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Trans-spanning acetylenic bispyridine ligands: synthesis and structural characterization of novel organic and organometallic pseudodehydroannulenes

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Abstract

The synthesis of a novel ferrocene based pincer ligand C_5H_5-Fe[C_5H_3(-≡-C_5H_4N)$_2$] is reported. This pincer ligand was prepared by the Pd-catalyzed reaction of 1,2-diethynylferrocene with 2-iodopyridine. The complex is a *trans*-spanning ligand and analogous to 1,2-bis(2-pyridinylethynyl)-4,5-dimethoxybenzene. A series of *trans*-coordinated 1:1 or 2:1 complexes (empirical formulae $C_{51}H_{37}ClCuF_3N_4O_7S$ and $C_{23}H_{18}Cl_4N_2O_2Pd$) that form from the ligands and $(CH_3CN)_2PdCl_2$ or $Cu(OTf)_2$ were obtained. These complexes form 13-membered rings. Structurally these complexes resemble a hexadehydro[14]annulene in which two benzene groups are replaced by pyridine rings and one alkyne group is replaced by the co-ordinated metal. All of the *trans*-spanning complexes were characterized by single crystal X-ray diffraction. Their molecular and solid-state structures are discussed. The Pd-complexes are of interest as potential high activity catalysts for Sonogashira-type couplings of alkynes to aryl halides. The 1,2-(bis-2′-pyridylethyn-1′-yl)ferrocene, was crystallized with $PdCl_2$ to obtain a novel organometallic *trans*-spanning complex of the formula $C_{24}H_{16}Cl_2FeN_2Pd$ that was crystallographically characterized.

Keywords: Alkynes; Heterocycles; Metallacycles; *N*-Pincer ligands; Self-assembly; Iron; Copper; $C_{51}H_{37}ClCuF_3N_4O_7S$

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1. Introduction

Here we report the complexation of **1a** with $Cu(OTf)_2$ and $(CH_3CN)_2PdCl_2$ and the synthesis and complexation of the novel pincer ligand **6** with $(CH_3CN)_2PdCl_2$ into the complex **7** (Schemes 1,2)

Supramolecular chemistry has evolved rapidly during the last 20 years. A fascinating subfield of supramolecular chemistry is the metal-assisted synthesis of platonic solids, regular or truncated polyhedra, which form by self-assembly processes. Stang, Atwood, and Zaworotko have made great strides in the generation of a host of these beautiful topologies by clever metal–ligand combinations [1–3].

We have an interest in the metal-assisted supramolecular assembly of conjugated organic ligands toward novel photonic, electroactive, and structural materials [4]. Particularly, exciting is the complexation chemistry of the ligand **1**. We demonstrated that the bispyridine **1a** is capable of forming a variety of different supramolecular assemblies that range from cyclic ‘metallodehydroannulenes’ or ‘pseudodehdroannulenes’ to a species that is a self-assembled version of the hitherto unknown poly(*ortho*-phenyleneethynylene) [4a]. Ueda [5,6], Bosch [7] and Thummel [8] have reported similar coordination compounds of the pincer ligand **1b.** Ueda prepared the Pd-complex **8** [6] that is an active catalyst in the Heck [9] reaction, increasing the interest in these structurally unique *trans*-spanning 10 ligands. As an additional twist, these *trans*-spanning ligands represent enediynes that could participate in a Bergman type rearrangement [11]. Zaleski [12], Buchwald [13] and König [14] have independently shown that Bergman reactions are trig-

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gered in specific enediyne systems by metal complexation. The critical parameter for the reactivity of endiyne systems is the distance between the termini of the two acetylene units (depicted by an arrow in structure **9**). In free enediynes this distance is 3.9–4.1 Å, and such materials are stable up to ca. 150–200 °C depending upon their substituent pattern. When this distance decreases below 3.5 Å, enediynes show dramatically increased Bergman activity at ambient temperature. It was of interest if metal coordination to **1a** and **6** could pull the alkyne termini together to modulate the reactivity of these enediynes.

2. Results and discussion

The conjugated ligand **1a** was synthesized according to Ref. [4a]. In the first experiment a solution of copper(II)triflate in methanol was layered over a solution of **1a** in dichloromethane. After several days, well-developed blue-green needles were harvested by filtration (30%). These needles are very sensitive to solvent loss when removed from the mother liquor. Attempts to obtain an ^{1}H-NMR spectrum of this compound was unsuccessful due to the paramagnetic nature of this d^{9} Cu(II) complex. The harvested specimens were of good quality and a single crystal X-ray structure determination of **2a** was possible.

Fig. 1 shows the molecular structure of **2a** and its packing in the solid state. Remarkable is the intramolecular shortening of the alkyne–alkyne distance upon co-ordination of the Cu^{2+} salt. This distance (arrow) decreases from 4.25 Å in the uncomplexed *cis*-form of **1a** (as calculated by 6-31G**) to 3.98 Å in the enediyne system of **2a**. The decrease in this distance is due to the decrease of the N–N-distance from the free ligand (model **1b,** 4.80 Å, 6-31G**) to 4.01 Å upon complexation into **2a**. While this shortening appears to be dramatic, the free ligand **1** may not be the best comparison because of the repulsive effect that the two pyridine nitrogen atoms exert on each other in the coplanar *cis*-form, which is only a local minimum. Upon complexation the electronic repulsion is removed and the structure of **2** and **3** should probably be compared to the (undisturbed) geometry of the dehydro[12]annulene **9**. Inspection of quantum chemical calculations of **8** (6-31G**) shows that it is indeed isostructural to **2** and **3**.

The octahedral molecules of **2a** arrange in a linear chain in the solid state. This chain is formed by the π–π stacking of dimethoxybenzene rings on top of each other. In this packing pattern the electron-rich methoxy groups of one ring are placed over the electron-deficient carbon atoms (C30A and C35A; Fig. 1) of a second dimethoxybenzene unit. The tight interaction (3.48 Å, dotted line) of these benzene rings is probably due to an electrostatic/charge effect.

After the successful determination of the structure of **2a**, the structure of the Pd-complex **3a** and their similarities was of interest. We obtained **1a**·$PdCl_2$, i.e. **3a**, by layering a solution of $(CH_3CN)_2PdCl_2$ in acetonitrile over a solution of **1a** in dichloromethane. Overnight block-shaped crystals formed in a 65% yield at the interface of the two solvents. Attempts to grow crystals of **3a** by mixing of **1a** and $(CH_3CN)_2PdCl_2$ in a suitable solvent did not work. Fig. 2 shows the ^{1}H-NMR spectra of the ligand **1a** (bottom) and that of the complex **3a** (top). The downfield shift of the signals of the pyridine ligand upon complexation is considerable and is due to the electron withdrawing effect of the $PdCl_2$ moiety. It is clear from the simple and clean spectrum that the crystallization experiment produces only one compound under these conditions. The isolated specimens were of good quality, and a single crystal structure analysis of **3a** was undertaken. The ORTEP of **3a** is displayed in Fig. 3. The overall topology and structure of the ligand **1a** in the structures of **2a** and **3a** is similar. The reason for the geometric similarity of the two complexes is the almost identical bond length of the Cu–N and Pd–N bonding distances that force the ligand into the observed pseudodehydroannulene geometry. The structure of **3a** is in excellent agreement with both of our recent structure of $Cu(OAc)_2$·**1a** [4a] and Bosch's analogous Pd-complex of **1b** [7].

While the structural features of the ligand **1a** were intriguing, a systematic change in ligand geometry would be desirable; of particular interest was the dependence of the *N*,*N*-, i.e. the *trans*-spanning distance upon the complexation behavior. If instead of a six membered ring a five membered ring could be utilized as scaffold for the 2-ethynylpyridines, the distance of the two pyridine nitrogen atoms would increase from (ideally) 4.01 Å to 5.06 Å in the projected ligand **6** according to a PM3 calculation Scheme 1.

The Pd-catalyzed reaction of **4** with **5** furnishes the ligand **6** (Scheme 2) in 70% yield after chromatography. A solution of the ligand **6** in dichloromethane was placed in a test tube; a solution of $(CH_3CN)_2PdCl_2$ in acetonitrile was layered above it. After several days red crystals formed at the interface in 45% yield. Only one type of coordination complex forms according to NMR spectroscopy of the harvested crystals. The ^{1}H-NMR spectra of **6** and its complex **7** are displayed in Fig. 4. As in the case of **3a**, a significant downfield shift of the ring protons of the coordinating pyridine units (in **7**) results. The spectra in the two series (**3a**,**7**) are almost superimposable, as would be expected for these similar complexes. The most interesting part of the proton NMR of **6** and **7** however, is its unique ferrocene region. All of the ferrocene signals in **7** (Fig. 4b) are downfield shifted by approximately 0.1–0.2 ppm. The proton H_b

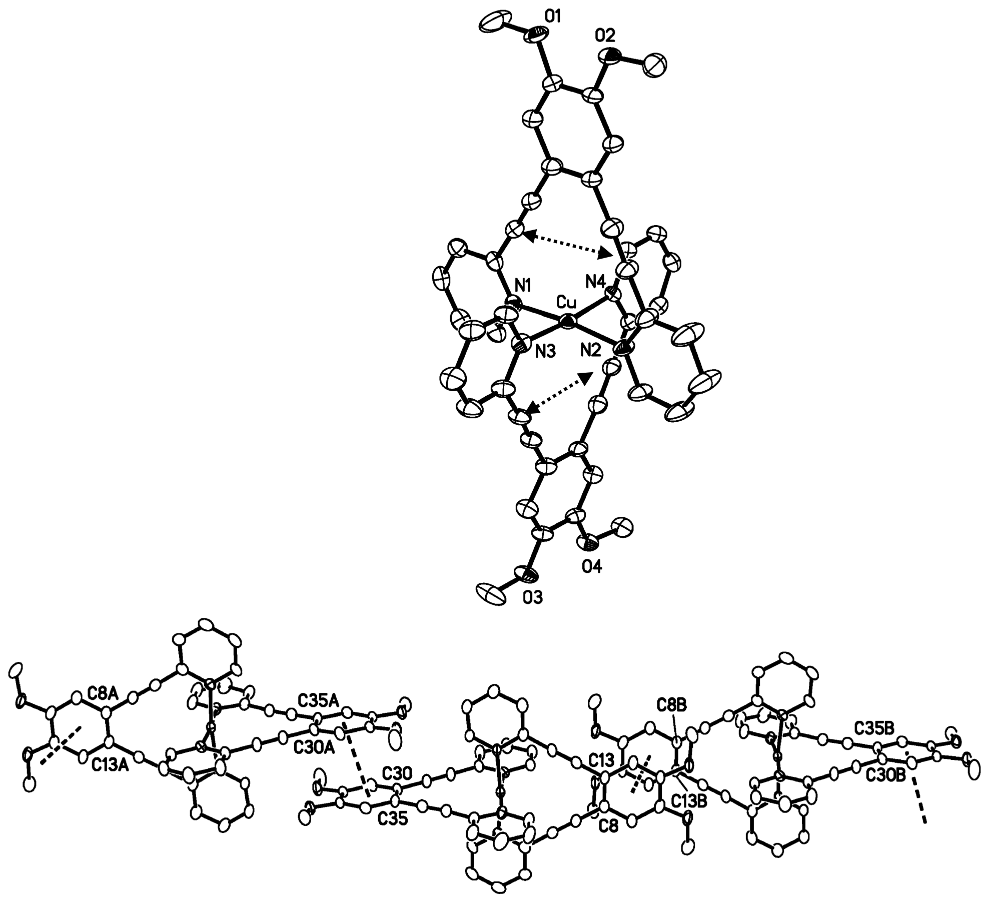


Fig. 1. Top: ORTEP (40% probability level) of **2a**. The dotted arrows mark the diyne distances that are relevant for a Bergman cyclization (3.96 and 3.99 Å). This distance in the model ligand **1b** is 4.25 Å according to 6-31G** calculation. The Cu–N distances are 2.01–2.02 Å. Bottom: linear chains of molecules of **2a** are held together by π–π stacking interactions. The centroid–centroid distances shown by the dotted lines are 3.47 and 3.51 Å, respectively.

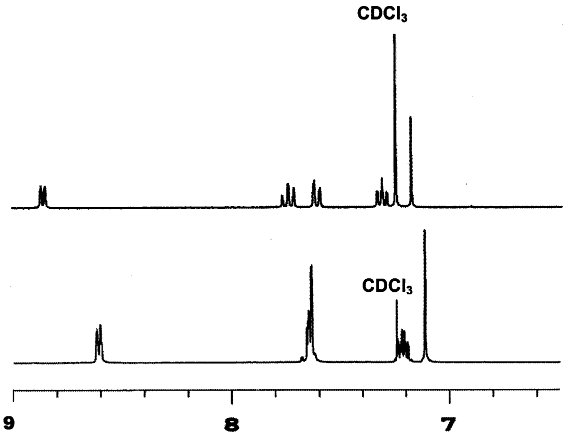


Fig. 2. Top: ^{1}H-NMR spectrum of **3a**. Bottom: ^{1}H-NMR spectrum of **1a**.

that is furthest away from the $PdCl_2$ group experiences the largest shift. A satisfactory explanation for this behavior is not available, but it could be due to the local deshielding effect and partial charge depletion effected by the $PdCl_2$ unit. These effects would be transmitted inductively by the ligand to the ferrocene nucleus.

The quality of the crystalline specimens of **7** was excellent and a single crystal X-ray structure was obtained. In Fig. 5 the molecular structure and in Fig. 6 details of the packing arrangement of **7** are shown. The molecular structure of **7** is somewhat different from that of **3a**. The distance between the two nitrogen atoms in the free ligand **6** is ca. 4.5 Å according to a force field calculation (MM2). The coordination of the $PdCl_2$ decreases the N–N distance to 4.03 Å according to our single crystal structure analysis and thus induces a modest amount of strain into this cyclic system. A second feature is that the two chlorine atoms bound to Pd are not perpendicularly oriented to the plane of the ligand, but show a torsion of 20.2°. This arrangement is unusual and brings the bottom chlorine atom closer to the ferrocene ring. The distance of 3.4 and 4.0 Å between the chlorine atom and the two closest hydrogen atoms of the bottom cyclopentadienyl ring in the ferrocene suggests that there is some hydrogen-bonding interaction. However, in the solid state there are quite short (2.80 A) *inter*molecular chlorine hydrogen contacts as shown in Fig. 6 (right picture, arrow). The combination of the π–π stacking and the strong inter-

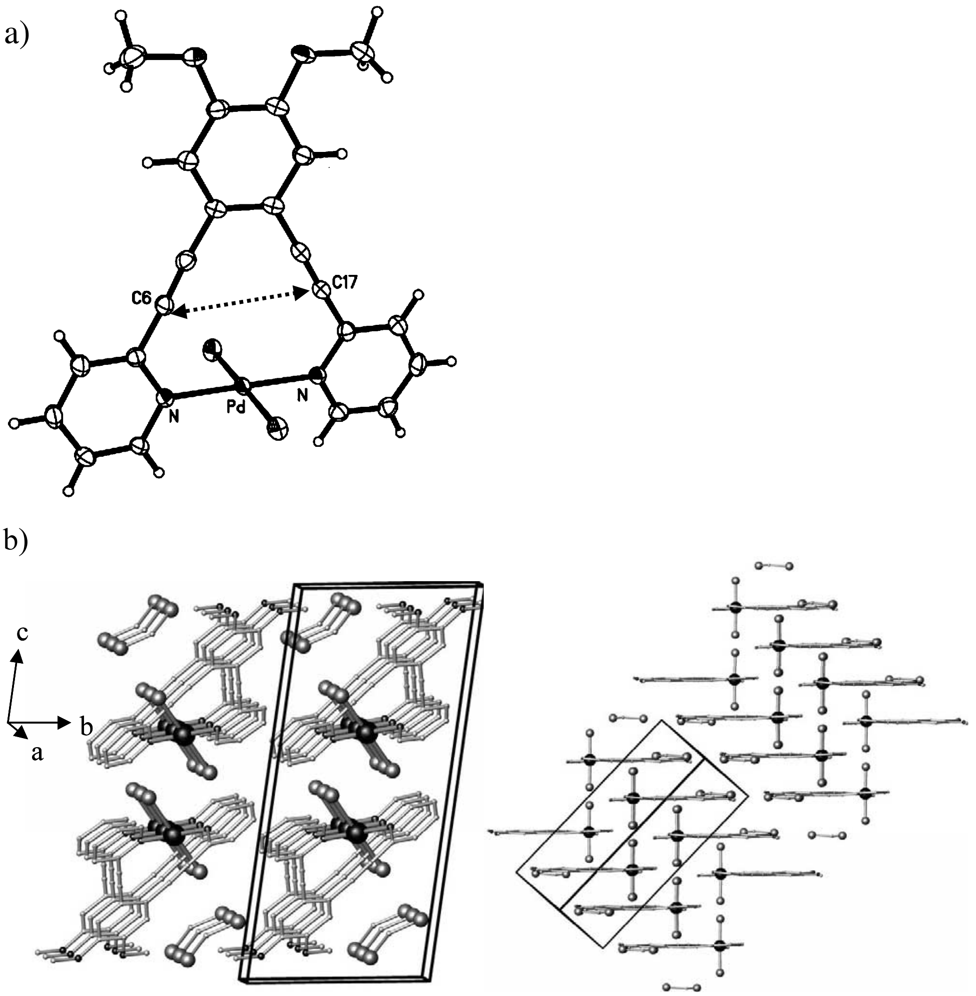
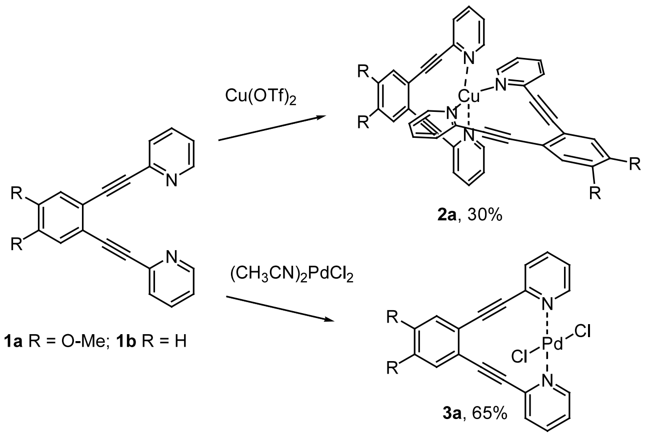


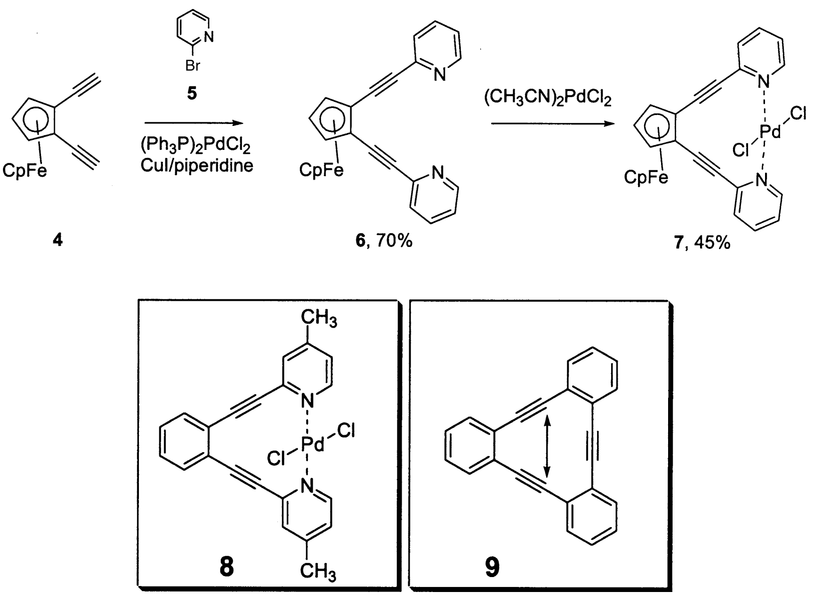
Fig. 3. (a) Molecular structure (ORTEP, 50% probability level) of **3a**. The dotted arrow marks the diyne distance that is relevant for a Bergman cyclization (3.96 Å) [10–13]. The Pd–N distances are 2.01 Å and identical to those reported by Bosch and Barnes [7] for a similar complex. The overall geometries of the ligands in **2a** and **3a** are very similar. (b) Packing of **3a** in the solid state. The packing is influenced by the proximity of the halogens in adjacent $PdCl_2$-units and the intercalated solvent molecules (CH_2Cl_2).



Scheme 1. Synthesis of the complexes **2a** and **3a**.

molecular Cl–H-bonds, i.e. a crystal packing effect, is probably the reason for the unusually tilted axis of the $PdCl_2$-unit in **7**, that however, leaves the complex in a square planar surrounding.

A cursory examination of the differential scanning calorimetry data of **1a**, **3a, 6** and **7** shows that these materials undergo Bergman type reactions at elevated temperatures [14,15]. The ligand **1a** melts at 168 °C and shows an exothermic reaction at 276 °C (62 kcal mol^{-1}). The ligand **6** melts at 141 °C and shows an exothermic reaction (35 kcal mol^{-1}) at 262 °C. Upon complexation neither **3a** nor **7** melt anymore, but instead a structural change is witnessed (319 °C, −4.6 kcal mol^{-1}, **3a**; 238 °C, 15 kcal mol^{-1}, **7**) that is followed by a strong exotherm (344 °C, −22 kcal mol^{-1}, **3a**; 295 °C, −27 kcal mol^{-1}, **7**). The second, larger exotherms are due to a Bergman-type rearrangement in the solid state. The coordination of $PdCl_2$ increases the temperature for this rearrangement significantly perhaps because the $PdCl_2$ acts as a 'stopper' between the enediyne termini. The complex **2a** was too sensitive (loss of solvent) to perform meaningful DSC measurements.



Scheme 2. Synthesis of the pincer ligand **6** and the Pd-complex **7**.

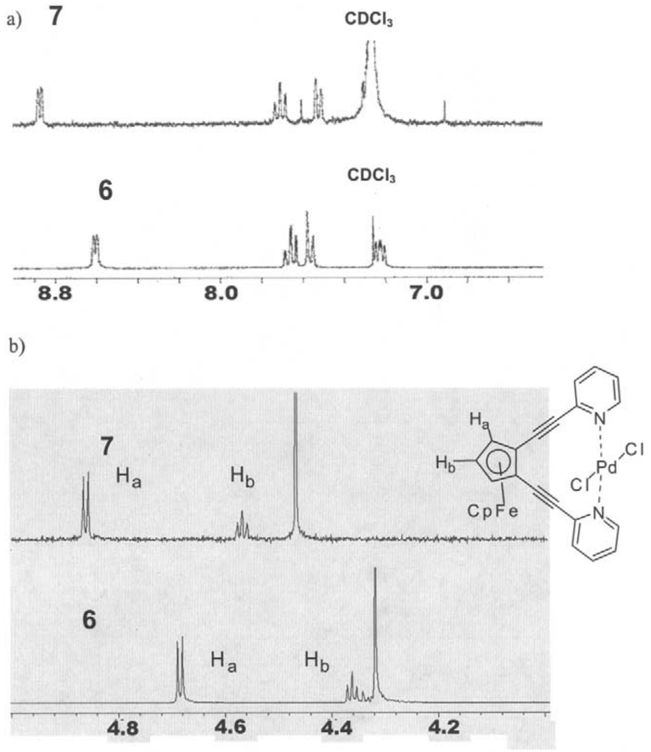


Fig. 4. ^{1}H-NMR spectra of **6** and **7**. (a) Top: aromatic region of **7**. Bottom: aromatic region of **6**. (b) Ferrocene region of the ^{1}H-NMR spectra of **6** and **7**. Top: spectrum of **7**. Remarkable is the large downfield shift of the ferrocene signals upon complexation to $PdCl_2$. Bottom: spectrum of the free ligand **6**.

In conclusion, we have been able to prepare a series of *trans*-spanning complexes **2**, **3** and **7** from the ligands **1a** and **6**. These *trans*-spanning complexes show a coordination geometry that is interesting from a structural point in that transition metal analogs of dehydroannulenes are formed. The distance between the 'terminal' alkyne carbons is very similar to that of the trisbenzo(dehydro[12]annulene)s of the type **9**, and the Bergman reactivity of these substrates is lower than that of its ligands; however, we are testing **3a** and **7** at the moment as catalysts in the Heck–Cassar–Sonogashira–Hagihara [16] couplings.

3. Experimental

3.1. General methods

Compounds **1a** and **4** were synthesized using literature procedures. All other reagents were of commercial grade and used as obtained. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker AM 300 or a Varian Mercury 400 spectrometer. The mass spectra were measured on a VG 70SQ. IR spectra were obtained using a Shimadzu FTIR-8400 with KBr pellets. X-ray crystal structure analyses were performed at 293 K using a Bruker SMART APEX CCD-based diffractometer system Mo–K$_\alpha$, ($\lambda = 0{,}71073$ Å).

3.2. Synthesis of the complex *2a* from *1a* and *Cu(OTf)$_2$*

A solution of Cu(OTf)$_2$ (3.6 mg, 10 μmol) in ethanol (1 ml) was layered over a solution of (**1a**) (6.8 mg, 20 μmol) in chlorobenzene (1 ml) with a layer of ethanol separating them. Upon diffusion of the layers, blue–green crystals formed of **2a** (3.1 mg, 30%). One needle was coated in inert oil and mounted on a thin glass fiber for single crystal structure determination.

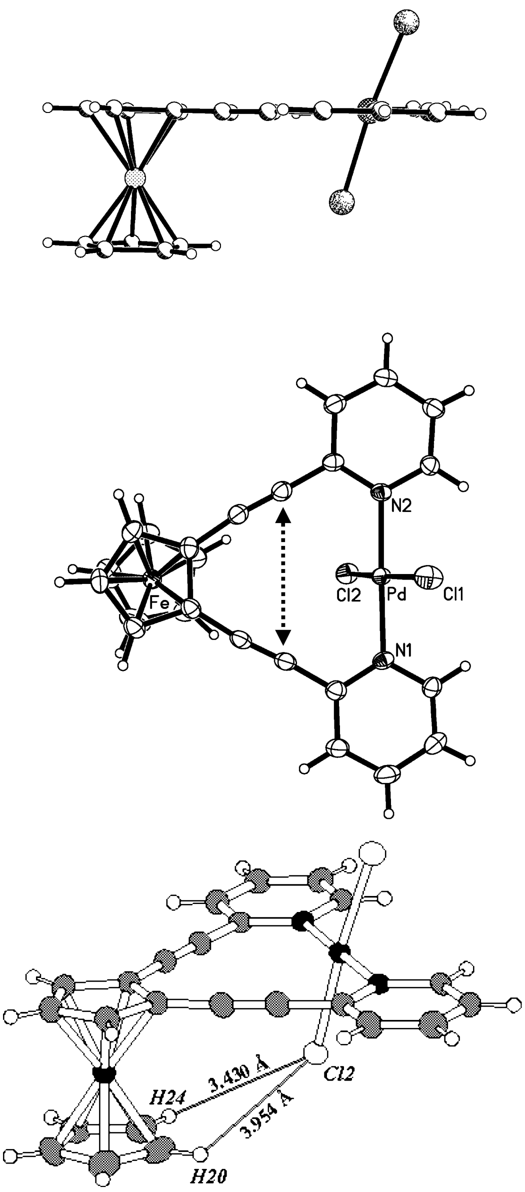


Fig. 5. ORTEP representation (displacement ellipsoids are at the 50% probability level) of **7**. The average Pd–N distance is 2.024 Å. The distance between the two alkyne carbon atoms (dotted arrow) is 4.093 Å, while the axis formed by the two chlorine atoms and the Pd is tilted by 20.2°.

3.3. Synthesis of **3a**

Compound **1a** (93.6 mg, 0.274 mmol) was dissolved in dichloromethane (3 ml) and placed in a vial. A solution of $(CH_3CN)_2PdCl_2$ (87.9 mg, 0.339 mmol) dissolved in 8 ml of acetonitrile was carefully layered on top of the dichloromethane solution. The vial was capped and placed in the dark for 12 h, after which brownish block-like crystals of **3a** (93.0 mg, 65%) were collected by vacuum filtration, washed with warm acetonitrile, and dried. IR (cm^{-1}): ν 2950, 2212, 1591, 1531, 1371, 1256, 991, 768. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.85 (dd, 2H, $^3J_{H,H} = 6.6$ Hz, $^4J_{H,H} = 0.83$ Hz, pyr-H), 7.73 (ddd, 2H, $^3J_{H,H} = 9.3$ Hz, $^4J_{H,H} = 1.7$ Hz, pyr-H), 7.60 (dd, 2H, $^3J_{H,H} = 8.8$ Hz, $^4J_{H,H} = 0.83$ Hz, pyr-H), 7.30 (dtd, 2H, $^3J_{H,H} = 9.1$ Hz, $^4J_{H,H} = 1.7$ Hz, pyr-H), 7.17 (s, 2H, arom.-H), 3.98 (s, 6H, OCH_3). MS (EI) *m*/*z* Calc. for M^+ ($C_{22}H_{16}Cl_2N_2O_2Pd$) 516.0, decomposition before could be M^+ determined.

3.4. Synthesis of the ferrocene pincer ligand **6**

In a 25 ml Schlenk flask, 1,2-diethynylferrocene **4** [17] (200 mg, 0.854 mmol), $(PPh_3)_2PdCl_2$ (12.0 mg, 0.0171 mmol), CuI (8.10 mg, 0.0425 mmol) were dissolved in dry triethylamine (3 ml). The resulting solution was subjected to three freeze–pump–thaw cycles, after which the vacuum was replaced with nitrogen. 2-Bromopyridine **5** (283 mg, 1.79 mmol) was added and the resulting solution stirred at 50 °C for 12 h before being quenched with water and diethyl ether. The water layer was separated and extracted with diethyl ether (50 ml). The combined organic layers were dried over magnesium sulfate and the solvent removed in vacuo. Column chromatography (SiO_2-hexanes/ethyl acetate, 10:1) furnished **6** (233 mg, 70%) as a red oily solid. IR (cm^{-1}): ν 2846, 2214, 1579, 1556, 1471, 1417, 1235, 1014, 773. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.58 (d, 2H, $^3J_{H,H} = 7.4$ Hz, pyr-H), 7.63 (td, 2H, $^3J_{H,H} = 9.4$ Hz, $^4J_{H,H} = 1.7$ Hz, pyr-H), 7.54 (d, 2H, $^3J_{H,H} = 7.7$ Hz, pyr-H), 7.20 (dddd, 2H, $^3J_{H,H} = 6.3$ Hz, $^4J_{H,H} = 1.4$ Hz, pyr-H), 4.68 (d, 2H, $^3J_{H,H} = 2.7$ Hz, sub. Cp ring), 4.35 (t, 1H, $^3J_{H,H} = 2.7$ Hz, sub. Cp ring), 4.31 (s, 5H, unsub. Cp ring). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 149.7, 143.6, 165.9, 126.9, 122.1, 88.00, 87.10, 72.35, 71.95, 69.62, 67.32. UV–vis ($CHCl_3$): λ 326 nm ($\varepsilon = 5274$ cm^{-1} M^{-1}). MS (EI) *m*/*z* Calc. for M^+ ($C_{24}H_{16}FeN_2$) 388.1, Found 388.0.

3.5. Synthesis of 7

Compound **6** (20 mg, 0.052 mmol) was dissolved in dichloromethane (3 ml) and placed in a vial. A solution of $(CH_3CN)_2PdCl_2$ (20 mg, 0.077 mmol) dissolved in 5 ml of acetonitrile was carefully layered atop the dichloromethane solution. The vial was capped and placed in the dark, and after 3 days red, block-like crystals appeared at the interface. Red block-like crystals of **7** (14 mg, 45%) were collected by vacuum filtration. IR (cm^{-1}): ν 2216, 1595, 1556, 1421, 1157. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.85 (d, 2H, $^3J_{H,H} = 7.0$ Hz, pyr-H), 7.69 (td, 2H, $^3J_{H,H} = 9.4$ Hz, $^4J_{H,H} = 1.7$ Hz, pyr-H), 7.51 (d, 2H, $^3J_{H,H} = 7.7$ Hz, pyr-H), 7.29–7.21 (m, 2H, pyr-H), 4.85 (d, 2H, $^3J_{H,H} = 3.0$ Hz, sub. Cp ring), 4.56 (t, 1H, $^3J_{H,H} = 3.0$ Hz, sub. Cp ring), 4.46 (s, 5H, unsub. Cp ring). UV–vis ($CHCl_3$): λ 326 nm ($\varepsilon =$ 5274 cm^{-1} M^{-1}). MS (EI) *m*/*z* Calc. for M^+ ($C_{24}H_{16}Cl_2FeN_2Pd$) 563.9, decomposition before M^+ could be determined.

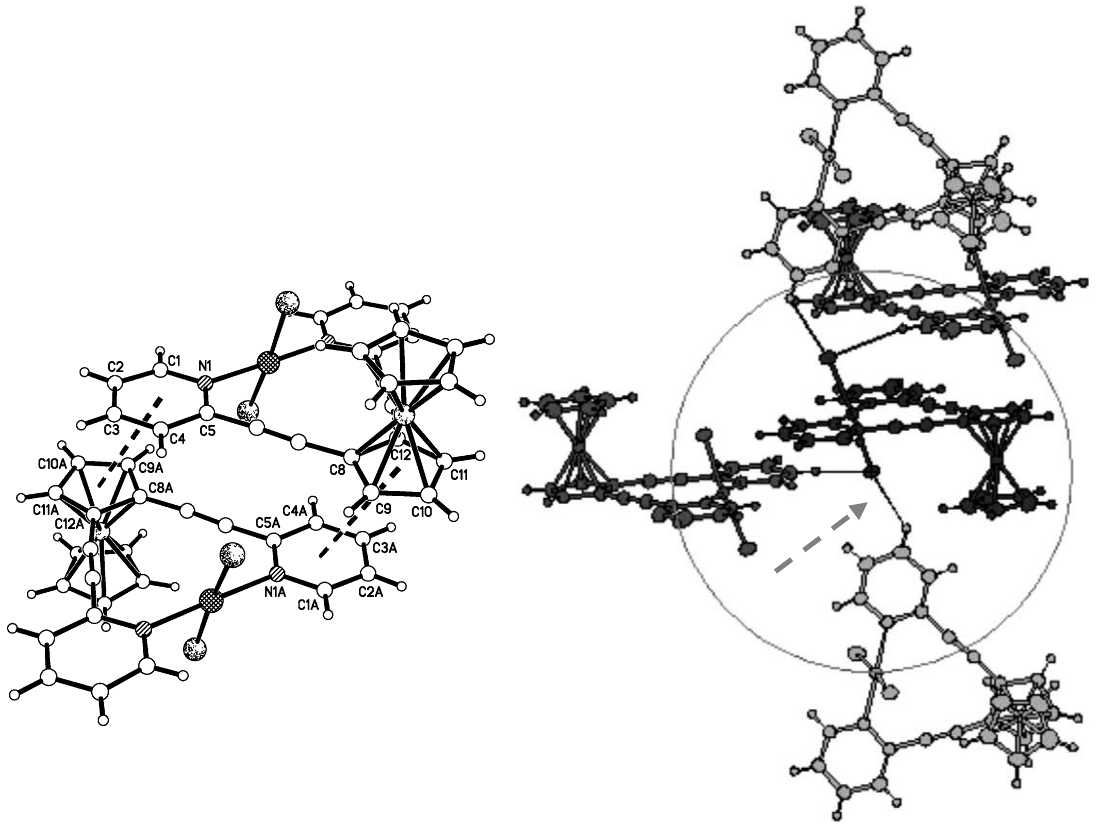


Fig. 6. Solid-state packing of **7** occurs in a herringbone fashion that promotes short intermolecular π–π interactions (left, from 3.4 to 3.8 Å, see dotted lines). In addition, there are short intermolecular hydrogen bonds that connect the chlorine atoms to the protons of the pyridine rings. The hydrogen bonding distance for the bottom chlorine atom is 2.8 Å (see arrow).

3.6. Crystallography of **2a**, **3a**, and **7**

3.6.1. Crystal data for **2a**

The empirical formula of **2a** $C_{51}H_{37}ClCuF_3N_4O_7S$ (1005.90). The data collection was performed at a temperature of 173(2) K utilizing Mo–K_α irradiation with a wavelength of 0.71073 Å. The crystal system is triclinic with $P\bar{1}$. The unit cell has the following dimension: $a = 12.2796(7)$ Å, $b = 13.0413(8)$ Å, $c = 19.496(1)$ Å, $\alpha = 89.346(1)°$, $\beta = 81.529(1)°$, $\gamma = 88.077(1)°$ and $V = 3086.3(3)$ Å^3. It contains $Z = 2$ crystallographically independent molecules. The calculated density is 1.082 g cm^{-3}. The absorption coefficient was determined to 0.483 mm^{-1} at the diffraction $F(0\,0\,0)$ with an intensity of 1032 counts. The crystal specimen was a small, elongated plate of the following dimensions: 0.48 × 0.12 × 0.08 mm^3. The data collection was performed in the Θ-range from 1.56 to 24.11° with index ranges $-14 \leqslant h \leqslant 14$, $-14 \leqslant k \leqslant 14$, $-22 \leqslant l \leqslant 22$. The data set contained 23 397 collected reflections of which 9801 were independent reflections with [$R_{int} = 0.0475$]. The completeness of data to $\Theta = 24.11°$ was 100.0%. The absorption correction was performed semi-empirically from equivalents utilizing max and min transmission of the crystalline specimen of 0.8309 and 0.5579. The data were refined by a full-matrix least-squares cycle on F^2. The ratio of data/restraints/parameters is 9801/0/617 with a resulting goodness-of-fit on F^2 of 1.012. The final R indices were obtained for reflections with intensity of [$I > 2\sigma(I)$] with R_1 is 0.0676, and wR_2 is 0.1683. If all data are utilized, R indices result for R_1 of 0.0848, and for wR_2 of 0.1756. The largest residual diffraction peak and hole were 0.843 and -0.771 e Å^{-3}.

3.6.2. Crystal data for **3a**

The empirical formula of **3a** is $C_{23}H_{18}Cl_4N_2O_2Pd$ (602.59). Data were acquired at 150.0(2) K at a wavelength of 0.71073 Å utilizing Mo–K_α radiation. The crystal system is triclinic with $P\bar{1}$. The unit cell has the following dimension: $a = 7.6929(4)$ Å, $b = 8.5391(4)$ Å, $c = 18.4042(9)$ Å, $\alpha = 80.124(1)°$, $\beta = 83.819(1)°$, $\gamma = 75.532(1)°$ and $V = 1150.6(1)$ Å^3. It contains $Z = 2$ molecules. The calculated density is 1.739 g cm^{-3}. The absorption coefficient was determined to 1.295 mm^{-1} F for $F(0\,0\,0)$ with an intensity of 600 counts. A crystal plate with the dimensions of 0.48 × 0.36 × 0.10 mm^3 was utilized. The data collection was performed in the Θ-range from 2.25 to 26.39°, with $-9 \leqslant h \leqslant 9$, $-10 \leqslant k \leqslant 10$, $-22 \leqslant l \leqslant 23$; 10 555 reflections were collected of which 4694 [$R_{int} = 0.0223$] were independent reflections. The completeness of the collected data is 99.6% to $\Theta =$

26.39°. The absorption correction was performed semi-empirically from equivalents utilizing max and min transmission of the crystalline specimen of 0.7191 and 0.5906. The data were refined by a full-matrix least-squares cycle on F^2. The ratio of data/restraints/parameters is 4694/0/309 with a goodness-of-fit on F^2 of 1.069. The final R indices were obtained for reflections with intensity of $[I > 2\sigma(I)]$. The indices R_1 were 0.0368, and wR_2 were 0.1058. The R indices for all data R_1 is 0.0406, and wR_2 is 0.1078. The largest residual diffraction peak and hole were 1.019, -1.364 e Å^{-3}.

3.6.3. *Crystal data for 7*

The empirical formula of **7** is $C_{24}H_{16}Cl_2FeN_2Pd$ (565.54). The temperature of the data collection was 150.0(2) K and the used wavelength was 0.71073 Å, Mo–K_α. The crystal system is monoclinic, $P2_1/n$. The unit cell has the following dimensions: $a = 12.4063(6)$ Å, $b = 14.2256(6)$ Å, $c = 12.7536(6)$, $\alpha = 90°$, $\beta = 112.2270(10)°$, $?\gamma = 90°$ and $V = 2083.59(17)$ Å^3. It contains $Z = 4$ crystallographically independent molecules. The density was calculated to 1.803 g cm^{-3}. The absorption coefficient was determined to 1.830 mm^{-1} for $F(0\,0\,0) = 1120$. The thin crystal plated measured $0.30 \times 0.18 \times 0.04$ mm^3. Data collection was performed from $\Theta = 1.95$ to 25.04° with index ranges from $-14 \leqslant h \leqslant 14$, $-16 \leqslant k \leqslant 15$, $-15 \leqslant l \leqslant 15$; 15 133 reflections were collected of which 3683 reflections were independent $[R_{int} = 0.0314]$. Completeness of the data to $\Theta = 25.04° = 100.0\%$. A Semi-empirical absorption correction was performed from equivalents with max and min transmission being determined to 0.8620 and 0.6487. The data were refined by a full-matrix least-squares cycle on F^2. The ratio of data/ restraints/parameters was 3683/0/287 with a goodness-of-fit on F^2 of 0.988. The final determined R indices for $[I > 2\sigma(I)]$ were $R_1 = 0.0268$, and $wR_2 = 0.0643$. The R indices of all data were $R_1 = 0.0348$, and $wR_2 = 0.0664$. The largest residual diffraction peak and hole were 0.694 and -0.292 e Å^{-3}.

4. Supporting information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 194 854 for compound **2a**, CCDC No. 194 615 for compound **3a**, and CCDC No. 194 614 for compound **7**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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