Linear homobimetallic palladium complexes with end-capped SC(O)Me units

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ABSTRACT

Rigid-rod structured homobimetallic palladium complexes of type [{*trans*-(Me(O)CS-4-C_6H_4-C_6H_4)(Ph_3P)$_2$Pd}$_2$(μ-N⌒N)](OTf)$_2$ (**8a**, μ-N⌒N = 4,4′-bipyridine, bpy; **8b**, μ-N⌒N = C_5H_4N-CH=N-N=CH-C_5H_4N; **8c**, μ-N⌒N = C_5H_4N-CH=CH-C_6H_4-CH=CH-C_5H_4N; **8d**, μ-N⌒N = C_5H_4N-CH=N-C_6H_4-N=CH-C_5H_4N) were synthesized by the reaction of *trans*-[(Me(O)CS-4-C_6H_4-C_6H_4)(Ph_3P)$_2$Pd](OTf) (**6**) with 0.5 equivalents of N⌒N (**7a**, N⌒N = bpy; **7b**, N⌒N = C_5H_4N-CH=N-N=CH-C_5H_4N; **7c**, N⌒N = C_5H_4N-CH=CH-C_6H_4-CH=CH-C_5H_4N; **7d**, N⌒N = C_5H_4N-CH=N-C_6H_4-N=CH-C_5H_4N) in high yield. Complex **6** was accessible by the subsequent reaction of I-4-C_6H_4-C_6H_4-4′-SC(O)Me (**2**) with [(PPh_3)$_4$Pd] (**3**) to produce *trans*-[(I)(Me(O)CS-4-C_6H_4-C_6H_4)(Ph_3P)$_2$Pd] (**4**) which further reacted with AgOTf (**5**) to give **6**.

The structures of **4** and **8c** in the solid state are reported. Most characteristic for these systems is the square-planer coordination geometry of palladium with *trans*-positioned PPh_3 groups. This automatically positions the iodo ligand and the Me(O)CS-4-C_6H_4-C_6H_4 unit (complex **4**) or the nitrogen donor atoms of the C_5H_4N-CH=CH-C_6H_4-CH=CH-C_5H_4N connectivity and the thio-acetyl group Me(O)CS-C_6H_4-C_6H_4 (complex **8c**) *trans* to each other. In **8c** a Pd–Pd separation of 20.156 Å is typical.

The electrochemical redox behavior of **2**, **4** and **8** is discussed.

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1. Introduction

There is a wide interest in the synthesis of one-dimensional organic and organometallic compounds because they might be of considerable use in, for example, the developing field of molecular electronics [1–4], as conducting wires [5] or as single-molecule insulators [6,7]. From literature reports it appeared that the properties of molecular wires strongly depend on the nature of the redox-active termini and the appropriate rigid-rod shaped connecting spacers [8]. Among them, conjugated end-capped organic thiols have received a great deal of attention because of their intrinsic semiconductor [5] or insulator properties [6], and of their unique capability to form well-ordered monolayers *via* self-assembly on gold or other metal surfaces [9]. The use of redox-active organometallic constituents assembled with all-carbon or heteroatomic π-spacers offer fascinating perspectives for the design and realization of rigid-rod structured species and hence, show several advantages over organic ones [10].

Recently, we got interested in the design of transition metal complexes featuring end-capped thiol or thio-acetyl groups and their use as appropriate precursors for self-assembling on gold sur-

faces [11]. The separation of the metal atoms from each other could, for example, be realized by the different size and length of nitrogen containing Lewis-base connecting units [11].

We here describe the synthesis of MeC(O)S end-capped linear homobimetallic palladium complexes in which the metal atoms are bridged by organic nitrogen containing units of different size. We chose palladium as metal centers because of their ability to form stable metal–carbon and metal–nitrogen bonds and also similar complexes are known, i.e. *trans*-[(C_6H_4-4-SC(O)Me)(Ph_3P)$_2$(X)Pd] (X = halide, OTf) for comparison [12]. Cyclovoltammetric studies of the newly prepared systems are reported as well.

2. Results and discussion

The synthesis protocol developed to prepare the homobimetallic rigid-rod structured palladium complexes [{*trans*-(MeC(O)S-4-C_6H_4-C_6H_4)(Ph_3P)$_2$Pd}$_2$(μ-N⌒N)](OTf)$_2$ (**8a**, μ-N⌒N = 4,4′-bipyridine (bpy); **8b**, μ-N⌒N = C_5H_4N-CH=N-N=CH-C_5H_4N; **8c**, μ-N⌒N = C_5H_4N-CH=CH-C_6H_4-CH=CH-C_5H_4N; **8d**, μ-N⌒N = C_5H_4N-CH=N-C_6H_4-N=CH-C_5H_4N) is illustrated in Scheme 1. The therefore necessary thiols 4-I-C_6H_4-C_6H_4-4′-SC(O)Me (**2**) and *trans*-[(MeC(O)S-4-C_6H_4-C_6H_4)(Ph_3P)$_2$Pd](OTf) (**6**) were synthesized *via* conventional methods as outlined in Scheme 1.

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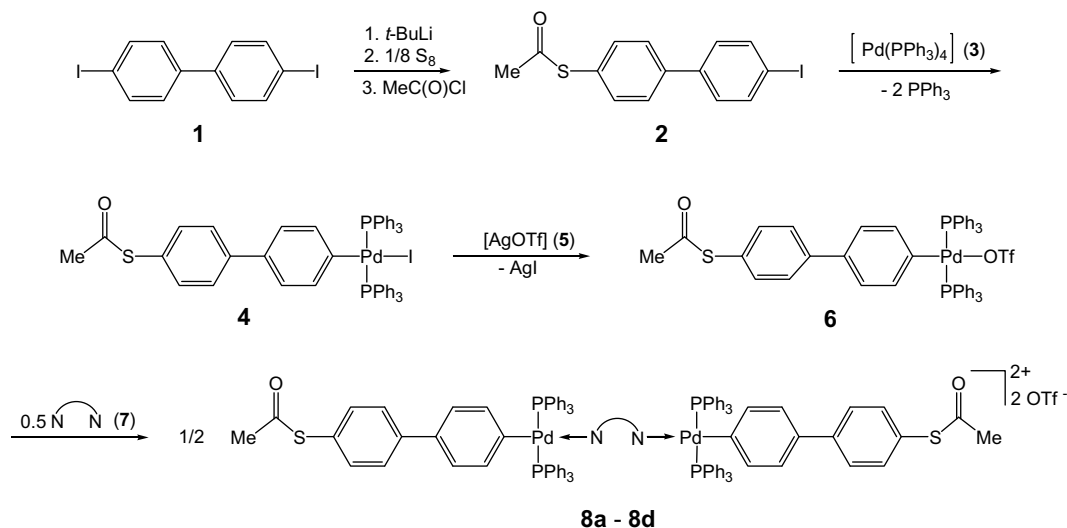
Scheme 1. Synthesis of **2**, **4**, **6** and **8a**–**8d** (Table 1).

4-Iodo-4′-thioacetylbiphenyl (**2**) was accessible by the subsequent reaction of commercially available 4,4′-diiodobiphenyl (**1**) with ^{t}BuLi, 1/8 S_8 and MeC(O)Cl in tetrahydrofuran at low temperature (Scheme 1). After appropriate work-up, thioacetate **2** could be isolated as a colorless solid in 80% yield. Treatment of **2** with a stoichiometric amount of [(PPh$_3$)$_4$Pd] (**3**) in toluene at 25 °C produced by an oxidative addition of the C–I bond to palladium mononuclear trans-[(I)(MeC(O)S-4-C$_6$H$_4$-C$_6$H$_4$)(Ph$_3$P)$_2$Pd] (**4**) as a stable yellow solid in excellent yield (Scheme 1).

For the preparation of **8a**–**8d** it was necessary to exchange the iodo ligand in **4** for a more labile group. Therefore, molecule **4**

was reacted with silver-tetrafluoroborate and -triflate. However, when [AgBF$_4$] was used as a halide abstracting reagent, decomposition of in situ-formed trans-[(MeC(O)S-4-C$_6$H$_4$-C$_6$H$_4$)(Ph$_3$P)$_2$-Pd](BF$_4$) occured even at low temperature. In contrast, treatment of **4** with equimolar amounts of AgOTf (**5**) (TfO = triflate, OSO$_2$CF$_3$) afforded trans-[(MeC(O)S-4-C$_6$H$_4$-C$_6$H$_4$)(Ph$_3$P)$_2$Pd](OTf) (**6**) in a toluene-dichloromethane mixture of ratio 5:2 at 25 °C (Scheme 1). While compound **6** could be handled in solution for a short period of time without any decomposition, it appeared that attempts to isolate **6** in crystalline form failed. Nevertheless, **6** could successfully be converted to the significant more stable homobimetallic complexes **8a**–**8d** by addition of 0.5 equivalents of the Lewis-bases N⌒N (**7a**, N⌒N = 4,4′-bpy; **7b**, N⌒N=C$_5$H$_4$N-CH=N-N=CH-C$_5$H$_4$N; **7c**, N⌒N = C$_5$H$_4$N-CH=CH-C$_6$H$_4$-CH=CH-C$_5$H$_4$N; **7d**, N⌒N = C$_5$H$_4$N-CH=N-C$_6$H$_4$-N=CH-C$_5$H$_4$N) (Scheme 1 and Table 1), whereby the labile OTf ligand in **6** was replaced by the better σ-donor/π-base N⌒N.

Yellow-colored crystals of **8a**–**8d** could be obtained by slow diffusion of n-pentane into a dichloromethane solution containing **8** at room temperature. They are air-, moisture- and temperature-sensitive. Due to their ionic nature, **8a**–**8d** are only soluble in polar organic solvents including tetrahydrofuran and dichloromethane, whereas in acetonitrile, dimethylsulfide and dimethylformamide

Table 1
Synthesis of **8a**–**8d**

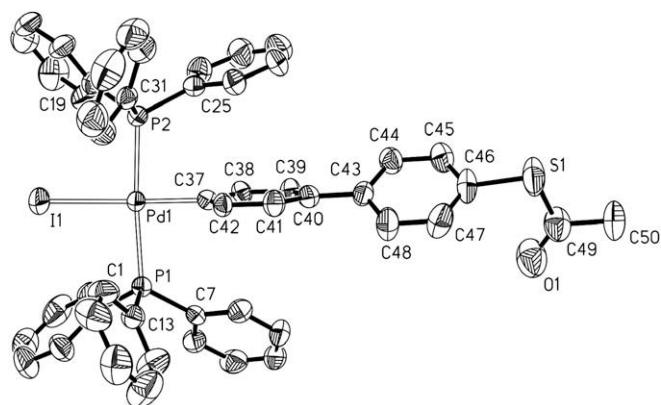| Compound	N⌒N	Yield[a] (%)
8a		75
8b		84
8c		83
8d		81

[a] Based on **4**.

Fig. 1. ORTEP diagram (50% probability level) of the molecular structure of **4** with the atom-numbering scheme. One CH$_2$Cl$_2$ molecule as packing solvent, the hydrogen atoms as well as the disordered atoms O1′ and C50′ have been omitted for clarity.
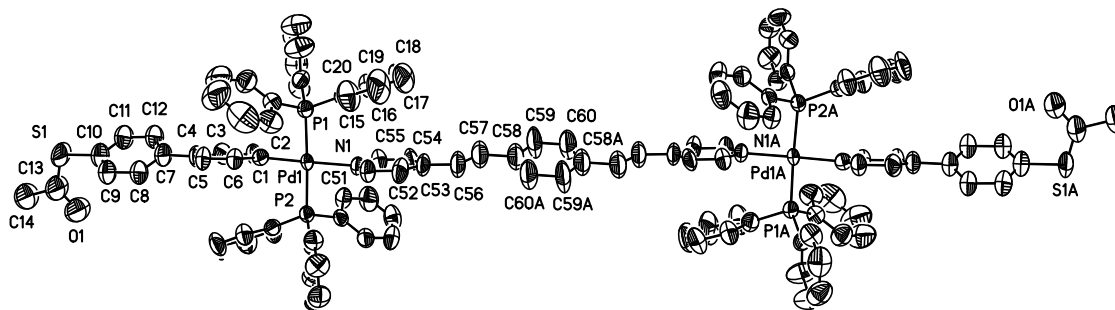
Fig. 2. ORTEP diagram (50% probability level) of **8c** with the geometry and atom-numbering scheme. The two triflate ions, the hydrogen atoms and the disordered atoms of the phenylenethioacetate unit (C7′–C14′, O1′, S1′) have been omitted for clarity. Selected bond distances and angles are given in Table 3.

they rapidly decompose even at low temperature to give black insoluble materials. On the other hand, solid **8a–8d** are stable for months under inert gas atmosphere at −30 °C.

Compounds **2**, **4** and **8a–8d** were characterized by elemental analysis, IR and NMR (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}) spectroscopy. From **4** and **8c** the molecular solid state structures were determined (see below).

The thioacetyl group in **2**, **4** and **8** gives rise to a very characteristic CO stretching vibration at ca. 1700 cm^{-1} [13a]. This band is, as expected, not significantly influenced, when one goes from **2** to **4** to **8**. The triflate ion in **8a–8d** shows a distinct v_{SO} absorption at ca. 1265 cm^{-1} which is in agreement with the *non*-coordinating character of this group [13]. This observation resembles to data found for other transition metal complexes, i.e. {[(dppp)Pd][C$_6$H$_4$-1,4-(C≡N)$_2$]$_2$(OTf)$_2$}$_4$ (1280 cm^{-1}) [13].

The ^{1}H NMR spectra of all complexes exhibit well-resolved resonance signals with the expected coupling pattern for each of the organic groups present (C$_6$H$_4$-C$_6$H$_4$-4-SC(O)Me, C$_6$H$_5$, C$_5$H$_4$N, C$_5$H$_4$N-CH=N, C$_5$H$_4$N-CH=CH, C$_6$H$_4$) (Section 3).

We were not able to obtain appropriate ^{13}C{^{1}H} NMR spectra for **8a–8d**, since these systems are less soluble in common organic solvents (vide supra). In addition, signal overlapping does not unequivocally allow assigning the appropriate resonance signals between 120 and 150 ppm in the ^{13}C{^{1}H} NMR spectra of **2** and

4. However, for the acetyl group two very distinct resonances could be observed at ca. 190 (CO) and 30 (CH$_3$) ppm, respectively.

The ^{31}P{^{1}H} NMR spectrum of **4** in CD$_2$Cl$_2$ consists of a sharp singlet at 22 ppm for the Pd(PPh$_3$)$_2$ unit. Compared with free Ph$_3$P [14] this signal is shifted to lower field, which is representative for the coordination of phosphanes to transition metal atoms. In addition, the ^{31}P{^{1}H} NMR spectra of **8a–8d** are coherent with the formation of single, highly symmetrical species, since only one sharp singlet appeared at ca. 20 ppm, 2 ppm up-field shifted relative to **4**.

Further structural informations for **4** and **8** were obtained by single X-ray structure determination. Slow vapor diffusion of *n*-pentane into a dichloromethane solution containing **4** or **8c** at 25 °C led to the formation of yellow crystals of **4** and **8c**, respectively. The molecular structure of **4** is depicted in Fig. 1, while Fig. 2 contains homobimetallic **8c**. Selected bond distances (Å) and angles (°) are listed in Table 2 (**4**) and Table 3 (**8c**). Crystallographic and structural refinement data are summarized in Table 5 (Section 3).

Complex **4** crystallizes in the monoclinic space group C2/c. The coordination geometry around Pd1 is planar caused by the two

Table 2
Selected bond distances (Å), bond angles (°), and torsion angles (°) for **4**[a]

Bond distances		Bond angles		Torsion angles	
Pd1–C37	2.023(6)	C37–Pd1–P2	86.0(2)	I1–Pd1–C37–C38	−162.5(9)
Pd1–P2	2.337(2)	C37–Pd1–P1	88.0(2)	C41–C40–C43–C44	−140.6(7)
Pd1–P1	2.350(2)	P2–Pd1–P1	172.87(6)	C41–C40–C43–C48	36.7(9)
Pd1–I1	2.6764(8)	C37–Pd1–I1	171.7(2)	C46–S1–C49–C50	174(2)
C46–S1	1.780(7)	P2–Pd1–I1	91.86(5)	S1–C46–C47–C48	174.8(7)
C40–C43	1.484(9)	P1–Pd1–I1	93.53(5)	C46–S1–C49–O1	−13(2)
S1–C49	1.709(9)	C49–S1–C46	103.0(4)	C45–C46–S1–C49	−100.7(7)

[a] The estimated standard deviations of the last significant digit(s) are shown in parentheses.

Table 3
Selected bond distances (Å), bond angles (°), and torsion angels (°) for **8c**[a]

Bond distances		Bond angles		Torsion angles	
Pd1–C1	2.040(9)	C1–Pd1–N1	177.7(4)	C53–C56–C57–C58	−174.6(13)
Pd1–P2	2.350(3)	C1–Pd1–P1	89.0(3)	C3–C4–C7–C8	146.5(15)
Pd1–P1	2.339(3)	P2–Pd1–P1	177.78(9)	C10–S1–C13–O1	5.4(18)
Pd1–N1	2.153(7)	N1–Pd1–P1	90.7(2)	C51–N1–Pd1–C1	160(8)
C10–S1	1.75(2)	C53–C56–C57	131.2(18)		
S1–C13	1.56(2)	C56–C57–C58	130(2)		

[a] The estimated standard deviation(s) of the last significant digit(s) are shown in parentheses.

Table 4
Peak potentials and formal (redox) potentials of **2**, **4** and **8a–8d** (irr. designates a current peak without a corresponding reverse peak)

	$E_{p,ox}$ (Pd(II)/Pd(IV))	$E_{p,ox}$ (S–C(O)Me)	$E_{p,ox}$ (C–I)	$E_{p,red}$	E_0 (μ-N⌒N)	E_0 (μ-N⌒N) [a] ligand **7a–7d** [30]
2	–	1.26 V (irr.)	1.66 V	−1.09 V	–	–
4	0.81 V (irr.)	1.48 V (irr.)	–	–	–	–
8a	0.87 V (irr.)	1.09 V (irr.)	–	–	−1.75 V (irr.)	−2.51 V (ΔE_p = 0.54 V) −3.08 V (ΔE_p = 0.54 V)
8b	0.82 V (irr.)	1.06 V (irr.)	–	–	−1.50 V (ΔE_p = 0.11 V) −1.67 V (ΔE_p = 0.10 V) −1.90 V (ΔE_p = 0.13 V)	−1.92 V (ΔE_p = 0.23 V) −2.30 V (ΔE_p = 0.23 V)
8c	0.74 V (irr.)	1.07 V (irr.)	–	–	−1.50 V (ΔE_p = 0.06 V) −1.70 V (ΔE_p = 0.06 V)	−2.21 V (ΔE_p = 0.35 V) −2.40 V (ΔE_p = 0.33 V)
8d	0.87 V (irr.)	1.16 V (irr.)	–	–	−1.10 V (ΔE_p = 0.29 V) −1.42 V (ΔE_p = 0.15 V) −1.71 V (ΔE_p = 0.16 V)	−2.00 V (ΔE_p = 0.31 V) −2.23 V (ΔE_p = 0.31 V) −2.48 V (ΔE_p = 0.27 V)

[a] Experiments were performed in THF, this explains in part the electrode potential differences.

Table 5
Experimental data for the X-ray diffraction studies of **4** and **8c**

	4	**8c**
Formula	$C_{50.5}H_{42}ClIOP_2PdS$	$C_{61}H_{49}F_3NO_4P_2PdS_2$
Formula weight	1027.59	1149.47
Space group	$C2/c$	$P\bar{1}$
Crystal system	Monoclinic	Triclinic
Z	8	2
a (Å)	21.758(4)	10.8177(10)
b (Å)	10.572(3)	11.0865(11)
c (Å)	39.496(10)	24.632(3)
α (°)	90	87.008(2)
β (°)	99.224(6)	89.541(2)
γ (°)	90	79.414(2)
Volume (Å^3)	8967(4)	2899.5(5)
d_{calc} (g cm^{-1})	1.522	1.316
Temperature (K)	298(2)	298(2)
$F(000)$	4120	1178
μ (Mo Kα) (mm^{-1})	1.317	0.502
Crystal size (mm)	$0.4 \times 0.3 \times 0.3$	$0.4 \times 0.2 \times 0.1$
θ^{min}, θ^{max} (°)	1.90, 25.69	1.66, 25.34
h, k, l (min, max)	−26, 0, 0; 26, 12, 48	−13, −13, −13; 13, 0, 29
No. of total, unique reflections	19425, 8574	23711, 10323
$R_{(int)}$	0.0593	0.0655
R_1 [$I > 2\sigma(I)$], all [a]	0.0610, 0.1024	0.1036, 0.1655
wR_2 [$I > 2\sigma(I)$], all [b]	0.1354, 0.1516	0.2199, 0.2515
S	1.015	1.139
Residual density (e/Å^{-3})	−0.868, 0.825	−1.275, 1.280

[a] $R_1 = \dfrac{\sum ||F_o| - |F_c||}{\sum |F_o|}$

[b] $wR_2 = \sqrt{\dfrac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$ with $w = \dfrac{1}{\sigma^2(F_o^2) + (g_1P)^2 + g_2P}$; $P = \dfrac{(\max(F_o^2, 0) + 2F_c^2)}{3}$

trans-positioned phosphorus atoms P1 and P2, the σ-bonded iodide I1, and C37 of the C_6H_4-C_6H_4-4-SC(O)Me unit (Fig. 1) (r.m.s. deviation of Pd1–P1–P2–I1–C37 is 0.0486 Å). The palladium-bonded phenylene group of the biphenylene unit is thereby nearly perpendicular oriented to the transition metal coordination plane (93.1°), while the second C_6H_4 entity forms an interplanar angle of 37.2°. The Pd1–P1 and Pd1–P2 separations with 2.350(2) and 2.337(2) Å are in the range expected for *trans*-positioned triphenyl phosphine ligands (2.319–2.360 Å) [15–17]. Both, the Pd1–I1 (2.6764(8) Å) and the Pd1–C37 distance (2.023(6) Å) (Table 2) agree well with those separations reported for other

trans-configurated iodo-palladium-carbon units in which likewise the Pd–I bond is *trans* to a C-sp^2 donor atom of high *trans*-influence [15–17].

The structure of **8c** in the solid state confirms the presence of a homobimetallic rigid-rod [{*trans*-(MeC(O)S-4-C_6H_4-C_6H_4)(Ph$_3$P)$_2$Pd}$_2$(μ-C_5H_4N-C=CH-C_6H_4-CH=CH-C_5H_4N)]$^{2+}$ system and two *non*-coordinated triflate ions, while the asymmetric unit of **8c** contains half of the cationic unit and one *non*-coordinated triflate entity. The second part of the molecule is generated by an inversion center in the center of the phenylene group of the connecting unit **7c**. The organometallic dicationic part consists of two planar MeC(O)S-4-C_6H_4-C_6H_4(Ph$_3$P)$_2$Pd moieties and the μ-bridging C_5H_4N-C=CH-C_6H_4-CH=CH-C_5H_4N entity (r.m.s. deviation of Pd1–P1–P2–N1–C1 is 0.0214 Å) (Fig. 2).

The interplanar angle between the two planes defined by the phenylene groups of the MeC(O)S-4-C_6H_4-C_6H_4 moieties is 34.7° which is characteristic for biaryls (for example, the interplanar angle in biphenyl is close to 0° [18a]). In contrast, the biphenyl moiety in **8c** is planar (with significant thermal libration even at low temperature) [18b]. Crystallographic interplanar angles for *para*-nitro-, [18c] -dinitro- [18d], and -dimethylbiphenyl [18e] derivatives exhibit values between 30° and 40°, whereas *para*-dihydroxy-biphenyl is planar in the solid state [18f,18g]. The palladium–nitrogen, palladium–phosphorus and palladium–carbon separations are in the typical range as observed for other palladium organometallic complexes [15,17].

Complex **8c** shows intra- and intermolecular π−π interactions resulting from the aryl ligands (N1, C51–C55 and C15–C20) forming a 2-D layer in the solid state (Fig. 3). As it can been seen from Fig. 3, five aryl rings interact with each other in a sandwich-type arrangement [18h]. Further details are presented in Fig. 4. The arrangement of these five aryl rings is thereby centrosymmetric, with a inversion center in the middle of the central aryl ring C58B–C60BA. The sandwich-type interaction is truncated after the fifth aryl ring at the expense of the formation of T-shaped π−π interactions [18h], as depicted in Fig. 5 together with geometrical details. The situation is further complicated with respect to the disorder of the MeC(O)S-4-C_6H_4-C_6H_4 entity, therefore Fig. 5 includes only one MeC(O)S-4-C_6H_4-C_6H_4 moiety. Between adjacent 2-D layers no further π−π interactions are present.
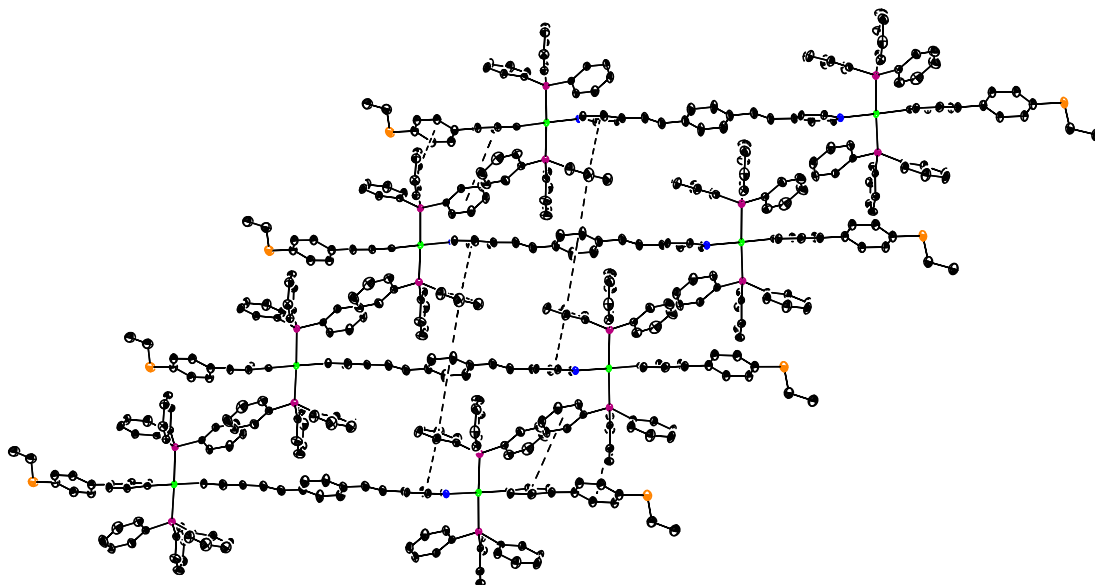

Fig. 3. Part of a 2-D layer of **8c** illustrating the sandwich-type and T-shaped π−π interactions between adjacent molecules. Hydrogen and oxygen atoms, and the triflate anions have been omitted for clarity.

In order to gain a first insight into the electrochemical behavior of the newly synthesized molecules, compounds **2**, **4** and **8a**–**8d** have been subjected to cyclic voltammetry (CV) [19]. Of particular importance is the behavior of molecule **2**, proper understanding of its electrochemistry provides the basis for the assignment of current peaks in **4** and **8a**–**8d** containing **2** as a building block.

A CV of **2** (Fig. 6) in dichloromethane shows two anodic oxidation waves at $E_{p,ox}$ = 1.26 V and $E_{p,ox}$ = 1.66 V, caused by oxidation of the thio-acetyl unit and the C–I unit, respectively, as reported previously for molecule MeC(O)S-4-C_6H_4-C_6H_4-SC(O)Me at $E_{p,ox}$ = 1.16 V and 1.65 V [20].

Oxidation of the thioacetyl-unit has been observed previously in the range $E_{p,ox}$ = 1.3–1.45 V with a selection of similar molecules [21–23], a discussion of the suggested reaction mechanism can be found in Ref. [21]. Oxidation of the iodo substituent has been reported for the structurally closely related 4,4′-diiodobiphenyl [20]. Two current peaks were observed at $E_{p,ox}$ = 1.65 V and at $E_{p,ox}$ = 1.76 V. This spacing implies intramolecular communication resulting in the measured shift of the second oxidation peak to more positive values. The peak potential found in the present study of the "mixed" molecule **2** falls well between the peak potentials observed before. The absence of a significant shift of the oxidation potential implies that the preceding oxidation of the thioacetyl unit has no influence *via* intramolecular communication.
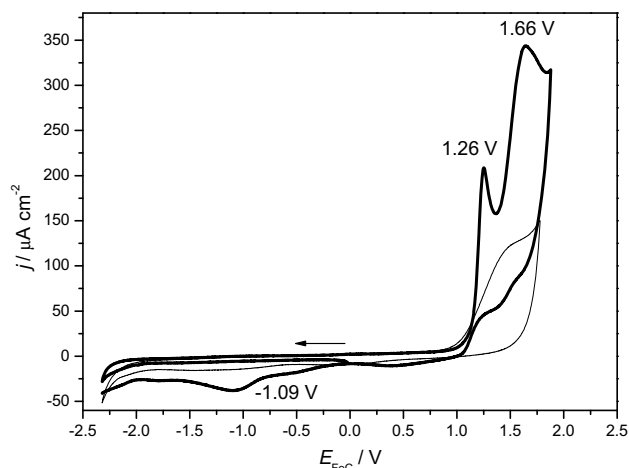

Fig. 6. Cyclic voltammogram of **2** in a solution of [n-Bu$_4$N][PF$_6$] (c = 0.1 mol dm^{-1}) in dichloromethane, 25 °C, argon, scan rate 100 mV s^{-1}, thin line: blank supporting electrolyte solution only.

Scanning from the positive potential limit into the negative direction yields a cathodic peak at $E_{p,red}$ = −1.09 V persisting in multicycle measurements. This peak does not appear, when the
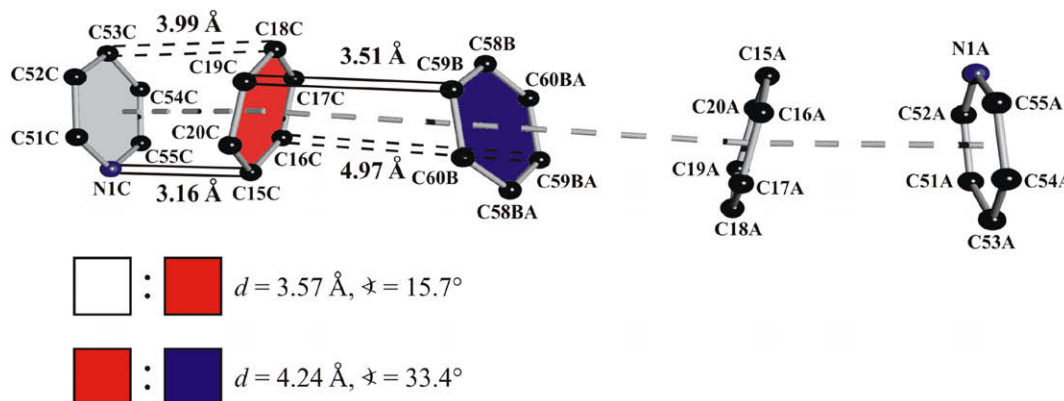

Fig. 4. Geometrical details of the sandwich-type π–π interactions of five aryl rings of **8c** within a 2-D layer. Label "A" refers to atoms of a first, labels "B" and "BA" to atoms of a second and label "C" to atoms of a third molecule of **8c**, with d giving the center-to-center distances as well as the shortest and longest C–C distance of adjacent aryl rings.
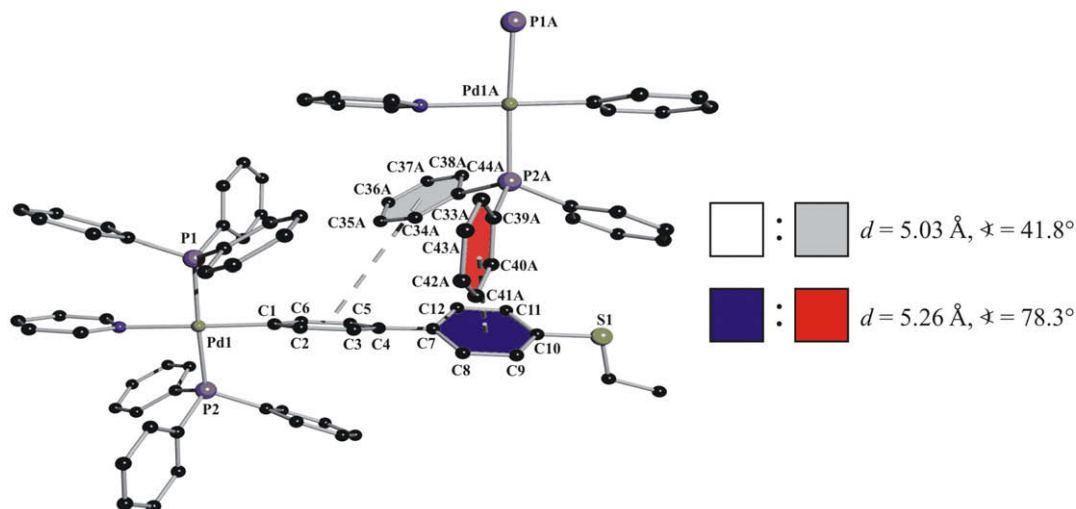

Fig. 5. Geometrical details of the T-shaped π–π interaction [14h] between aryl rings of **8c** within a 2-D layer. Label "A" refers to atoms of a second molecule of **8c**, with d giving the center-to-center distances.
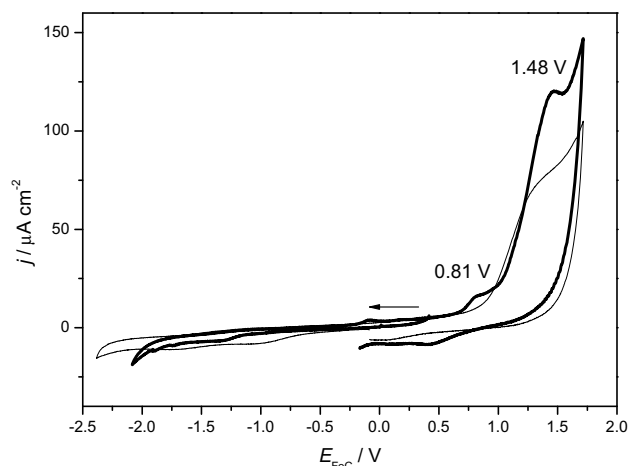
Fig. 7. Cyclic voltammogram of **4** in a solution of $[n\text{-}Bu_4N][PF_6]$ ($c = 0.1$ mol dm^{-1}) in dichloromethane, 25 °C, argon, scan rate 100 mV s^{-1}; thin line: blank supporting electrolyte solution only.

Fig. 8. Cyclic voltammogram of *trans*-$[(Ph_3P)_2Cl_2Pd]$ (bold line) in a solution of $[n\text{-}Bu_4N][PF_6]$ ($c = 0.1$ mol dm^{-1}) in dichloromethane, 25 °C, argon, scan rate 100 mV s^{-1}; thin line: blank supporting electrolyte solution only.

initial scan was performed from the starting potential $E = 0.0$ V into the negative going direction. This implies that the reduction peak at $E_{p,red} = -1.09$ V (Fig. 6) results from species formed by the oxidation of the S–C(O)Me or the I entity. The assignment to the direct reduction of the iodo ligand (as stated with $E_{p,red} = -1.49$ V elsewhere [20]) can be excluded because the peak appears only after a positive going potential excursion. This peak has been observed instead in CV studies of 4-iodo-4′-thioacetylbiphenyl at $E_{p,red} = -1.03$ V confirming the lack of association with I reduction. The suggested reduction of electrooxidation products of the thioacetyl unit has been discussed elsewhere in detail [21].

The CV of mononuclear *trans*-$[(I)(C_6H_4\text{-}C_6H_4\text{-}4\text{-}SC(O)Me)(PPh_3)_2$ Pd] (**4**) (Fig. 7) shows an oxidation current shoulder at $E_{p,ox} = 0.81$ V which can be assigned to the oxidation of Pd(II).

Based on evidence reported elsewhere a transition from Pd(II) to Pd(IV) has to be expected because Pd(III) is unstable [24,25]. Oxidation potentials pertaining to this reaction are scant. An oxidation peak observed in a CV study of $[(PPh_3)_2Hal_2Pd]$ turned out to be caused by the reoxidation of Pd(0) generated in a negative going potential excursion [26], Campora et al. have reported a current peak in CVs of Pd(II) complexes in the range from 1.06 V > $E_{p,ox}$ > 1.24 V[1] which they assigned to the oxidation of Pd(II) to Pd(IV) [27].

With *trans*-$[(Ph_3P)_2Cl_2Pd]$ a CV as displayed in Fig. 8 was obtained, the oxidation of Pd(II) proceeds at $E_{p,ox} = 1.15$ V. The negative going peak at $E_{p,red} = -1.1$ V may indicate reduction of Pd(II) to Pd(0).

The lower oxidation potential observed here can be explained by invoking the higher σ-electron-donating capability of the aryl moiety (and perhaps even the iodo ligand) as compared to the two chloro ligands resulting in a higher charge density at the palladium atom and hence, easier oxidation. The oxidation peak found at $E_{p,ox} = 1.48$ V is assigned to the oxidation of the SC(O)Me group, the upshifted value results from a transfer of charge density to the palladium making oxidation more difficult. The absence of a corresponding reduction peak implies a chemical follow-up reaction resulting in species without redox activity in the scanned potential region.
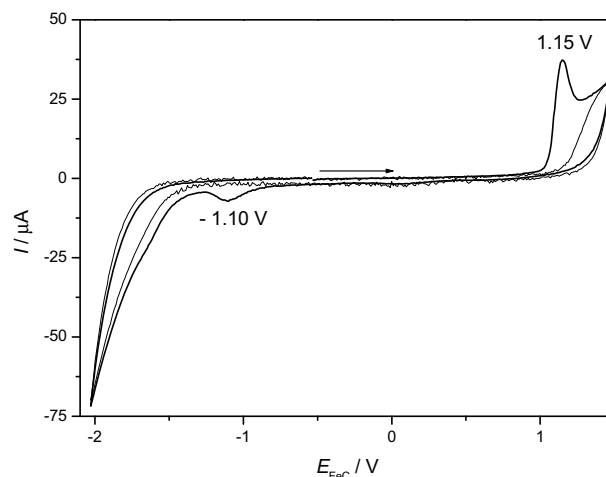
The cyclic voltammograms of **8a–8d** display current shoulders at $E_{p,ox} = 0.87$ and 1.09 for **8a**, 0.82 and 1.06 V for **8b**, 0.74 and 1.07 V for **8c** and 0.87 and 1.16 V for **8d**, respectively (for a complete listing see Table 4). The former peaks can be assigned to the oxidation of palladium(II), the latter to oxidation of the SC(O)Me unit. The palladium oxidation shows a more positive value than with **4** indicating that the palladium atoms in **8a–8d** are more difficult to oxidize which can be explained by the π-donor/acceptor character of the connecting μ-N∩N units. A similar behavior was previously reported for related compounds with similar bridging units between ruthenium ions [28]. In addition, complexes **8a–8d** show, depending on the nature of the bridging N∩N moieties, one to three reduction peaks in the anodic region between −1.10 and −1.75 V. A similar electrochemical behavior was found for $[((PEt_3)_2)_4(\mu\text{-}4,4'\text{-}bpy)_2(\text{anthracenyl})_2Pt]^{4+}$ [29]. The ligand reductions in **8a–8d** are shifted to substantially less negative potentials in comparison with free **7a–7d** (see Table 4) [30]. The differences are consistent with the expected electrostatic stabilization of the negatively charged, reduced forms of the linking units by the coordinated palladium cations [28,31,32].

3. Experimental

General methods. All reactions were carried out in an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen, Germany; H_2O 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 CD_2Cl_2, δ 5.32); $^{13}C\{^1H\}$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to CD_2Cl_2, δ 53.50). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane with the solvent signal as reference signal. $^{31}P\{^1H\}$ NMR were recorded at 101.202 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ 139.0, relative to 85% H_3PO_4, δ 0.00). Cyclic voltammograms (CVs) were recorded in a dried cell, purged with purified argon at 25 °C. Platinum wires served as working and as counter electrode. A calomel electrode served as reference electrode. For ease of comparison, all potentials are converted using the redox potential of the ferrocene-ferrocenium cou-

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[1] In the original report a saturated calomel electrode was used, as a reference the redox process of $[Fe(II)/(III)(\eta^5\text{-}C_5H_4(COMe))_2]$ was used. The potential range given here refers to this redox system, its formal potential may slightly differ from that of the ferrocene/ferrocenium system used throughout this work.

ple FcH/FcH$^+$ (FcH = (η^5-C$_5$H$_5$)$_2$Fe) as reference (E_0 = 0.00 V, ΔE_P = 0.10 V) [33,34]. Electrolyte solutions were prepared from freshly distilled tetrahydrofuran and [n-Bu$_4$N]PF$_6$ (dried in *oil-pump vacuum* at 120 °C). The organometallic complexes were added at c = 1.0 mM. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} using a Radiometer system (VoltaLab 3.1) and a Radiometer Analytical PGZ 100 VoltaLab. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 melting point apparatus. Microanalyses were performed by the Organic Department at Chemnitz, Technical University and the Institute of Organic Chemistry at the University of Heidelberg.

4. General remarks

Chemicals were purchased from commercial suppliers and were used as received.

4.1. Synthesis of **2** (modified procedure Ref. [35])

4,4′-Diiodobiphenyl (**1**) (5.00 g, 12.31 mmol) was dissolved in tetrahydrofuran (300 mL) and *t*-BuLi (14.49 mL, 24.62 mmol, 1.7 M in *n*-pentane) was drop-wise added during 10 min at −78 °C. After stirring this reaction solution at this temperature for 10 min, sulfur (394 mg, 12.31 mmol) dissolved in tetrahydrofuran (75 mL) was drop-wise added and the reaction mixture was allowed to warm to 0 °C and stirred for 45 min at this temperature. The solution was again cooled to −78 °C and acetylchloride (966 mg, 13.31 mmol) was added in one portion. After warming the reaction solution overnight to 25 °C, water (20 mL) was added and the mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over magnesium sulfate. All volatiles were removed by rotary evaporation and the residue was purified by chromatography (column size: 20 × 2.5 cm; Silica gel; *n*-hexane–dichloromethane (ratio 10:3). Removal of the solvents in *oil-pump vacuum* gave **2** as a colorless solid. Yield: 3.5 g (9.88 mmol, 80% based on **1**).

M.p.: 110–112 °C. IR (KBr): 2922 (m), 1904 (w), 1695 (vs) (ν_{CO}), 1475 (s), 1378 (m), 1351 (m), 1260 (m), 1121 (s), 1092 (s), 999 (s), 844 (m), 808 (vs), 762 (s), 693 (w), 679 (w), 618 (s), 555 (w), 526 (w), 496 (w) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 2.4 (s, 3H, CH$_3$), 7.3 (d, 2H, J_{HH} = 8.2 Hz, ^{o}H, C$_6$H$_4$-4-SC(O)CH$_3$), 6.5 (d, 2H, J_{HH} = 8.2 Hz, ^{m}H, C$_6$H$_4$SC(O)CH$_3$), 7.1 (d, 2H, J_{HH} = 8.2 Hz, ^{m}H, I-C$_6$H$_4$), 7.4 (d, 2H, J_{HH} = 8.2 Hz, ^{o}H, I-C$_6$H$_4$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 30.2 (CH$_3$), 93.7 (C–I), 127.3 (^{i}C/C$_6$H$_4$), 127.6 (C$_6$H$_4$), 128.9 (C$_6$H$_4$), 134.9 (C$_6$H$_4$), 137.9 (C$_6$H$_4$), 139.64 (^{i}C/C$_6$H$_4$), 141.2 (^{i}C/C$_6$H$_4$), 194.4 (CO). HRMS calcd. for C$_{12}$H$_{11}$IOS (M$^+$) 354.9515, found 354.965.

4.2. Synthesis of **4**

Compound **2** (405 mg, 1.14 mmol) was dissolved in 50 mL of toluene and one equivalent of [(PPh$_3$)$_4$Pd] (**3**) (1.32 g, 1.14 mmol) was added in a single portion at 25 °C. During 2 h of stirring at this temperature a yellow precipitate formed. All volatiles were removed in *oil-pump vacuum* and the residue was dissolved in dichloromethane (5 mL). *n*-Hexane (60 mL) was added, whereby a yellow solid precipitated. The supernatant layer was decanted and the residue was washed twice with *n*-hexane (20 mL) to gave **4** as a yellow solid. Yield: 0.95 g (0.96 mmol, 85% based on **2**).

M.p.: 154 °C (dec.). Anal. Calc. for C$_{50}$H$_{41}$IOP$_2$PdS (985.20): C, 60.96; H, 4.19; S, 3.25. Found: C, 61.09; H, 4.37; S, 3.87%. IR (KBr): 3050 (m), 1697 (s) (ν_{CO}), 1575 (m), 1477 (s), 1434 (vs), 1401 (m), 1308 (w), 1261 (w), 1185 (w), 1158 (w), 1117 (s), 1095 (sh), 1060 (m), 999 (s), 952 (m), 803 (s), 744 (s), 692 (vs), 618 (s), 519 (vs) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 2.4 (s, 3H, CH$_3$), 6.4

(d, 2H, J_{HH} = 8.2 Hz, ^{o}H, C$_6$H$_4$-C$_6$H$_4$SC(O)CH$_3$), 6.5 (dd, 2H, J_{HH} = 8.2 Hz, $^4J_{HP}$ = 3.9 Hz, ^{m}H, C$_6$H$_4$-C$_6$H$_4$SC(O)CH$_3$), 7.2–7.6 (m, 34H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$ and PPh$_3$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ = 21.7. ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 30.1 (CH$_3$), 125.2 (^{i}C/C$_6$H$_4$), 126.3, 127.2 (C$_6$H$_4$), 127.7 (pt, C$_6$H$_5$, J_{CP} = 4.9 Hz), 129.9 (C$_6$H$_5$), 131.9 (pt, ^{i}C/C$_6$H$_5$, J_{CP} = 23.2 Hz), 134.0 (^{i}C/C$_6$H$_4$), 134.5 (C$_6$H$_4$), 134.9 (pt, C$_6$H$_5$, J_{CP} = 6.4 Hz), 136.0 (pt, C$_6$H$_4$, J_{CP} = 5.0 Hz), 143.5 (^{i}C/C$_6$H$_4$), 159.9 (^{i}C/C$_6$H$_4$), 194.3 (CO).

4.3. Synthesis of **8a**

AgOTf (**5**) (46.6 mg, 0.181 mmol) was added in a single portion to **4** (178 mg, 0.181 mmol) dissolved in toluene–dichloromethane (ratio 5:2) (40 mL) at 25 °C. After 30 min of stirring, the reaction mixture was filtered through a pad of Celite. To this solution **7a** (14.0 mg, 0.090 mmol) was added and the resulting suspension was stirred for 30 min. By addition of 50 mL of *n*-hexane a yellow precipitate formed. The supernatant solution was removed by filtration (canula) and the residue was dried in *oil-pump vacuum*. Complex **8a** was obtained as a yellow solid (147.1 mg, 0.065 mmol, 75% based on **4**).

M.p.: 150 °C (dec.). Anal. Calc. for C$_{112}$H$_{90}$F$_6$N$_2$O$_8$P$_4$Pd$_2$S$_4$ · 0.5 CH$_2$Cl$_2$ (2213.38): C, 61.05; H, 4.14; N, 1.27. Found: C, 60.88; H, 4.17; N, 1.36%. IR (KBr): 3058 (m), 2924 (m), 1706 (s) (ν_{CO}), 1608 (s), 1480 (s), 1434 (s), 1395 (sh), 1269 (vs) (ν_{SO}), 1153 (s), 1098 (s), 1065 (s), 1030 (s) (ν_{CF}), 1000 (s), 804 (s), 749 (s), 691 (s), 636 (s), 520 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 2.4 (s, 6H, CH$_3$), 5.29 (s, 0.5 CH$_2$Cl$_2$), 6.8 (d, 4H, J_{HH} = 7.9 Hz, ^{o}H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$), 6.9 (m, 8H, ^{o}H, C$_6$H$_4$-C$_6$H$_4$SC(O)CH$_3$, C$_5$H$_4$N), 7.2–7.5 (m, 68H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$ and PPh$_3$), 8.2 (m, 4H, ^{m}H, C$_5$H$_4$N). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 19.7. ^{13}C{^{1}H} NMR data could not be obtained, due to the low solubility of **8a** in common NMR solvents.

4.4. Synthesis of **8b**

Compound **4** (181.3 mg, 0.184 mmol) was dissolved in 40 mL of a toluene–dichloromethane mixture of ratio 5:2 and one equivalent of AgOTf (**4**) (47 mg, 0.184 mmol) was added at 25 °C in a single portion. After 30 min of stirring at this temperature, the reaction mixture was filtered through a pad of Celite. To the eluate, **7b** (19 mg, 0.092 mmol) was added at 25 °C and the resulting suspension was additionally stirred for 30 min. After appropriate work-up (see synthesis of **8a**), complex **8b** could be isolated as a yellow solid (168 mg, 0.076 mmol, 82% based on **4**).

M.p.: 155 °C (dec.). Anal. Calc. for C$_{114}$H$_{92}$F$_6$N$_4$O$_8$P$_4$Pd$_2$S$_4$ (2224.96): C, 61.54; H, 4.17; N, 2.52. Found: C, 61.26; H, 4.29; N, 2.58%. IR (KBr): 3054 (s), 2369 (w), 1703 (s) (ν_{CO}), 1609 (m), 1479 (sh), 1476 (s), 1434 (s), 1353 (w), 1266 (vs ($\nu_{s(SO)}$), 1224 (sh), 1152 (s), 1095 (s), 1062 (m), 1028 (vs) (ν_{CF}), 998 (s), 949 (m), 806 (s), 747 (s), 695 (vs), 636 (vs), 570 (sh), 516 (vs) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ = 2.4 (s, 6H, CH$_3$), 6.8 (d, 4H, J_{HH} = 7.9 Hz, ^{m}H, C$_6$H$_4$C$_6$H$_4$-4-SC(O)CH$_3$), 7.0 (d, 4H, J_{HH} = 8.1 Hz, ^{m}H, C$_5$H$_4$N-CH=N-N=CH-C$_5$H$_4$N), 7.2 (m, 8H, ^{o}H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$, C$_5$H$_4$N-CH=N-N=CH-C$_5$H$_4$N), 7.2–7.4 (m, 68H, PPh$_3$, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$), 8.1 (d, 4H, J_{HH} = 8.1 Hz, ^{o}H, C$_5$H$_4$N-CH=N-N=CH-C$_5$H$_4$N), 8.2 (s, 2H, C$_5$H$_4$N-CH=N-N=CH-C$_5$H$_4$N). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ = 19.7. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ = 30.4 (CH$_3$), 127.3 (C$_5$H$_4$N), 127.6 (C$_6$H$_4$), 128.5(C$_6$H$_5$), 128.6 (C$_6$H$_4$), 129.4 (C$_6$H$_5$), 130.9, 134.3 (C$_6$H$_4$), 135.2, 137.2 (C$_6$H$_5$), 151.9 (C$_5$H$_4$N), 194.5 (CO).

4.5. Synthesis of **8c**

Complex **4** (157.9 mg, 0.160 mmol) was dissolved in a mixture of toluene–dichloromethane (ratio 5:2) (40 mL) and then one equivalent of AgOTf (**4**) (41.0 mg, 0.160 mmol) was added in a single portion at 25 °C. After stirring this reaction solution for 30 min

it was filtered through a pad of Celite. To the thus obtained eluate, **7c** (22.8 mg, 0.080 mmol) was added in a single portion at room temperature and the resulting suspension was stirred for additional 30 min. On addition of 50 mL of *n*-hexane a yellow precipitate formed. The supernatant solution was decanted and the residue was dried in *oil-pump vacuum*. Complex **8c** was obtained as a yellow solid (153.0 mg, 0.067 mmol, 83% based on **4**).

M.p.: 160 °C (dec.). Anal. Calc. for $C_{122}H_{98}F_6N_2O_8P_4Pd_2S_4 \cdot CH_2Cl_2$ (2384.01): C, 61.97; H, 4.23; N, 1.18. Found: C, 62.20; H, 4.28; N, 1.30%. IR (KBr): 3053 (m), 2922 (w), 1703 (s) (ν_{CO}), 1606 (s), 1476 (m), 1435 (s), 1401 (sh), 1266 (vs) (ν_{SO}), 1223 (sh), 1152 (s), 1095 (m), 1062 (w), 1029 (s) (ν_{C-F}), 998 (m), 965 (sh), 835 (s), 805 (s), 747 (s), 695 (s), 636 (s), 617 (sh), 559 (m), 518 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.4$ (s, 6H, CH$_3$), 5.29 (s, 0.5 CH$_2$Cl$_2$), 6.8 (m, 8H, ^{o}H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$/^{m}H, C$_5$H$_4$N-CH=CH-C$_6$H$_4$-CH=CH-C$_5$H$_4$N), 7.1 (s, 2H, C$_5$H$_4$N-CH=CH-C$_6$H$_4$-CH=CH-C$_5$H$_4$N), 7.2 (s, 2H, C$_5$H$_4$N-CH=CH-C$_6$H$_4$-CH=CH-C$_5$H$_4$N), 7.3–7.4 (m, 68H, PPh$_3$, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$), 7.6 (s, 4H, C$_5$H$_4$N-CH=CH-C$_6$H$_4$-CH=CH-C$_5$H$_4$N), 7.9 (d, 4H, J_{HH} = 6.8 Hz, ^{o}H, C$_5$H$_4$N-CH=CH-C$_6$H$_4$-CH=CH-C$_5$H$_4$N). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = 19.9$. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = 30.0$ (CH$_3$), 122.2 (C$_5$H$_4$N), 126.8 (C$_6$H$_4$), 127.9, 128.3 (C$_6$H$_5$), 128.7 (C$_6$H$_4$), 128.8 (CH=CH), 130.8 (C$_6$H$_4$), 133.7 (C$_6$H$_5$), 133.9, 134.3 (C$_6$H$_4$), 135.1 (C$_6$H$_5$), 146.2 (CH=CH), 150.7 (C$_5$H$_4$N), 194.1 (CO).

4.6. Synthesis of **8d**

AgOTf (**5**) (39 mg, 0.153 mmol) was added to **4** (150.5 mg, 0.153 mmol) dissolved in a mixture of toluene-dichloromethane in the ratio of 5:2 (40 mL) at 25 °C. After 30 min of stirring, the reaction solution was filtered through a pad of Celite. To the eluate, **7d** (22 mg, 0.076 mmol) was added at 25 °C and the resulting suspension was stirred for additional 30 min. Addition of 50 mL of *n*-hexane afforded a yellow precipitate. The solvents were removed by filtration and the yellow residue was dried in *oil-pump vacuum*. Yield: 142 mg (0.062 mmol, 81% based on **4**).

M.p.: 144 °C (dec.). Anal. Calc. for $C_{120}H_{96}F_6N_4O_8P_4Pd_2S_4$ (2301.06): C, 62.64; H, 4.21; N, 2.43. Found: C, 62.40; H, 4.21; N, 2.43%. IR (KBr): 3054 (m), 2954 (w), 2274 (w), 1705 (s) (ν_{CO}), 1610 (m), 1575 (sh), 1476 (s), 1435 (s), 1351 (w), 1263 (vs) (ν_{SO}), 1223 (sh), 1152 (s), 1096 (s), 1060 (m), 1029 (vs) (ν_{CF}), 998 (s), 805 (s), 747 (s), 694 (vs), 637 (vs), 616 (s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 2.4$ (s, 6H, CH$_3$), 6.8 (d, 4H, J_{HH} = 7.9 Hz, ^{m}H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$), 7.0 (d, 4H, J_{HH} = 7.5 Hz, ^{o}H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$), 7.2 (m, 4H, ^{m}H, C$_5$H$_4$N-CH=CN-C$_6$H$_4$-CN=CH-C$_5$H$_4$N), 7.3–7.6 (m, 68H, C$_6$H$_4$-C$_6$H$_4$-4-SC(O)CH$_3$, PPh$_3$), 8.1 (d, 4H, J_{HH} = 5.9 Hz, ^{o}H, C$_5$H$_4$N-CH=CN-C$_6$H$_4$-CN=CH-C$_5$H$_4$N), 8.2 (s, 2H, C$_5$H$_4$N-CH=CN-C$_6$H$_4$-CN=CH-C$_5$H$_4$N). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta = 19.8$. ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): $\delta = 30.2$ (CH$_3$), 122.7 (C$_5$H$_4$N), 127.1 (C$_6$H$_4$), 128.3 (C$_6$H$_5$), 128.9, 129.0 (C$_6$H$_4$), 129.1, 131.1 (C$_6$H$_5$), 133.7, 134.1 (C$_6$H$_4$), 134.9 (C$_6$H$_4$), 151.7 (C$_5$H$_4$N), 194.3 (CO).

5. X-ray structure determination

The structures of **4** and **8c** in the solid state were determined from single-crystal X-ray diffraction. For data collection a Bruker Smart 1K CCD diffractometer with graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) was used. Crystallographic data of **4** and **8c** are given in Table 4. Data collection and cell determination has been done with the program SMART [36,37]. For data integration and refinement of the unit cells the program SAINT was used. [37] The space groups were determined using the program XPREP [37] and the absorption has been corrected semi-empirically with SADABS [38]. The structures were solved by direct methods with the program SHELX-97 and structure refinement was based on least-square based F^2 using SHELX-97 [39]. All *non*-hydrogen atoms were

fully refined anisotropically in their local positions. The hydrogen atom positions have been refined with a riding model. In **4** the half occupied dichloromethane solvent molecule and the thioacetate substituent are disordered and have been refined to split occupancies of 0.35/0.65 (CH$_2$Cl$_2$) and 0.71/0.29 (O1, C50). In **8c** the triflate ion and the phenylenethioacetate unit are disordered and have been refined to split occupancies of 0.77/0.23 (O$_3$SCF$_3$) and 0.50/0.50 (C7–C14, O1, S1).

Supplementary material

CCDC 679544 and 679545 contains the supplementary crystallographic data for **4** and **8c**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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