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Rigid-rod structured palladium complexes

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Dedicated to Professor Gerard van Koten.

Abstract

Mononuclear and homobimetallic palladium complexes of structural type [*trans*-(Me(O)CS-4-C₆H₄)(Ph₃P)₂Pd(N^{\circ}N)]OTf (8a, N^{\circ}N=C₄H₄N₂; 8b, N^{\circ}N=C₅H₄N-4-C=N) and {[*trans*-(Me(O)CS-4-C₆H₄)(Ph₃P)₂Pd]₂N^{\circ}N}(OTf)₂ (9a, N^{\circ}N = 4,4'-bipyridine (=bipy); 9b, N^{\circ}N = C₆H₄-1,4-(C=N)₂; 9c, N^{\circ}N = (C₆H₄-4-C=N)₂) are accessible by the reaction of *trans*-(Ph₃P)₂Pd(C₆H₄-4-SC(O)-Me)(OTf) (6) with 1 or 0.5 equivalents of the Lewis-bases N^{\circ}N (7a, N^{\circ}N = C₄H₄N₂; 7b, N^{\circ}N = C₅H₄N-4-C=N; 7c, N^{\circ}N = bipy; 7d, N^{\circ}N = C₆H₄-1,4-(C=N)₂; 7e, N^{\circ}N = (C₆H₄-4-C=N)₂) in high yield. Complex 6 can be prepared in a two-step synthesis procedure. Oxidative addition of I-1-C₆H₄-4-SC(O)Me (2) to Pd(PPh₃)₄ (3) gives *trans*-(Ph₃P)₂Pd(C₆H₄-4-SC(O)Me)(I) (4), which further reacts with [AgOTf] (5) to afford 6.

The formation of **8** and **9** strongly depends on the size of the Lewis-bases $N^{\cap}N$. It is obvious that the co-ordination of the second N-ligated site of **8a** or **8b** to a further bulky $[(PPh_3)_2Pd(C_6H_4-4-SC(O)Me)]^+$ unit is not possible. In contrast, more extended $N^{\cap}N$ species such as **7c–7e** will result in the formation of linear structured homobimetallic **9a–9c**.

The solid-state structures of **4** and **4** · **CH**₂**Cl**₂ are reported. Complex **4** is packed in the orthorhombic space group *Pbca*. The assembly of dichloromethane into the crystal lattice breaks the symmetry, whereby **4** · **CH**₂**Cl**₂ crystallises in the triclinic space group $P\overline{1}$. In both modifications a square-planar palladium(II) ion is present, with the iodo atom and the Me(O)CS-C₆H₄ unit *trans*-positioned. The different crystal packing has no significant influence onto the geometry around the d⁸-configurated palladium atoms. © 2005 Elsevier B.V. All rights reserved.

Keywords: Palladium; Nitrogen Lewis-bases; Oxidative addition; Homobimetallic; Molecular wire; X-ray structure

1. Introduction

With the advancement in nanoscale molecular electronic devices, organic and organometallic functionalised thiols have recently received great attention [1-10]. This is attributed to their intrinsic or insulator properties [11-21]. Among them, conjugated thiol end-capped molecules, such as 1,4-ethynyl-phenylene and bis-9,10-phenyl-ethynylan-thracene have been widely studied as molecular wires [22,23]. In addition, such molecules can be used in molecular electronics to form well-ordered monolayers by self-

assembly processes onto metal surfaces of gold or silver [24]. In contrast to ultra-thin films made by, i.e., molecular beam epitaxy or chemical vapour deposition, self-assembled monolayers (SAMs) are highly ordered and orientated and can incorporate a wide range of diverse groups into as well as at the end of the chain [25]. This means that by chemical control a variety of functionalised surfaces with specific interactions can be produced.

One-dimensional dithiols are also very unique in their use as molecular wires to span two metal surfaces allowing through-bridge exchange of electrons [26].

Next to organic, for example, biphenyl- and fluorenylbased end-capped dithiols, also very recently thiol end-grafted organometallic compounds, i.e., *trans*-(Ph₃P)₂-Pt(C \equiv C-C₆H₄-4-SC(O)Me)₂ became available [27]. As it

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could be shown by Mayor et al. [27] such complexes act as a single-molecular insulator. More recently, we became interested in this field of study [28].

We describe here the synthesis and properties of monoand homo-bimetallic acetyl-S end-capped palladium complexes.

2. Results and discussion

For the preparation of $[trans-(Me(O)CS-4-C_6H_4) (Ph_3P)_2Pd(N^{\cap}N)$]OTf (8a, $N^{\cap}N = C_4H_4N_2$; 8b, $N^{\cap}N =$ $C_5H_4N-4-C \equiv N$ and {[*trans*-(Me(O)CS-4-C₆H₄)(Ph₃P)₂- $Pd_2N^{\cap}N$ (OTf)₂ (9a, $N^{\cap}N = 4,4'$ -bipyridine (=bipy); 9b, $N^{\cap}N = C_6H_4 - 1, 4 - (C \equiv N)_2; 9c, N^{\cap}N = (C_6H_4 - 4 - C \equiv N)_2)$ we decided to use trans-(Ph₃P)₂Pd(C₆H₄-4-SC(O)Me)(I) (4) as precursor complex, which can be synthesised by the oxidative addition of 1-I-C₆H₄-4-SC(O)Me (2) to Pd(PPh₃)₄ (3). However, it appeared that the synthesis of thiol 2 was the critical step in the synthesis protocol of 4, since this molecule is only available in a low yield reaction [29]. Out of this reason we had to develop an improved synthetic procedure to obtain 2 in much higher yield. This problem could be solved by using stronger aprotic solvents. Subsequent treatment of C_6H_4 -1,4-(I)₂ (1) with ^tBuLi, 1/8 S₈ and MeC(O)Cl in tetrahydrofuran at low temperature affords thiol 2 as a colourless solid in yields up to 85% (Eq. (1)). Further reaction of 2 with stoichiometric amounts of $Pd(PPh_3)_4$ (3) produces by loss of two Ph₃P ligands mononuclear trans- $(Ph_3P)_2Pd(C_6H_4-4-SC(O)Me)(I)$ (4) (Eq. (1)). After appropriate work-up, complex 4 can be isolated as a vellow solid in excellent yield (Section 4).



Surprisingly, iodide abstraction from 4 by using $[AgBF_4]$ resulted in the decomposition of 4. However, when [AgOTf] (5) (TfO = triflate, OSO₂CF₃) is reacted with 4 in toluene-dichloromethane mixtures of ratio 5:2 the in situ formation of *trans*- $(Ph_3P)_2Pd(C_6H_4-4-SC(O)Me)$ (OTf) (6) is observed (Scheme 1). Addition of the Lewisbases $N^{\cap}N$ (7a, $N^{\cap}N = C_4H_4N_2$; 7b, $N^{\cap}N = C_5H_4N$ -4-C=N; 7c, $N^{\cap}N = bipy$; 7d, $N^{\cap}N = C_6H_4-1, 4-(C=N)_2$; 7e, $N^{\cap}N = (C_6H_4-4-C \equiv N)_2$) to 6 in a 1:2 stoichiometry gives either the mono-nuclear palladium complexes 8a and 8b, or the respective homobimetallic rigid-rod structured molecules 9a-9c (Scheme 1, Table 1). This result was at first astonishing, because we expected the only formation of linear homobimetallic species. Complexes 8a and **8b** can be synthesised in a more straightforward way by using a 1:1 molar ratio of 6 and 7 (Scheme 1).

Table 1 Synthesis of complexes 8 and 9



Scheme 1. Synthesis of mononuclear 8a and 8b, and homobimetallic 9a-9c (Table 1).

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Complexes 8 and 9 can be precipitated as yellow solids from the reaction medium by slow addition of *n*-hexane. Due to their ionic nature, they only dissolve in polar organic solvents including tetrahydrofuran, dichloromethane and chloroform. However, in acetonitrile, dimethylsulfide and dimethylformamide they decompose even at low temperature. They also decompose on exposure to air and moisture. Under inert gas atmosphere 8 and 9 can be stored for months at -30 °C.

Compounds 4, 8 and 9 were fully characterised by elemental analysis, IR and NMR (${}^{1}H$, ${}^{31}P{}^{1}H$) spectroscopy. Additionally, from 4 and 4 \cdot CH₂Cl₂ the solid-state structures could be determined.

In the IR spectra of **8** and **9** the triflate counter ion gives rise to one very characteristic v_{SO} -absorption at ca. 1265 cm⁻¹ which is consistent with the non-coordinating character of the triflate group [30]. For the acetyl moiety a distinct CO stretching vibration is found at ca. 1700 cm⁻¹ which appears at the same wave-number as **2** (Section 4). The $v_{C = N}$ absorption of the cyano group(s) in **8b**, **9b** and **9c** is observed at 2280, 2275 and 2260 cm⁻¹. These bands are shifted to higher wave-numbers, when compared to **7b** (2244 cm⁻¹), **7d** (2234 cm⁻¹) or **7e** (2228 cm⁻¹) [30]. This clearly indicates the coordination of the cyano units to the palladium(II) centres in **8b**, **9b** and **9c**, respectively. This finding resembles to data found for other transition metal complexes, i.e., {[(dppp)Pd][C₆H₄-1,4-(C=N)₂]₂(OTf)₂}₄ (2280 cm⁻¹) [30].

The ¹H NMR spectra of **4**, **8** and **9** show well-resolved resonance signals for the corresponding organic groups Me(O)CS, C_6H_4 , C_6H_5 , C_5H_4N , $C_4H_4N_2$ and bipy with the expected coupling pattern. The spectra further show the formation of mono- (**8**) or dinuclear molecules (**9**), which can be concluded from the signal intensities of the latter units.

However, it was not possible to obtain ${}^{13}C{}^{1}H$ NMR spectra of all palladium complexes, since it appeared that some of these species are less soluble in common organic solvents (vide supra and Section 4).

Characteristic for the ${}^{31}P{}^{1}H$ NMR spectra of 8 and 9 is the appearance of one sharp signal at ca. 21 ppm, which can be assigned to the Ph₃P units. Compared with free Ph₃P [31] the signals in 8 and 9 are shifted to lower field. When one compares the ${}^{31}P{}^{1}H$ NMR chemical shift of 4 (22 ppm) with that ones typical for 8 and 9 a high-field shift by ca. 1 ppm is characteristic. This allows to monitor the reaction of 4 with 5 and 7 to give 8 and 9, respectively.

Single crystals suitable for X-ray structure determination could be obtained by diffusion of *n*-hexane into a dichloromethane solution containing 4 at -30 °C, whereby two different type of crystals were formed. One sort is solvent free (4), while in the second crop of crystals one dichloromethane molecule is assembled into the crystal lattice (4 · CH₂Cl₂). The molecular structure of 4 is depicted in Fig. 1, while the different crystal packing of 4 and 4 · CH₂Cl₂ is shown in Fig. 2. Selected geometrical details for 4 and 4 · CH₂Cl₂ are listed in Table 2, and the experi-



Fig. 1. XP-plot (50% probability level) of complex 4 with the atomnumbering scheme.

mental data for the X-ray diffraction studies are given in Table 3 (Section 4).

The palladium(II) ion in both modifications possesses a square-planar environment, caused by the two trans-positioned Ph_3P groups (P1, P2), the σ -bound iodide I1 and the Me(O)CS-4-C₆H₄ group (Fig. 1) (4: r.m.s.d. 0.0919 Å, $4 \cdot CH_2Cl_2$: 0.0773 Å). The latter building block is perpendicular orientated to the transition metal co-ordination plane (93.2° (4) and 89.9° (4 · CH₂Cl₂)). The Pd-I, Pd-P and Pd-C separations (Table 2) are in the typical range as reported for similar species [32]. Complex 4 is packed in the orthorhombic space group Pbca. The assembly of dichloromethane into the crystal lattice breaks the symmetry, whereby $4 \cdot CH_2Cl_2$ crystallises in the triclinic space group P1. Complex 4 is build-up by the formation of tubes along the crystallographic axes a of equal oriented species of 4. These tubes are forming along the crystallographic axes b four different layers with the iodo atom positioned up and down, to the left and to the right, and are staggered into each other by the PPh₃ phenyl groups (Fig. 2, left).

In $4 \cdot CH_2Cl_2$ equal orientated tubes are formed by 4 with an alternate up and down orientation of the iodo atoms. These tubes are forming a layer along the crystallographic axes *a*. Between these layers the dichloromethane solvent molecules are assembled into the crystal lattice (Fig. 2, right). The different crystal packing in 4 and $4 \cdot CH_2Cl_2$ has no significant influence onto the geometries around palladium.

3. Conclusion

A straightforward synthesis method for the preparation of thiol end-capped mono- and homo-bimetallic palladium complexes is reported. The key steps are the oxidative

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Fig. 2. Crystal lattices of 4 (left) and $4 \cdot CH_2Cl_2$ (right).

Table 2 Selected bond distances (Å) and angles (°) for 4 and $4 \cdot CH_2 Cl_2^a$

	4	$4\cdot\mathbf{CH}_{2}\mathbf{Cl}_{2}$
Pd(1)-C(37)	2.007(7)	2.008(5)
C(40)–S(1)	1.780(9)	1.765(5)
Pd(1)-P(2)	2.3546(2)	2.3286(12)
Pd(1)-I(1)	2.7021(9)	2.6874(5)
Pd(1) - P(1)	2.342(2)	2.3411(12)
S(1)-C(43)	1.747(17)	1.68(3)
P(1)–Pd(1)–C(37)	87.2(2)	88.45(12)
P(2)-Pd(1)-C(37)	87.3(2)	87.48(12)
P(2)-Pd(1)-P(1)	174.02(7)	172.38(5)
C(37) - Pd(1) - I(1)	168.3(2)	176.50(13)
P(1)-Pd(1)-I(1)	91.40(5)	94.06(3)
P(2)-Pd(1)-I(1)	93.61(5)	90.29(3)

^a The estimated standard deviations of the last significant digits are shown in parentheses.

addition of 1-I-C₆H₄-4-SC(O)Me to Pd(PPh₃)₄ and the conversion of trans-(Ph₃P)₂Pd(Me(O)CS-4-C₆H₄)(I) with [AgOTf] to $[trans-(Ph_3P)_2Pd(Me(O)CS-4-C_6H_4)](OTf).$ The latter molecule allows the synthesis of mono- and homo-bimetallic palladium complexes featuring thiol end-capped phenylene units, whereby the palladium centres are spanned by carbon-rich nitrogen-containing bridging units. The control over these reaction is given by the different size of the Lewis-bases NⁿN and resembles to the bulkiness of the organometallic entity [(Me(O)CS-4- C_6H_4)(Ph₃P)₂Pd⁺. The newly synthesised complexes are rigid-rod structured. Their use for the application of self-assembled monolayers and/or to span two metal surfaces to allow through-bridge exchange of electrons (or act as single-molecular insulator) is subjected to further studies.

Table 3 Crystal data and structure refinement for 4 and $4\cdot CH_2Cl_2$

Compound	4	$4 \cdot CH_2Cl_2$
Empirical formula	C44H37IOP2PdS	C45H39Cl2IOP2PdS
M	909.04	993.96
Space group	Pbca	$P\bar{1}$
a (Å)	10.4205(12)	13.3448(8)
b (Å)	23.294(3)	13.7490(8)
<i>c</i> (Å)	32.716(4)	14.0713(8)
α (°)	90	70.919(1)
β (°)	90	62.358(1)
γ (°)	90	77.858(1)
$V(\text{\AA}^3), Z$	7941.1(16), 8	2156.1(2), 2
$D_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.521	1.531
$\mu (\mathrm{mm}^{-1})$	1.411	1.426
θ Range (°)	1.24-26.43	1.73-28.48
Reflections collected/ unique/R _{int}	69477/8980/0.1302	25011/10393/0.0557
Data/restraints/parameter	8131/0/452	10393/130/537
$R_1^{a} [I > 2\sigma(I)]$	0.0717	0.0521
wR_2^{b} (all data)	0.2060	0.1438
Largest difference in peak	1.161, -1.725	1.062, -1.252
and hole (e $Å^{-3}$)		
^a $R_1 = \frac{\sum F_o - F_c }{\sum F_o }.$		
^b $wR_2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$	with $w = \frac{1}{\sigma^2(F_2^2) + (g_2^2)}$	$\frac{1}{\left(g_1P\right)^2+g_2P};$

$$\frac{\sqrt{\sum w(F_{o}^{2})^{2}}}{(\max(F_{o}^{2},0)+2F_{c}^{2})}, \qquad \sigma^{2}(F_{o}^{2})+(g_{1}P)$$

4. Experimental

P =

4.1. General methods

All reactions were carried out in an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG,

Ludwigshafen, Germany; H₂O traces: molecular sieve, 4 Å, Roth company) using standard Schlenk techniques. Solvents were purified by distillation (*n*-hexane and dichloromethane: calcium hydride; toluene. sodium: tetrahydrofuran: sodium/benzophenone ketyl). FT-IR spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer (KBr). NMR spectra were recorded with a Bruker Advance 250 spectrometer, operating in the Fourier transform mode. ¹H NMR spectra were recorded at 250.123 MHz (internal standard, relative to CDCl₃, δ $^{13}C{^{1}H}$ 7.26). NMR spectra were recorded at 67.890 MHz (internal standard, relative to CDCl₃, δ 77.16). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane (δ 0.00) with the solvent signal as reference. ³¹P{¹H} NMR were recorded at 101.202 MHz in CDCl₃ with P(OMe)₃ as external standard (δ 139.0, relative to 85% H₃PO₄, δ 0.00). Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries with a Gallenkamp MFB 595 010 melting point apparatus. Microanalyses were performed by the Organic Department at Chemnitz the University of Technology and the Institute of Organic Chemistry at the University of Heidelberg.

4.2. General remarks

Chemicals were purchased from commercial suppliers and were used as received. For **8a** and **8b** no ${}^{13}C{}^{1}H{}$ NMR data could be obtained, since these species are only less soluble in common organic solvents.

4.3. Modified synthesis of 2 [29,33]

1,4-Diiodobenzene (1) (5.00 g, 15.20 mmol) is dissolved in tetrahydrofuran (300 mL) and ^tBuLi (17.88 mL, 30.40 mmol. 1.7 M in *n*-pentane) is drop-wise added at -78 °C during 10 min. After stirring the reaction mixture for another 10 min at this temperature, sulfur (0.48 g, 15.20 mmol) dissolved in tetrahydrofuran (75 mL) is added drop-wise at 0 °C, and the reaction mixture is allowed to warm to 0 °C and stirred for additional 45 min at this temperature. Afterwards, the reaction mixture is again cooled to -78 °C and acetyl chloride (1.19 g, 15.20 mmol) is added in one portion. The thus obtained reaction solution is allowed to warm to room temperature overnight. Water (20 mL) is added and extraction with dichloromethane $(3 \times 50 \text{ mL})$ is carried out. The combined layers are dried over magnesium sulfate. The solvent is removed by rotary evaporation and the residue is purified by chromatography (Silica gel, column size 20×2.5 cm; *n*-hexane/dichloromethane, ratio 10:3). The solvents are removed from the eluate in oil-pump vacuum to leave a colourless solid. Yield: 3.5 g (12.77 mmmol, 84% based on 1).

M.p.: 54 °C. IR (KBr): 3082 (m), 1904 (w), 1698 (vs) (ν_{CO}), 1470 (s), 1378 (m), 1121 (s), 1092 (s), 999 (s), 808 (vs) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.4$ (s, 3H, CH₃), 7.1 (d, 2H, $J_{HH} = 8.2$ Hz, C₆H₄), 7.7 (d, 2H, $J_{HH} = 8.2$ Hz,

 C_6H_4). ¹³C{¹H} NMR (CDCl₃): $\delta = 30.3$ (CH₃), 96.0 (C-I/C₆H₄), 127.7 (CH/C₆H₄), 135.88 (CH/C₆H₄), 138.5 (ⁱC/C₆H₄), 194.0 (CO).

4.4. Synthesis of 4

Molecule 2 (0.1 g, 0.36 mmol) is dissolved in 30 mL of toluene and one equivalent of $Pd(Ph_3)_4$ (3) (0.412 g, 0.36 mmol) is added in one portion at 25 °C. During 24 h of stirring at this temperature a yellow precipitate forms. All volatiles are removed in oil-pump vacuum and the residue is dissolved in dichloromethane (5 mL). *n*-Hexane (60 mL) is added, whereby a yellow solid precipitates. The supernatant layer is decanted and the residue is washed twice with *n*-hexane (20 mL) to give 4 as a yellow solid. Yield: 0.32 g (0.25 mmol, 70% based on 2).

M.p.: 150 °C (dec.). Anal. Calc. for $C_{44}H_{37}IOP_2PdS$ (909.10): C, 58.13; H, 4.10; S, 3.53. Found: C, 58.42; H, 4.35; S, 3.41%. IR (KBr): 2962 (m), 1705 (s) (v_{CO}), 1636 (s), 1478 (s), 1432 (vs), 1400 (vs), 1261 (s), 1092 (sh), 1025 (s), 796 (s), 744 (s), 692 (vs), 612 (m), 517 (vs) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.2$ (s, 3H, CH₃), 6.2 (d, 2H, $J_{HH} = 8.2$ Hz, C₆H₄), 6.6 (dt, 2H, $J_{HH} = 8.2$ Hz, ${}^{4}J_{HP} = 3.9$ Hz, C₆H₄), 7.2–7.6 (m, 30H, PPh₃). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta = 21.7$. ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): $\delta = 30.1$ (CH₃), 127.6 (${}^{i}C/C_{6}H_{4}$), 127.8, 127.9, 128.0 (C₆H₄), 129.9 (${}^{i}C/C_{6}H_{4}$), 131.4, 132.2, 133.1, 134.5, 134.8, 134.9, 135.0, 135.2, 136.6 (C₆H₅), 178.5 (CO).

4.5. Synthesis of 8a

[AgOTf] (5) (48.0 mg, 0.187 mmol) is added in one portion to 4 (170.7 mg, 0.187 mmol), which is dissolved in a toluene-dichloromethane mixture of ratio 5:2 (50 mL) at 25 °C. After 30 min of stirring, the reaction mixture is filtered through a pad of Celite. To this solution pyrazine (7a) (1.5 mg, 0.187 mmol) is added and the resulting suspension is stirred for additional 30 min. On addition of 50 mL of *n*-hexane a yellow precipitate forms. The supernatant solution is removed by filtration with a canula and the residue is dried in oil-pump vacuum. Complex **8a** is obtained as a yellow solid. Yield: 136 mg (0.133 mmol, 75% based on 4).

M.p.: 78 °C (dec.). Anal. Calc. for $C_{48}H_{41}F_3N_2O_4P_2Pd_S_4 \cdot 0.5CH_2Cl_2$ (1061.84): C, 56.42; H, 4.02; N, 2.66. Found: C, 56.21; H, 4.14; N, 2.38%. IR (KBr): 3053 (m), 2924 (m), 1701 (s) (v_{CO}), 1654 (m), 1479 (m), 1434 (s), 1416 (sh), 1260 (vs) ($v_{s(SO)}$), 1223 (m), 1153 (s), 1094 (s), 1051 (m), 1028 (s) (v_{CF}), 1009 (m), 811 (s), 745 (s), 693 (s), 636 (s), 518 (vs) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.3$ (s, 3H, CH₃), 6.5 (d, 2H, $J_{HH} = 7.4$ Hz, C_6H_4), 6.9 (m, 8H, C_6H_4), 7.2–7.3 (m, 30H, PPh₃), 8.2 (m, 2H, $C_4H_4N_2$), 8.6 (m, 2H, $C_4H_4N_2$). ³¹P{¹H} NMR (CDCl₃): $\delta = 19.1$.

4.6. Synthesis of 8b

To 4 (164.7 mg, 0.184 mmol) dissolved in 30 mL of a toluene–dichloromethane mixture of ratio 5:2 one equivalent of [AgOTf] (5) (47 mg, 0.184 mmol) is added in one portion at 25 °C. After 30 min of stirring, the reaction mixture is filtered through a pad of Celite. To the eluate *iso*-nicotinonitrile (7b) (19 mg, 0.092 mmol) is added in one portion at 25 °C and the resulting suspension is stirred for 30 min. After appropriate work-up (see synthesis of 8a), complex **8b** can be isolated as a yellow solid. Yield: 155 mg (0.15 mmol, 75% based on 4).

M.p.: 60 °C (dec.). Anal. Calc. for $C_{51}H_{41}F_3N_2O_4$ -P₂PdS₂ (1035.37): C, 59.16; H, 3.99; N, 2.71. Found: C, 59.17; H, 4.01; N, 2.44%. IR (KBr): 3054 (s), 2280 (w) ($v_{C=N}$), 1703 (s) (v_{CO}), 1609 (m), 1551 (w), 1480 (m), 1435 (s), 1416 (sh), 1260 (vs) ($v_{s(SO)}$), 1223 (sh), 1153 (s), 1118 (w), 1095 (s), 1051 (m), 1029 (vs) (v_{CF}), 1009 (m), 944 (m), 812 (s), 746 (s), 693 (vs), 637 (vs), 570 (w), 519 (vs) cm⁻¹. ¹H NMR (CDCl₃): δ = 2.3 (s, 3H, CH₃), 6.5 (d, 2H, J_{HH} = 7.7 Hz, C₆H₄), 6.9 (d, 2H, J_{HH} = 7.7 Hz, C₆H₄), 7.2–7.3 (m, 30H, PPh₃), 8.0 (bs, 2H, C₅H₄NCN), 8.2 (bs, 2H/C₅H₄NCN). ³¹P{¹H} NMR (CDCl₃): δ = 19.1.

4.7. Synthesis of 9a

trans-(PPh₃)₂Pd(C₆H₄-4-SC(O)CH₃)(I) (4) (201 mg, 0.22 mmol) is dissolved in a mixture of toluene-dichloromethane (ratio 5:2) (50 mL) and then one equivalent of [AgOTf] (5) (56 mg, 0.22 mmol) is added at 25 °C. After stirring the reaction mixture for 30 min, it is filtered through a pad of Celite. To the thus obtained eluate, 4,4'-bipyridine (7c) (17 mg, 0.11 mmol) is added at 25 °C and the resulting suspension is stirred for 30 min. On addition of 80 mL of *n*-hexane a yellow precipitate is formed. The supernatant solution is decanted and the residue is dried in oil-pump vacuum. Complex **9a** is obtained as a yellow solid. Yield: 192 mg (0.095 mmol, 86% based on **4**).

M.p.: 142 °C (dec.). Anal. Calc. for C₁₀₀H₈₂F₆N₂O₈P₄-Pd₂S₄ (2018.72): C, 59.50; H, 4.09; N, 1.39. Found: C, 59.45; H, 4.02; N, 1.43%. IR (KBr): 3054 (m), 2964 (w), 1702 (s) (v_{CO}), 1636 (s), 1609 (s), 1481 (m), 1435 (s), 1401 (sh), 1265 (vs) (v_{s(SO)}), 1223 (sh), 1154 (s), 1096 (m), 1030 (s) (v_{CF}), 1008 (s), 959 (w), 806 (s), 749 (s), 694 (s), 637 (s), 573 (w), 521 (s) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.2$ (s, 6H, CH₃), 6.5 (d, 4H, $J_{\rm HH} = 8.0$ Hz, C₆H₄), 6.9 (d, 4H, $J_{\rm HH} = 8.0$ Hz, C₆H₄), 7.0 (d, 4H, $J_{\rm HH} = 6.3$ Hz, bipy), 7.2–7.3 (m, 60H, PPh₃), 8.1 (d, 4H, $J_{\rm HH} = 6.3$ Hz, bipy). ³¹P{¹H} NMR (CDCl₃): $\delta = 19.6$. ¹³C{¹H} NMR (CDCl₃): $\delta = 30.0$ (CH₃), 118.6 (^{*i*}C/C₆H₄), 122.4, 123.2 (C₆H₅), 123.7 (ⁱC/C₆H₄), 125.2, 127.4, 127.8, 128.2, 128.9, 129.0, 129.1 (C_6H_4/C_6H_5), 130.8 (^{*i*}C/bipy), 133.7, 133.8, 133.9, 137.3, 137.8, 144.3 (C₆H₅), 148.7 (bipy), 151.9 (bipy), 194.1 (CO).

4.8. Synthesis of 9b

[AgOTf] (5) (62.6 mg, 0.244 mmol) is added to 4 (226.6 mg, 0.244 mmol) in a mixture of toluene and dichloromethane (ratio 5:2) (60 mL) at 25 °C. After 30 min of

stirring, the reaction mixture is filtered through a pad of Celite. Terephthalonitrile (7d) (15.6 mg, 0.122 mmol) is added to the eluate and the resulting suspension is stirred for 30 min. Addition of 80 mL of *n*-hexane affords a colorless precipitate. The solvents are removed by filtration and the residue is dried in oil-pump vacuum. Complex **9b** is obtained as a yellow solid (194 mg, 0.098 mmol, 80% based on **4**).

M.p.: 125 °C (dec.). Anal. Calc. for C₉₈H₇₈F₆N₂O₈P₄-Pd₂S₄ (1990.66): C, 59.13; H, 3.95; N, 1.41. Found: C, 59.45; H, 4.02; N, 1.43%. IR (KBr): 3052 (m), 2275 (m) $(v_{C=N})$, 1700 (s) (v_{CO}) , 1553 (m), 1480 (s), 1466 (s), 1435 (s), 1402 (s), 1266 (vs) (v_{s(SO)}), 1223 (sh), 1187 (w), 1151 (s), 1094 (s), 1051 (m), 1030 (vs) (v_{CF}), 1009 (sh), 998 (m), 943 (w), 849 (w), 807 (s), 751 (s), 693 (vs), 636 (vs), 568 (m), 520 (s), 508 (s) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.4$ (s, 6H, CH₃), 6.5 (d, 4H, $J_{HH} = 8.0$ Hz, C₆H₄), 6.6 (d, 4H, $J_{\rm HH} = 8.0$ Hz, C_6H_4), 7.0 (s, 4H, NCC₆H₄NC), 7.3-7.4 (m, 60H, PPh₃). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta = 20.5$. ¹³C{¹H} NMR (CDCl₃): $\delta = 30.2$ (CH₃), 118.2 (^{*i*}C/ C₆H₄), 122.3, 125.3, 127.6, 127.9, 128.2 (C₆H₅), 128.4, 129.0 (C_6H_4/C_6H_5) , 129.1 $({}^{t}C/C_6H_4CN)$, 129.3 (C_6H_4) , 130.6 (${}^{i}C/C_{6}H_{4}CN$), 131.4 (${}^{i}C/C_{6}H_{4}$), 133.4 ($C_{6}H_{4}CN$), 133.8, 133.9 (C₆H₅), 134.0 (C₆H₄CN), 134.2, 135.9 (C₆H₅), 194.0 (CO).

4.9. Synthesis of 9c

[AgOTf] (5) (56 mg, 0.22 mmol) is added in one portion to 4 (199.2 mg, 0.22 mmol) in a mixture of toluene–dichloromethane (ratio 5:2) (40 mL) at 25 °C. After 30 min of stirring, the reaction mixture is filtered through a pad of Celite. 4,4'-Biphenyldicarbonitrile (7e) (22.3 mg, 0.11 mmol) is added in one portion to the eluate. After 30 min of stirring, 50 mL of *n*-hexane are added, whereby a colourless precipitate is formed. The solvents are removed by filtration and the residue is dried in oil-pump vacuum. Complex 9c is obtained as a colourless solid (197 mg, 0.095 mmol, 87% based on 4).

M.p.: 132 °C (dec.). Anal. Calc. for C104H82F6N2O8-P₄Pd₂S₄ (2066.76): C, 60.44; H, 4.00; N, 1.36. Found: C, 59.99; H, 4.02; N, 1.55%. IR (KBr): 2933 (m), 2260 (m) $(v_{C=N})$, 1702 (s) (v_{CO}) , 1553 (m), 1480 (s), 1468 (sh), 1435 (s), 1398 (w), 1264 (vs) (v_{s(SO)}), 1222 (sh), 1151 (s), 1118 (m), 1095 (s), 1030 (vs) (v_{CF}), 1007 (sh), 947 (w), 825 (m), 804 (s), 747 (s), 693 (vs), 637 (vs), 572 (m), 520 (s), 508 (s) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 2.4$ (s, 6H, CH₃), 6.5 (d, 4H, $J_{HH} = 7.9$ Hz, C_6H_4), 6.6 (d, 4H, $J_{HH} = 8.1$ Hz, C_6H_4CN), 6.7 (d, 4H, $J_{HH} = 7.9$ Hz, C_6H_4), 7.3–7.4 (m, 60H, PPh₃), 7.7 (d, 4H, $J_{\rm HH} = 8.1$ Hz, C₆H₄CN). ³¹P{¹H} NMR (CDCl₃): $\delta = 20.9$. ¹³C{¹H} NMR (CDCl₃): $\delta = 30.0$ (CH₃), 118.8 (^{*i*}C/C₆H₄), 122.9 (C_6H_4CN) , 125.3, 127.7, 128.1 (C_6H_4/C_6H_5) , 128.2 $(^{1}C/$ C_6H_4CN , 128.5 (C_6H_5), 129.1 (C_6H_4), 129.2 (C_6H_5), 129.3 (C₆H₄CN), 130.6 (ⁱC/C₆H₄CN), 131.6 (C₆H₅), 133.2 (C₆H₄), 133.7, 133.8, 133.9, 134.2 (C₆H₅), 135.9 (C₆H₄CN), 193.9 (CO).

5. X-ray structure determination

For data collection of 4 and $4 \cdot CH_2Cl_2$ a Bruker Smart 1K CCD diffractometer with graphite monochromatised Mo K α radiation ($\lambda = 0.71073$ Å) was used. For protection against oxygen and moisture, the preparation of single crystals was preformed in perfluoro alkyl ether (ABCR GmbH&Co KG; viscosity 1600 cSt). Data collection and cell determination has been done with the program SMART [34,35]. For data integration and refinement of the unit cell the program SAINT was used [35]. The space group was determined using the program XPREP [35] and the absorption has been corrected semi-empirically with SADABS [36]. The structure of 4 was solved by direct methods with the program shelxs-97 and refined by full-matrix least-squares procedures on F^2 , using SHELXL-97 [37]. **4** · CH₂Cl₂ crystallised as a non-monohedral twin. Therefore reflections of both domains are separated with the program RLATT [38]. After refinement of the matrices in the program SMART [34,35] integration of the data is performed with fixed matrices and fixed box sizes. With the program GEMINI⁴ a new raw file of the reflections of the first domain is written without reflections overlapping stronger than 0.015 Å. The structure was solved by Patterson methods using SHELXS-97 [37].

All non-hydrogen atoms in **4** and $\mathbf{4} \cdot \mathbf{CH}_2\mathbf{Cl}_2$ were fully refined anisotropically in their local positions. The hydrogen atom positions have been refined with a riding model.

In $4 \cdot CH_2Cl_2$ the dichloromethane and the thioacetate group are disordered and have been refined to split occupancies of 0.47/0.53 (O1–C44) and 0.67/0.23 (CH₂Cl₂), respectively.

5. Supplementary material

The crystallographic data for 4 and $4 \cdot CH_2Cl_2$ have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 280925 (4) and CCDC 280926 ($4 \cdot CH_2Cl_2$). Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1ET, UK [fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

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