaction gave **7** in very low yield (Scheme 2).



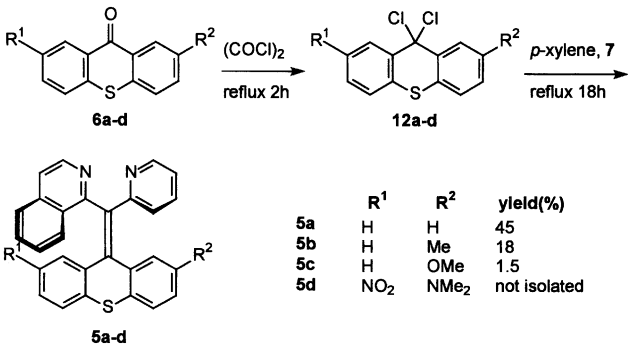
Scheme 2. Attempted synthesis of **7** by addition of (2-pyridinylmethyl)-lithium **9** to isoquinoline **8**.

More efficient was a four step approach using Reissert compound **10**.[15] Compound **10** could readily be prepared from isoquinoline, benzoylchloride and KCN. Initially, **10** was deprotonated using NaH in dry toluene, but the use of *t*BuOK in dry THF proved to be more efficient. The dark blue–purple solution of deprotonated **10** was treated with picolylchloride providing the Reissert compound **11** in moderate yield together with **7**. This prompted the development of a more efficient route in which **11** was not isolated, but immediately hydrolyzed under basic conditions giving **7** in good yield (Scheme 3).



Scheme 3. Synthesis of 1-(2-pyridinylmethyl)isoquinoline **7**.

The thioxanthenes, prepared by standard procedures,[3,16] were converted into the corresponding *gem*-dichlorides **12a–d** by treatment with pure oxalyl chloride. These highly moisture sensitive compounds were not isolated, but immediately used in the subsequent reaction with **7**. Refluxing the *gem*-dichlorides **12a–c** in *p*-xylene in the presence of **7** afforded target compounds **5a–c** (Scheme 4).



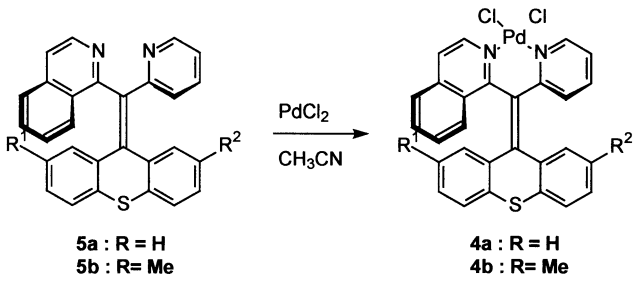
	R^1	R^2	yield(%)
5a	H	H	45
5b	H	Me	18
5c	H	OMe	1.5
5d	NO_2	NMe_2	not isolated

Scheme 4. Synthesis of ligands **5a–c**.

Whereas **5a** could be isolated in 45% yield, yields dropped considerably when a substituent was introduced in the thioxanthene. The alkene **5b** with a methyl substituent was obtained in 18% yield and the methoxy-substituted alkene **5c** was isolated in only 1.5% yield. ^{1}H NMR spectra of **5b** and **5c**, indicated the presence of both the *cis* and *trans* isomer as is evident from characteristic resonances of the methyl (1.84 and 2.04 ppm) and methoxy groups (3.33 and 3.45 ppm). Both geometrical isomers are obtained in a one to one ratio. Attempts to synthesize **5d** failed as only starting material could be isolated (Scheme 4).

Most probably this is due to steric hindrance, since for increasing substituent sizes in **5a–c** yields drop considerably. It has been reported[13c] that the addition of base results in increased yields in the *gem*-dichloride-coupling reactions. The same reaction, performed with **7** and **12a** in the presence of piperidine, however, did not provide product **5a**.

The palladium complexes **4a** and **4b** were obtained quantitatively by heating the ligand and $PdCl_2$ for 2.5 h at 50°C and subsequently at room temperature overnight in acetonitrile (Scheme 5).



Scheme 5. Synthesis of palladium complexes **4a** and **4b**.

Pure palladium complexes **4a** and **4b**, showing low solubility, were isolated as yellow/orange powders. Upon complexation of $PdCl_2$ to the ligands **5a** and **5b**, a shift of approximately 0.4 ppm downfield was observed in the ^{1}H NMR-spectrum for the pyridinic protons in the complexes **4a** and **4b**. Crystals of **4b** suitable for X-ray analysis (Fig. 3) could be obtained by slow diffusion of acetonitrile in a chloroform solution of this complex.

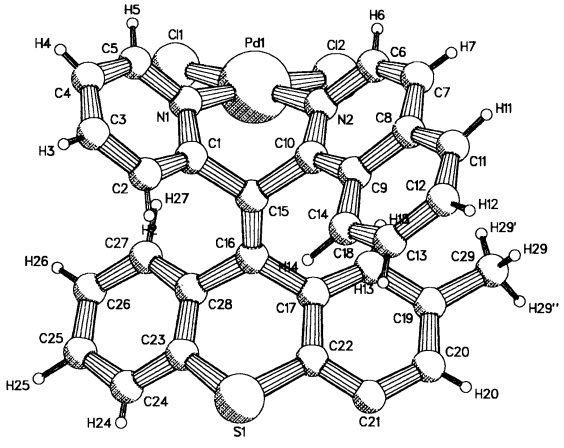


Figure 3. A Pluton representation of the structure of complex **4b**.

The X-ray structure clearly shows the non-planar, helical shaped structure with folded upper and lower parts of the molecule. The tri- and tetracyclic units on both sides of the central double bond are positioned in opposite directions (i.e. *anti*-folded). The central six-membered rings, embedding the palladium and sulfur atom in the upper and lower parts of the molecule, clearly have a boat conformation. This conformation is necessary to allow the aromatic rings to adopt an *anti*-folded configuration to diminish the steric strain around the central double bond caused by *peri*-hydrogen interactions between H_2 and H_{27} and H_{13}–H_{14} and H_{18}. The folded configuration is also evident from the torsion angles: C_9–C_{10}–C_{15}–C_1=113.6°; C_2–C_1–C_{15}–C_{10}=−115.7°; C_{17}–C_{16}–C_{28}–C_{27}=−135.8°; C_{28}–C_{16}–C_{17}–C_{18}=137.4°.

The bond length of the central double bond (C_{15}–C_{16}, 1.348 Å) in the Pd-complex is similar to values found for other chiral overcrowded alkenes.[3,7] However, the central double bond is, compared to those in other chiroptical molecular switches, considerably distorted: C_1–C_{15}–C_{16}–C_{28}=5.2°; C_1–C_{15}–C_{16}–C_{17}=−174.8°; C_{10}–C_{15}–C_{16}–C_{17}=7.4°; C_{10}–C_{15}–C_{16}–C_{28}=−172.6°.

The bond lengths to palladium for the square planar palladium complex (Pd–N 2.014/2.023 Å and Pd–Cl bonds 2.284/2.290 Å) can be considered normal and show no strong deviation from values reported in literature for other bipyridine complexes[17] and the previously reported metallo-based sterically overcrowded alkene.[8]

Both **4a** and **4b** are chiral compounds. The groups around the central double bond are forced by steric interactions into non-planar, helical orientation. The chirality in these inherently dissymmetric alkenes therefore originates from this helical shape of the molecule and is controlled by the metal-coordination in the upper part which 'locks' the pyridine and isoquinoline moieties.

3. Conclusion

In conclusion, the first chiral metallo-based sterically overcrowded alkenes have successfully been synthesized. The new methylene-bridged isoquinoline–pyridine moiety is introduced as a bidentate metal binding site. The X-ray analysis of the palladium complexe **4b** clearly show the helical shape. The resolution of these new chiral overcrowded alkenes and photochemical behavior are subject to current investigation.

4. Experimental

4.1. General

^{1}H NMR data were recorded on a Varian VXR 300 or a Varian Unity 500 (at 300, or 500 MHz, respectively). ^{13}C NMR data were recorded on a Varian VXR 300 or a Varian Unity 500 (at 75.48 or 125.80 MHz, respectively). The chemical shifts are denoted in (units ppm) with the solvent as an internal standard and converted to the TMS scale. High Resolution Mass Spectra (HRMS) were recorded on

a AEI MS-902 mass spectrometer by electron impact (EI) and were performed by Mr A. Kiewiet. Elemental analyses were performed in the microanalytical department of our laboratory by Mr H. Draayer, Mr J. Ebels and Mr J. Hommes. Melting points were taken on a Mettler FP-2 melting point apparatus, equipped with a Mettler FP-21 microscope and are uncorrected. All chemicals were obtained from Acros, Aldrich, or Merck. Solvents were dried using standard procedures.

4.1.1. 2-Benzoyl-1-pyridin-2-ylmethyl-1,2-dihydro-isoquinoline-1-carbonitrile (11). To a refluxing solution of **10** (2.08 g, 8.0 mmol) in dry toluene (30 ml) under a nitrogen atmosphere was added NaH (0.72 g, 15.0 mmol, 50% dispersion in oil). The reaction mixture immediately turned deep red. After refluxing for 3 min, picolylchloride (0.96 g, 7.5 mmol) in dry toluene (10 ml) was added whereupon the reaction mixture was refluxed for 2 h. The reaction mixture was then cooled to room temperature and a solution of saturated NH_4Cl (50 ml) was added. The reaction mixture was extracted with CH_2Cl_2 (2×50 ml), dried on Na_2SO_4, filtered and the organic layers were evaporated under reduced pressure giving a brown oil. This oil was purified using column chromatography (SiO_2, hexane/EtOAc/Et_3N=9:3:1, R_f=0.23) yielding the product as white crystals which precipitated from the eluent (0.64 g, 1.8 mmol, 23%, decomposition when $T>140$°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.61 (d, J=12.5 Hz, 1H), 3.88 (d, J=12.5 Hz, 1H), 5.50 (d, J=7.7 Hz, 1H), 6.33 (d, J=8.1 Hz, 1H), 7.0–7.6 (m, 12H), 8.35 (d, J=4.8 Hz, 1H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 45.8, 60.4, 106.4, 117.7, 122.3, 124.9, 125.3, 126.5, 126.7, 127.9, 128.0, 128.5, 129.1, 129.4, 131.6, 133.3, 135.9, 149.1, 153.8, 169.4; m/z (EI, %)=351 (M^+, 0.5), 260 (3), 259 (13), 246 (2), 220 (7), 219 (19), 218 (4), 198 (2), 197 (10), 196 (1), 169 (3), 168 (5), 154 (2), 131 (2), 106 (8), 105 (100), 92 (3), 78 (3), 77 (28), 76 (2), 65 (3), 51 (5); m/z (CI, %)=354 (5), 353 (26), 352 ($M+H^+$, 100), 326 (6), 325 (25), 222 (11), 221 (62), 139 (8), 122 (2), 105 (6); Anal. Calcd: C, 78.60; H, 4.80; N, 12.00%; Found: C, 79.19; H, 4.86; N, 12.03%.

4.1.2. 1-(2-Pyridinylmethyl)isoquinoline (7). Under a nitrogen atmosphere **11** (1.65 g, 6.3 mmol) was dissolved in dry THF (30 ml) and then cooled to −50°C. At −50°C the Reissert compound **10**[15] was deprotonated by dropwise addition of a solution of KO*t*Bu (0.52 g, 7.0 mmol) in dry THF (30 ml). Already when the first drop was added the mixture turned deep purple. After adding all of the KO*t*Bu, the reaction mixture was stirred for 1 h at −40°C. Upon addition of picolylchloride (0.89 g, 7.0 mmol) the reaction mixture slightly decolorized. After stirring for 1 h at −30°C, the reaction mixture was allowed to reach room temperature. The reaction mixture was then stirred for an additional 2 h whereupon a solution of 2 M KOH in H_2O/EtOH (30 ml) was added. The now red/orange solution was stirred overnight. The reaction mixture was acidified with 2 M HCl solution (100 ml), diluted with CH_2Cl_2 (100 ml) and extracted with 2 M HCl (2×100 ml). The combined acidic layers were neutralized with $NaHCO_3$ and then extracted with CH_2Cl_2 (3×100 ml). The organic layers were dried on Na_2SO_4, filtered and the solvent removed under reduced pressure resulting in a yellow brownish oil. This oil was purified using column chromatography (SiO_2, hexane/EtOAc/Et_3N=10:3:1, R_f=0.35) giving **7** as a yellow oil (0.99 g, 4.5 mmol, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (s, 2H), 7.05 (m, 1H), 7.15 (d, J=8.1 Hz, 1H), 7.4–7.6 (m, 4H), 7.77 (d, J=8.1 Hz, 1H), 8.27 (d, J=8.4 Hz, 1H), 8.47 (d, J=5.9 Hz, 1H), 8.53 (d, J=4.0 Hz, 1H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 44.0 (t), 118.8 (d), 120.2 (d), 122.2 (d), 125.0 (d), 126.0 (d), 126.2 (d), 126.2 (s), 128.8 (d), 135.2 (d), 135.2 (s), 140.9 (d), 148.0 (d), 158.0 (s), 158.2 (s); m/z(EI, %)=221 (6), 220 (M^+, 41), 219 (100), 218 (19), 217 (4), 191 (3), 115 (3), 110 (5), 109.5 (9), 109 (4), 95.5 (3), 51 (3); HRMS: calcd for $C_{15}H_{12}N_2$: 220.10004, found 220.09898.

4.1.3. 1-(Pyridyl-2-yl-thioxanthen-9-ylidene-methyl)-isoquinoline (5a). In a magnetically stirred flask under a nitrogen atmosphere **6a** (2.58 g, 12 mmol) was dissolved in oxalyl chloride (50 ml). This mixture was refluxed for 3 h which resulted in a yellow solution. The oxalyl chloride was removed under reduced pressure with an oil pump using three liquid nitrogen traps. When the oxalyl chloride was removed beige solid was obtained, which turned pink after 2.5 h in vacuo. Dry *p*-xylene (30 ml) was added giving a pink solution, to which was added a solution of **7** (2.68 g, 12 mmol) in dry *p*-xylene (20 ml) giving a dark green mixture. This mixture was then refluxed overnight (18 h). The reaction mixture had turned overnight orange/red and a solid had precipitated. After cooling to room temperature the reaction mixture was diluted with CH_2Cl_2 (200 ml) and extracted with 6 M HCl solution (3×200 ml). The red acid layers were washed with CH_2Cl_2 (2×100 ml) and then neutralized with $NaHCO_3$. Upon addition of the $NaHCO_3$ a yellow/red suspension was obtained. This suspension was extracted with CH_2Cl_2 (3×250 ml). The combined organic layers were dried on Na_2SO_4 and the solvent removed under reduced pressure giving a red oil. The compound was purified by column chromotography (neutral Al_2O_3 activity V, CH_2Cl_2, R_f=0.43). After evaporation of the CH_2Cl_2, **5a** is obtained as a white foam (2.26 g, 0.68 mmol, 45%, mp 191.5–192.0°C). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.64–6.69 (dt, J=7.7, 1.1 Hz, 1H), 6.85–6.90 (dt, J=7.5, 1.1 Hz, 1H), 6.94–7.00 (dt, J=7.5, 1.1 Hz, 1H), 7.02–7.51 (m, 10H), 7.55–7.57 (d, J=6.2 Hz, 2H), 7.68–7.66 (d, J=8.1 Hz, 1H), 8.57–8.59 (td, J=5.1, 1.3 Hz, 1H), 8.75–8.77 (d, J=5.1 Hz, 1H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 119.7 (d), 121.4 (d), 124.9 (d), 125.2 (d), 125.6 (d), 125.9 (d), 126.26 (d), 126.34 (d), 126.4 (d), 126.6 (d), 126.9 (d), 128.2 (d), 129.4 (d), 129.5 (d), 133.3 (s), 134.0 (s), 135.2 (s), 135.4 (d), 135.6 (s), 136.0 (s), 138.4 (s), 141.6 (d), 149.1 (d), 157.7 (s),158.9 (s); m/z (EI, %)=417 (2), 416 (9), 415 (30), 414 (M^+, 97), 413 (100), 412 (6), 411 (7), 410 (3), 382 (3), 381 (7), 380 (4), 379 (7), 338 (3), 337 (8), 336 (27), 308 (3), 304 (4), 287 (5), 286 (20), 207.5 (4), 207 (12), 206.5 (3), 206 (9), 205 (6), 197 (3), 190 (5), 189 (4), 149 (3), 44 (4); HRMS: calcd for $C_{28}H_{18}N_2S$: 414.11906, found 414.11856; Anal. Calcd: C, 81.13; H, 4.38; N, 6.76%; Found: C, 80.71; H, 4.46; N, 6.83%.

4.1.4. 1-[(2-Methyl-thioxanthen-9-ylidene)-pyridin-2-yl]-isoquinoline (5b). This compound was prepared using the procedure for the synthesis of 1-(pyridyl-2-yl-thioxanthen-9-ylidene-methyl)-isoquinoline **5a**. Starting from **6b** (0.41 g, 1.8 mmol) and **7** (0.36 g, 1.6 mmol), the product was obtained after column chromatography (neutral Al_2O_3

activity V, CH_2Cl_2, R_f=0.45) as a white foam (0.12 g, 0.28 mmol, 18%, mp 99.3–99.7°C). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84 (s, 3H), 2.04 (s, 3H), 6.59–6.69 (m, 2H), 6.81–6.86 (t, J=7.7 Hz, 1H), 6.90–7.54 (m, 33 H), 7.64–7.66 (d, J=8.1 Hz, 2H), 8.18 (br. s, 2H), 8.54–8.58 (m, 2H), 8.72 (m, 2H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 20.4, 20.7, 119.77, 119.84, 121.50, 121.60, 125.11, 125.22, 125.66, 125.74, 126.13, 126.42, 126.47, 126.52, 126.69, 127.06, 127.44, 127.67, 128.32, 129.29, 129.55, 129.71, 129.74, 130.05, 130.39, 130.71, 133.77, 134.48, 135.08, 135.22, 135.42, 135.57, 135.63, 135.80, 136.17, 136.20, 138.79, 141.49, 141.78, 149.10, 149.24, 157.88, 158.06, 159.10, 159.31; *m/z* (EI, %)=431 (2), 430 (9), 429 (33), 428 (M^+, 100), 427 (82), 413 (3), 411 (2), 397 (2), 396 (4), 395 (6), 394 (3), 393 (4), 379 (2), 352 (4), 351 (11), 350 (36), 349 (2), 348 (3), 334 (2), 322 (2), 318 (2), 302 (3), 301 (7), 300 (29), 299 (3), 298 (3), 282 (3), 215 (2), 214.5 (6), 214 (19), 213.5 (3.6), 213 (9), 212 (2), 211 (5), 210 (2), 206.5 (2), 206 (5), 205.5 (3), 205 (6), 198.5 (2), 198 (2), 197.5 (2), 197 (2), 196 (2), 190 (4), 189 (4); HRMS: calcd for $C_{29}H_{20}N_2S$: 428.13471, found 428.13331; Anal. Calcd: C, 81.28; H, 4.70; N, 6.54%; Found: C, 80.56; H, 4.83; N, 6.46%.

4.1.5. 1-[(2-Methoxy-thioxanthen-9-ylidene)-pyridin-2-yl-methyl]-isoquinoline (5c). This compound was prepared using the procedure for the synthesis of **5a**. Starting from **6c** (0.75 g, 3.1 mmol) and **7** (0.68 g, 3.1 mmol), **5c** is obtained after column chromatography (neutral Al_2O_3 activity V, CH_2Cl_2, R_f=0.43) as a white foam (20 mg, 0.045 mmol, 1.5%, mp 88.2–89.0°C). ^{1}H NMR ($CDCl_3$, 125.80 MHz) δ 3.33 (bs, 3H), 3.45 (s, 3H), 6.47–6.49 (dd, J=8.4, 2.6 Hz, 1H), 6.62–6.65 (dt, J=7.4, 1.2 Hz, 1H), 6.74–7.72 (m, 26H), 8.17 (bs, 2H), 8.59–8.60 (d, J=4.8 Hz, 1H), 8.65–8.66 (dd, J=3.3, 1.1 Hz, 1H), 8.75 (s, 2H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 54.4, 54.6, 111.7, 113.0, 114.7, 119.3, 119.4, 121.1, 122.2, 121.7, 124.0, 124.4, 124.7, 125.1, 125.6, 125.9, 126.0, 126.1, 126.2, 126.2, 126.5, 126.6, 126.7, 126.8, 126.9, 127.0, 127.8, 129.0, 129.1, 129.4, 133.5, 134.3, 134.6, 133.9, 135.1, 135.3, 135.6, 135.7, 136.0, 136.3, 138.3, 138.4, 141.1, 141.2, 141.2, 148.8, 157.0, 157.2, 157.5, 158.3, 158.7; *m/z* (EI, %)=445 (33), 444 (100, M^+) 443 (56), 429 (10), 401 (5), 400 (6), 368 (5), 367 (13), 366 (38), 351 (5), 323 (6), 317 (6), 316 (26), 222 (17), 206 (5), 200 (7), 199 (6).

4.1.6. Dichloro[1-(pyridyl-2-yl-thioxanthen-9-ylidene-methyl)-isoquinoline] palladium (4a). Ligand **5a** (150 mg, 0.36 mmol) and an equimolar amount of $PdCl_2$ (64 mg, 0.36 mmol) were stirred for 2.5 h at 50°C in CH_3CN (15 ml) and then overnight at room temperature. The orange suspension becomes bright yellow after 30 min at 50°C. After removal of the solvent the palladium complex **4a** was obtained quantitatively as a yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66–6.69 (t, J=7.7 Hz, 1H), 6.95–7.11 (m, 4H), 7.29–7.38 (m, 4H), 7.44–7.46 (d, J=7.7 Hz, 1H), 7.57–7.69 (m, 4H), 7.74–7.76 (d, J=8.1 Hz, 1H), 7.80–7.83 (d, J=8.4 Hz, 1H), 9.02–9.04 (d, J=6.2 Hz, 1H), 9.13–9.15 (d, J=5.9 Hz, 1H); *m/z* (DEI, %)=594 (2.1), 592 (M^+, 3.0), 591 (1.6), 590 (2.3), 589 (1.5), 555 (1.2), 554 (0.8), 521 (0.8), 416 (8), 415 (32), 414 (100), 413 (100), 412 (8), 411 (11), 381 (7), 379 (8), 336 (32); *m/z* (DCI, %)=614 (0.7), 612 (2.0), 610 ($M+NH_4^+$, 3), 608 (2.4), 417 (10), 416 (32), 415 (100); Anal. Calcd: C, 56.82; H, 3.07; N, 4.73; Pd, 17.98%; Found: C, 56.08; H, 3.10; N, 4.76; Pd 17.75%.

4.1.7. Dichloro[1-[(2-methyl-thioxanthen-9-ylidene)-pyridin-2-yl]-isoquinoline] palladium (4b). Ligand **5b** (72.6 mg, 0.17 mmol) and an equimolor amount of $PdCl_2$ (25 mg, 0.17 mmol) were stirred for 2.5 h at 50°C in CH_3CN (15 ml) and then overnight at room temperature. The orange suspension becomes bright yellow after 30 min at 50°C. After removal of the solvent the palladium complex **5b** was obtained quantitatively as a yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77 (s, 3H), 2.08 (s, 3H), 6.63–6.66 (t, J=7.7 Hz, 1H), 6.75–6.78 (d, J=7.7 Hz, 1H), 6.87 (s, 1H), 6.93–7.79 (m, 35H), 7.83–7.86 (d, J=8.4 Hz, 2H), 9.00–9.02 (d, J=2.3 Hz, 1H), 9.03–9.04 (d, J=2.9 Hz, 1H), 9.14–9.15 (m, 2H); *m/z* (DEI, %)=610 (0.1), 608 (0.2), 606 (0.3), 604 (M^+, 0.2), 429 (32), 428 (100), 427 (88), 425 (5), 351 (35), 300 (27), 214 (16); *m/z* (DCI, %)=628 (2), 626 (6), 624 (9), 622 ($M+NH_4^+$, 8), 431 (10), 430 (34), 429 (100); Anal. Calcd: C, 57.49; H, 3.33; N, 4.62; Pd, 17.56%; Found: C, 56.22; H, 3.26; N, 4.54; Pd 17.31%.

4.2. Crystal structure determination (4b)

Crystals suitable for X-ray diffraction were grown by slow diffusion of acetonitrile in a chloroform solution containing the palladium complex **4b**. $C_{29}H_{20}Cl_2N_2PdS$, bright orange/yellow block-shaped crystal (0.08×0.15×0.45), triclinic, space group P-1, a=9.293(1) Å, b=11.124(1) Å, c=13.205(1) Å, α=101.043(7)°, β=92.150(9)°, γ=105.467(7)°, V=1285.6(2) Å^3, Z=2, d_x=1.565 g cm^{-3}. X-Ray data were collected on an ENRAF–NONIUS CAD4T [Mo Kα, Graphite monochromated, λ=0.71073 Å, Θ_{max}=20.33; ω-scan, T=150 K]. The structure was solved using Paterson methods (DIRDIF) nd refined on F^2 (SHELXL-93). Hydrogen atoms were taken into account at calculated positions. Final R value 0.0357 (4830 reflections). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 170549. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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