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Linear homobimetallic palladium complexes

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Abstract

The oxidative addition of C_6H_4-1,4-I_2 (**1**) to $Pd(PPh_3)_4$ (**2**) gives mononuclear *trans*-$(Ph_3P)_2Pd(C_6H_4$-4-I)(I) (**3**), which can be converted to *trans*-$(Ph_3P)_2Pd(C_6H_4$-4-I)(OTf) (**5**) by its reaction with [AgOTf] (**4**). Complex **5** can be used in the high-yield preparation of a series of unique cationic mono- and dinuclear palladium complexes of structural type $[trans\text{-}(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}I)(L)]^+$ (**7**, L = $C_4H_4N_2$; **9a**, L = C_5H_4N-4-C≡N; **9b**, L = N≡C-4-C_5H_4N) and $[trans\text{-}(C_6H_4\text{-}4\text{-}I)(Ph_3P)_2Pd \leftarrow N^{\frown}N \rightarrow Pd(PPh_3)_2(C_6H_4\text{-}4\text{-}I)]^{2+}$ (**14a**, N⌒N = C_6H_4-1,4-(C≡N)$_2$; **14b**, N⌒N = (C_6H_4-4-C≡N)$_2$; **14c**, N⌒N = 4,4′-bipyridine (=bipy)). Complexes **7**, **9** and **14** rearrange in solution to give $[trans\text{-}(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}PPh_3)(L)]^{2+}$ (**10**, L = $C_4H_4N_2$; **12a**, L = C_5H_4N-4-C≡N; **12b**, L = N≡C-4-C_5H_4N) and $[trans\text{-}(C_6H_4\text{-}4\text{-}PPh_3)(Ph_3P)_2Pd \leftarrow N^{\frown}N \rightarrow Pd(PPh_3)_2(C_6H_4\text{-}4\text{-}PPh_3)]^{4+}$ (**15a**, N⌒N = C_6H_4-1,4-(C≡N)$_2$; **15b**, N⌒N = (C_6H_4-4-C≡N)$_2$) along with $\{[(Ph_3P)_2(Ph_3P\text{-}4\text{-}C_6H_4)Pd(\mu\text{-}I)]_2\}^{2+}$ (**11**).

The solid state structures of **3**, **9a**, **10**, **11** and **15b** are reported. Most characteristic for all complexes is the square-planar coordination geometry of palladium with *trans*-positioned PPh_3 ligands. In **3** the iodide and the 4-iodo-benzene are linear oriented laying with the palladium atom on a crystallographic C_2 axes. In **9a** this symmetry is broken by steric interactions of the PPh_3 ligands with the 4-cyano-pyridine and 4-iodobenzene groups. Compound **11** contains two μ-bridging iodides with different Pd–I separations showing that the $C_6H_4PPh_3^+$ ligand induces a stronger *trans*-influence than PPh_3. In **15b**, the $Ph_3PC_6H_4$—Pd ← N≡C—C_6H_4—C_6H_4—C≡N → Pd—$C_6H_4PPh_3$ building block is rigid-rod structured with the C_6H_4 units perpendicular oriented to the Pd coordination plane, while the biphenylene connecting moiety is in-plane bound.

Keywords: Palladium; Homobimetallic; Lewis-bases; 1-Dimensional complexes; X-ray structure

1. Introduction

There is a wide interest in the synthesis of one-dimensional molecules [1], because they possess considerable attention in, for example, the developing field of molecular electronics [2]. The ability of molecular wires is to transport in a very efficient way electrons through the wire between two redox-active fragments [3]. The properties of such complexes depend on the nature of the redox termini and the π-conjugated linking units [4]. The use of redox-active organometallic building blocks assembled with all-carbon chains [5], or hetero atom consisting units [6], offer a fascinating perspective for the design of nanoscopic molecular devices. However, it appeared that, when the chain length of the bridging unit is increased, the synthesis of the compounds becomes more difficult and the stability of the compounds decreases [6]. Out of this reason, we decided to systematically study homobimetallic late-transition metal complexes in which the organometallic fragments are bridged by π-conjugated nitrogen-containing Lewis-bases of different length [6,7]. This would enable us to prepare in a straightforward manner linear transition metal complexes.

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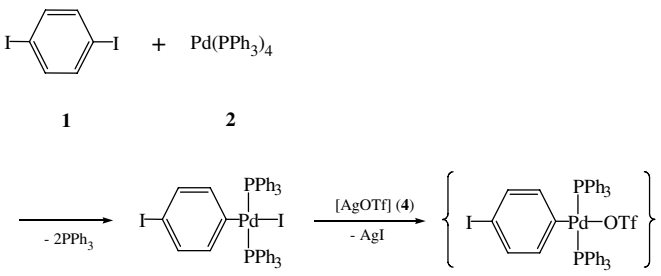
We here report full details for the synthesis, the spectral characterization and X-ray molecular structures of unique mono- and dinuclear palladium species featuring bidentate Lewis-base ligands spanning the appropriate organometallic building blocks.

2. Results and discussion

Mononuclear $[trans\text{-}(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}I)(L)]^+$ (**7**, L = $C_4H_4N_2$; **9a**, L = C_5H_4N-4-C≡N; **9b**, L = N≡C-4-C_5H_4N) and $[trans\text{-}(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}PPh_3)(L)]^{2+}$ (**10**, L = $C_4H_4N_2$; **12a**, L = C_5H_4N-4-C≡N; **12b**, L = N≡C-4-C_5H_4N) as well as homobimetallic $\{[(Ph_3P)_2(Ph_3P\text{-}4\text{-}C_6H_4)Pd(\mu\text{-}I)]_2\}^{2+}$ (**11**), $[trans\text{-}(C_6H_4\text{-}4\text{-}I)(Ph_3P)_2Pd \leftarrow N^{\frown}N \rightarrow Pd(PPh_3)_2\text{-}(C_6H_4\text{-}4\text{-}I)]^{2+}$ (**14a**, $N^{\frown}N = C_6H_4$-1,4-(C≡N)$_2$; **14b**, $N^{\frown}N = (C_6H_4\text{-}4\text{-}C{\equiv}N)_2$; **14c**, $N^{\frown}N$ = 4,4′-bipyridine (=bipy)) and $[trans\text{-}(C_6H_4\text{-}4\text{-}PPh_3)(Ph_3P)_2Pd \leftarrow N^{\frown}N \rightarrow Pd(PPh_3)_2\text{-}(C_6H_4\text{-}4\text{-}PPh_3)]^{4+}$ (**15a**, $N^{\frown}N = C_6H_4$-1,4-(C≡N)$_2$; **15b**, $N^{\frown}N = (C_6H_4\text{-}4\text{-}C{\equiv}N)_2$) can be synthesized from *trans*-$(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}I)(OTf)$ (**5**) (OTf = triflate, OSO_2CF_3). Complex **5** itself is accessible in a two-step synthesis procedure as shown in Eq. (1). An irreversible chemoselective oxidative addition of C_6H_4-1,4-I_2 (**1**) to $Pd(PPh_3)_4$ (**2**) gives the insertion product *trans*-$(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}I)(I)$ (**3**) [8]. The palladium-bonded iodide in **3** can be exchanged for more label triflate to form **5** by the reaction with equimolar amounts of [AgOTf] (**4**) in toluene–dichloromethane mixtures. Complex **3** could be isolated as a colorless crystalline material, while compound **5** could only be prepared in situ, since it is unstable both in solution and in the solid state and decomposes even at low temperature to give a black insoluble precipitate [9].



(1)

Complex **3** was characterized by elemental analysis, ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR and IR spectroscopy (Section 3).

The $^{31}P\{^1H\}$ NMR spectrum of **3** displays a resonance signal at 21 ppm. The key spectroscopic ^1H NMR feature of **3** is that the protons of the C_6H_4-4-I ligand show a doublet-of-doublet (^oH) and doublet (^mH), attributable to the *ortho* and *meta* hydrogen nuclei, magnetically coupled to each other over three bonds (^oH, ^mH) and additionally coupled to the phosphorus nuclei over four bonds (^oH) [10].

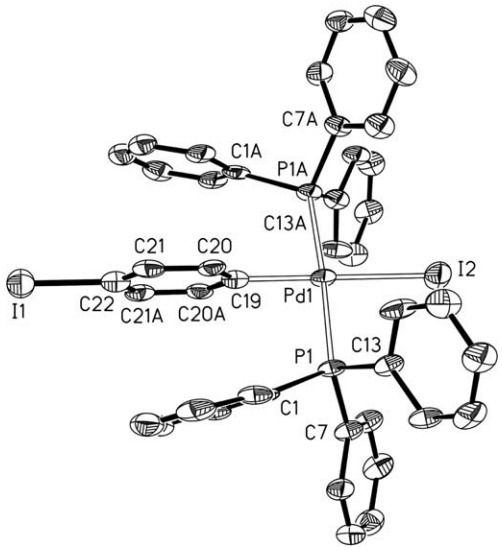
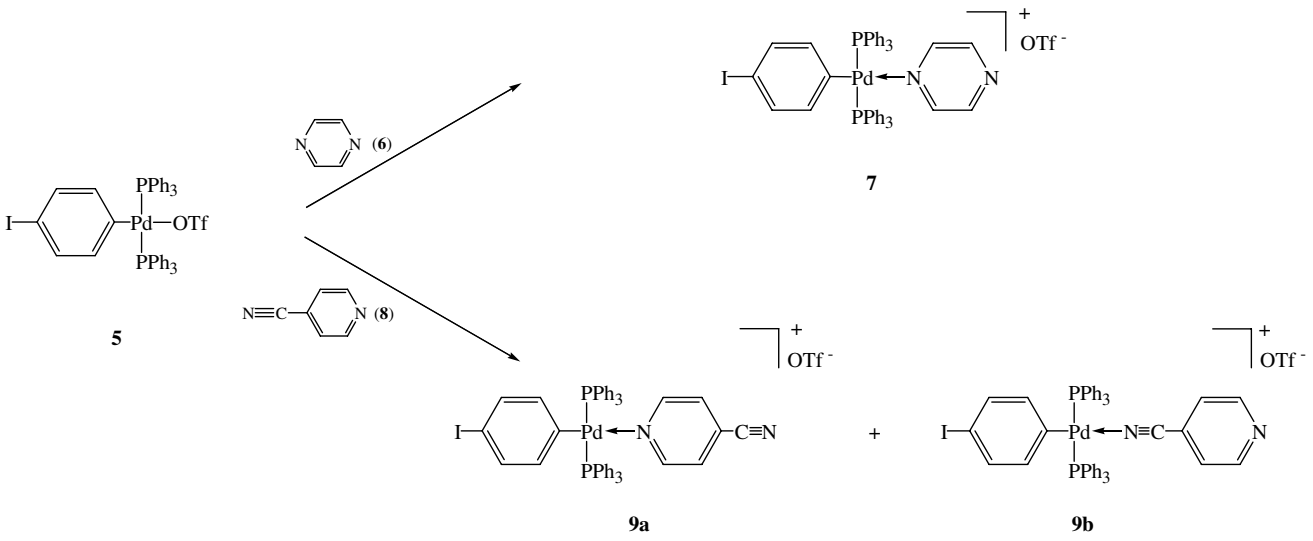


Fig. 1. ORTEP plot (50% probability level) of **3** with the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Pd(1)–P(1) 2.342(2), Pd(1)–P(1A) 2.342(2), Pd(1)–C(19) 2.04(1), Pd(1)–I(2) 2.699(1); and I(2)–Pd(1)–C(19) 180.0, P(1A)–Pd(1)–P(1) 176.6(1), P(1)–Pd(1)–I(2) 91.70(5), P(1)–Pd(1)–C(19) 88.30(5).

Single crystals of **3**, suitable for X-ray diffraction studies could be grown by slow vapor diffusion of *n*-pentane into a dichloromethane solution of **3** at room temperature. The structure of **3** (Fig. 1) shows a perfect square-planar coordination geometry around Pd1 with *trans*-oriented PPh_3 groups. Complex **3** features a C_2 symmetry (symmetry generated atoms are indicated with the suffix A; symmetry code $0.5 - x$, y, $-z$) with the axis lying onto I1, C22, C19, Pd1 and I2. Thus, the benzene ring is exactly perpendicular oriented to the square plane of the palladium coordinated atoms. The Pd1–P1 separation with 2.342(2) Å is in the range expected for *trans*-positioned triphenyl phosphine ligands (2.319–2.342 Å). Both the Pd1–I2 (2.699(1) Å) and the Pd1–C19 distances (2.04(1) Å) (Fig. 1) 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 [11–16].

Complex **5** can successfully be used in the synthesis of mononuclear $[trans\text{-}(Ph_3P)_2Pd(C_6H_4\text{-}4\text{-}I)(L)]^+$ (**7**, L = $C_4H_4N_2$; **9a**, L = C_5H_4N-4-C≡N; **9b**, L = N≡C-4-C_5H_4N). The reaction of **5** with one equivalent of the nitrogen donors $C_4H_4N_2$ (**6**) and C_5H_4N-4-C≡N (**8**) proceeds essentially quantitatively as outlined in Scheme 1. In an attempt to synthesize linear molecules of type $[trans\text{-}(C_6H_4\text{-}4\text{-}I)(Ph_3P)_2Pd \leftarrow N^{\frown}N \rightarrow Pd(PPh_3)_2(C_6H_4\text{-}4\text{-}I)]^{2+}$ ($N^{\frown}N$ = $C_4H_4N_2$, C_5H_4N-4-C≡N) by reacting **5** with 0.5 equiv. of **6** and **8**, respectively, also resulted in the formation of mononuclear **7** and **9**. This can be explained by either steric requirements (solid state structure of **9a**) or electronic effects, since upon coordination of palladium to nitrogen the second nitrogen atom becomes too electron poor to interact with a further palladium atom.

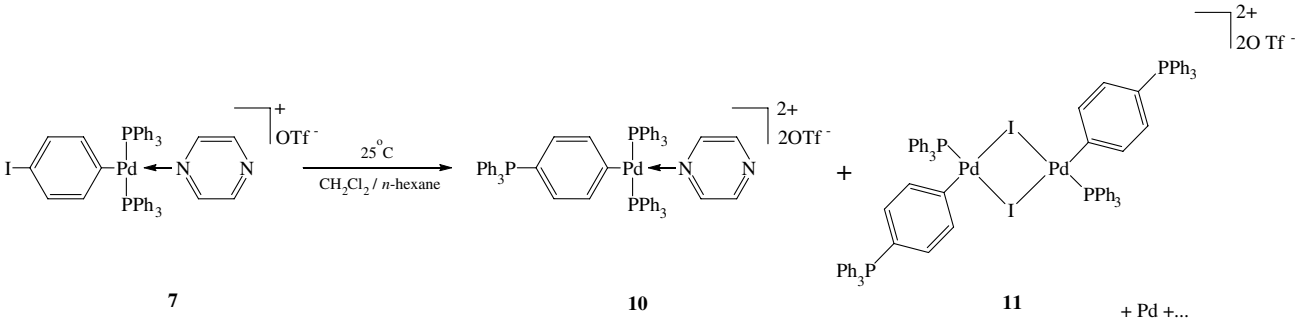


Scheme 1. Synthesis of mononuclear **7**, **9a** and **9b**.

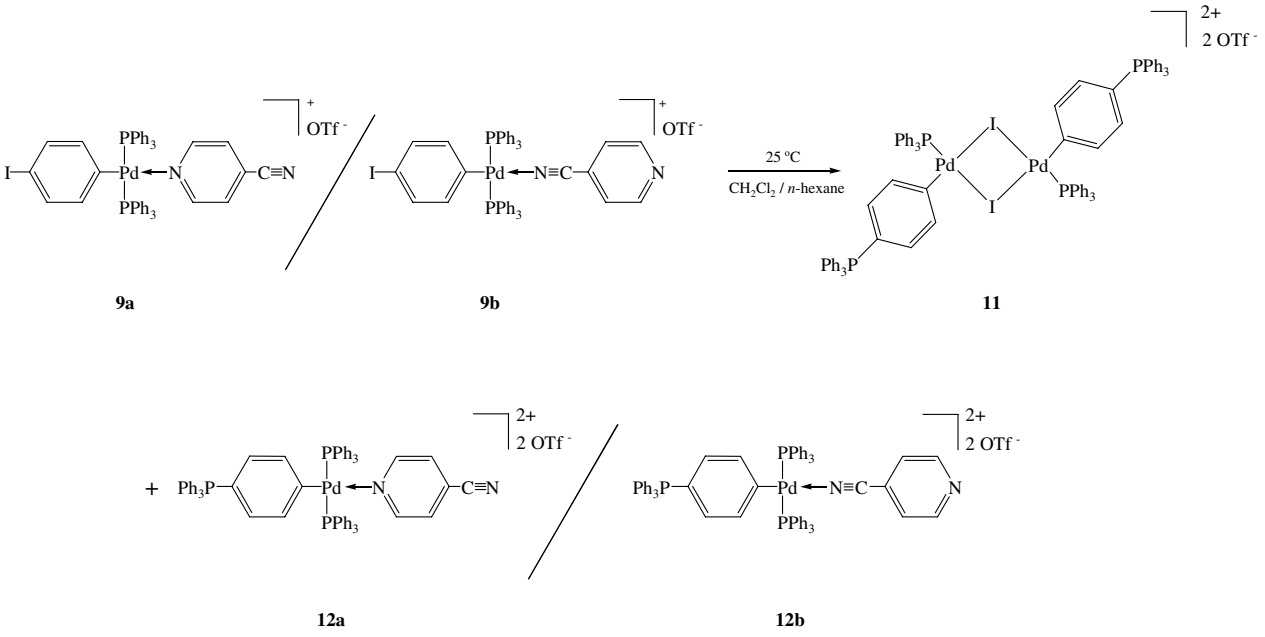
The most noteworthy feature of complex **9** is that it exists as two isomers (**9a** and **9b**) differing in the coordination of the ambident Lewis-base 4-cyanopyridine **8** to palladium (cyano group or pyridine nitrogen atom (Scheme 1)). In an independent study we were able to show that complex **9a**, which preferentially crystallizes in form of colorless single crystals (Fig. 2), rearranges in solution during days to give a mixture of **9a** and **9b**, respectively. The C≡N stretching vibration for **9a** is found at 2244 cm^{-1}, while for **9b**, where the cyano unit is datively bonded to palladium, shows one absorption at 2277 cm^{-1}.

Unequivocal conformation of the proposed structure of **9a** was obtained from a single-crystal structure determination. The molecular structure of **9a** and relevant bond lengths and angles are shown in the legend of Fig. 2. The overall structural features of **9a** are similar to those of related palladium complexes [11,13]. The metal square-plane is slightly distorted and includes *trans*-positioned triphenyl phosphino groups (P1–Pd1–P2 and C1–Pd1–N1 are 173.08(6) and 179.7(2)°). The aromatic rings of the C_6H_4-4-I and C_5H_4N-4-C≡N moieties are, in comparison with **3**, not perpendicular oriented to the palladium coordination plane (78.9° for C_6H_4-4-I and 68.4° for C_5H_4N-4-C≡N). This might be effected by sterical interactions of the benzene rings with the two PPh_3 ligands. The Pd1–C1, Pd1–N1, Pd1–P1 and Pd1–P2 bond distances are in the typical range as reported for similar palladium complexes [12].

Complexes **7** and **9** are not stable in solution at room temperature for a long period of time. We observed that the color of, for example, dichloromethane solutions containing either **7** or **9**, changed during days from pale yellow to orange, whereby elemental palladium precipitated (Eqs. (2) and (3)). After filtration through a pad of Celite and addition of *n*-hexane to the filtrates colorless crystals of $[trans\text{-}(C_6H_4\text{-}4\text{-}PPh_3)(Ph_3P)_2PdL]^{2+}$ (**10**, L = $C_4H_4N_2$; **12a**, L = C_5H_4N-4-C≡N; **12b**, L = N≡C-4-C_5H_4N) are produced. Concentration of the supernatant solution gave crystals of $\{[(Ph_3P\text{-}4\text{-}C_6H_4)(Ph_3P)_2Pd(\mu\text{-}I)]_2\}^{2+}$ (**11**).



(2)



(3)

Due to the ionic character of **10**–**12** they only dissolve in chlorinated solvents. They are air-, moisture- and temperature sensitive.

Most representative for **10** and **12** are their $^{31}P\{^{1}H\}$ NMR spectra, since two resonance signals can be detected at ca. 21 and 27 ppm [17]. This differs from the starting materials **7** and **9**, where only one resonance signal is found (**7**, **9**: 21.2 ppm).

Noteworthy for **10** and **12** is the lowfield shift for the ^{o}H and ^{m}H protons of the C_6H_4, 4-cyano pyridine and pyrazine units in the ^{1}H NMR spectra, when compared with the starting materials **7** and **9**, respectively (Section 3). Further characteristic is the increase of intensity for the PPh_3 protons in **10** and **12** which indicates the presence of a third PPh_3 group and is in agreement with the proposed structures.

The formation of **10**–**12** from **7** and **9** most likely suggests a interchange reaction occurring through a P–C reductive elimination to form the 4-iodo tetraphenyl phosphonium cation followed by irreversible palladium mediated oxidative addition of the C–I bond to palladium(0) as described in Ref. [18].

Crystals of **10** were grown from diffusion of benzene into dichloromethane solutions containing **7**. The solid-state structure and selected bond distances and angles of **10** are given in Fig. 3.

The palladium atom Pd1 is held in a distorted square-planar environment (mean deviation of the atoms Pd1, P2, P3, N1 and C5 from the best plane is 0.1411 Å) with the coordinated pyrazine unit in a position *trans* to C_{ipso} (C5) of the $C_6H_4PPh_3^+$ moiety (Fig. 3). This coordination geometry is typical for molecules containing a $(Ph_3P)_2Pd$ entity [14,16]. A comparison with compound **9a** shows that the angles between the palladium coordinated aromatic rings and the palladium coordination plane are in the same range (84.7° C_6H_4 and 68.6° $C_4H_4N_2$). The Pd1–C5 (1.997(4) Å), Pd1–N1 (2.124(3) Å), Pd1–P2 (2.325(1) Å) and Pd1–P3 (2.345(1) Å) distances are within the range of reported palladium-aryl, coordinated-nitrogen heterocycles and -phosphane bonds [15]. As well, the P1–C8 bond length resembles with 1.782(4) Å to distances characteristic for this type of structural bonding motif [16,18].

Colorless crystals of **11** which are suitable for single X-ray structure determination could be obtained by slow evaporation of chloroform from dissolved **10** at room temperature (vide supra). The result of the X-ray structure

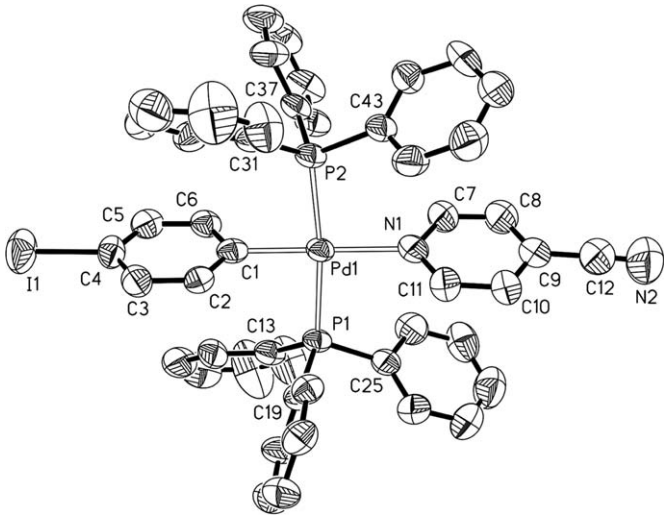


Fig. 2. ORTEP plot (50% probability level) of **9a** with the atom numbering scheme (the hydrogen atoms, the chloroform molecule and the OTf^- ion are omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)–P(1) 2.358(2), Pd(1)–P(2) 2.355(2), Pd(1)–C(1) 2.023(6), Pd(1)–N(1) 2.138(5); and N(1)–Pd(1)–C(1) 179.7(2), P(1)–Pd(1)–P(2) 173.08(6), P(1)–Pd(1)–N(1) 93.0(2), P(1)–Pd(1)–C(1) 87.0(2), N(1)–Pd(1)–C(1)–C(2)–4(44), C(1)–Pd(1)–N(1)–C(11) 17(44).

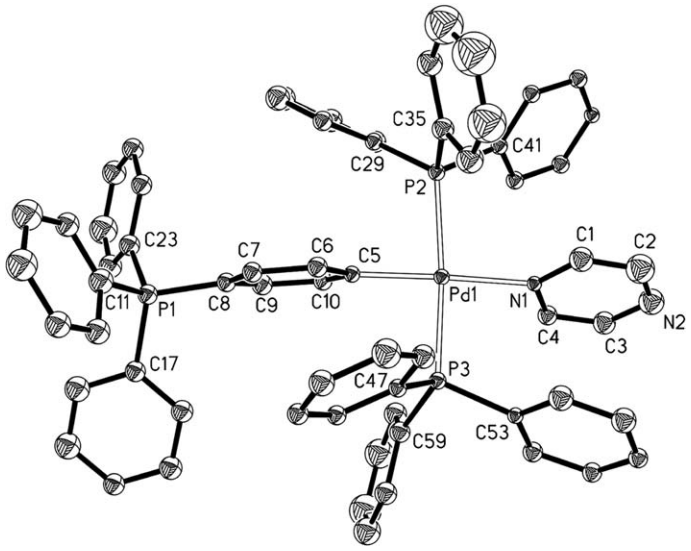


Fig. 3. ORTEP plot (50% probability level) of the asymmetric unit of **10** with the atom numbering scheme (the hydrogen atoms, 1.5 benzene molecules and the two OTf^- ions are omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)–P(2) 2.325(1), Pd(1)–P(3) 2.345(1), Pd(1)–C(5) 1.997(4), Pd(1)–N(1) 2.124(3), P(1)–C(8) 1.782(4); and N(1)–Pd(1)–C(5) 173.5(2), P(2)–Pd(1)–P(3) 167.29(4), P(2)–Pd(1)–N(1) 95.24(9), P(2)–Pd(1)–C(5) 86.2(2), N(1)–Pd(1)–C(5)–C(6) –166.0, C(5)–Pd(1)–N(1)–C(1) –167.7.

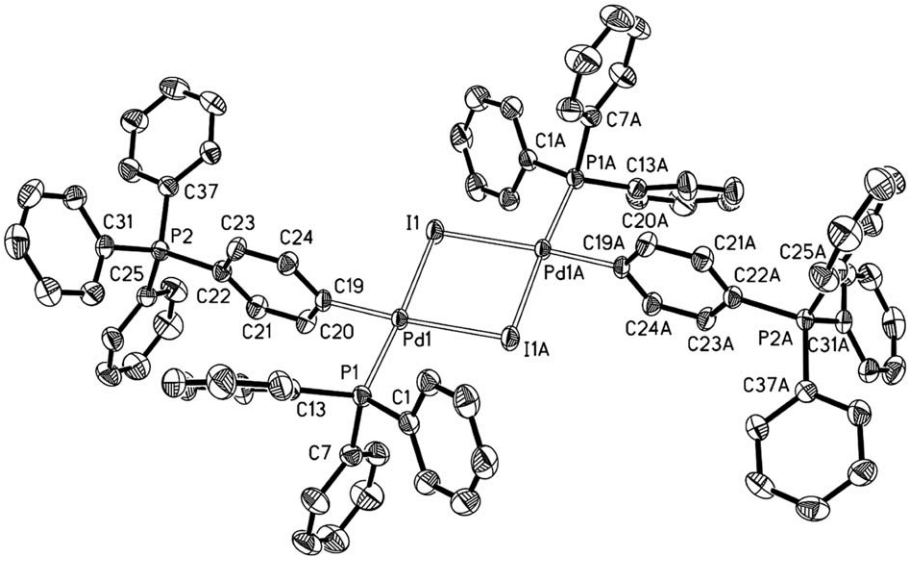


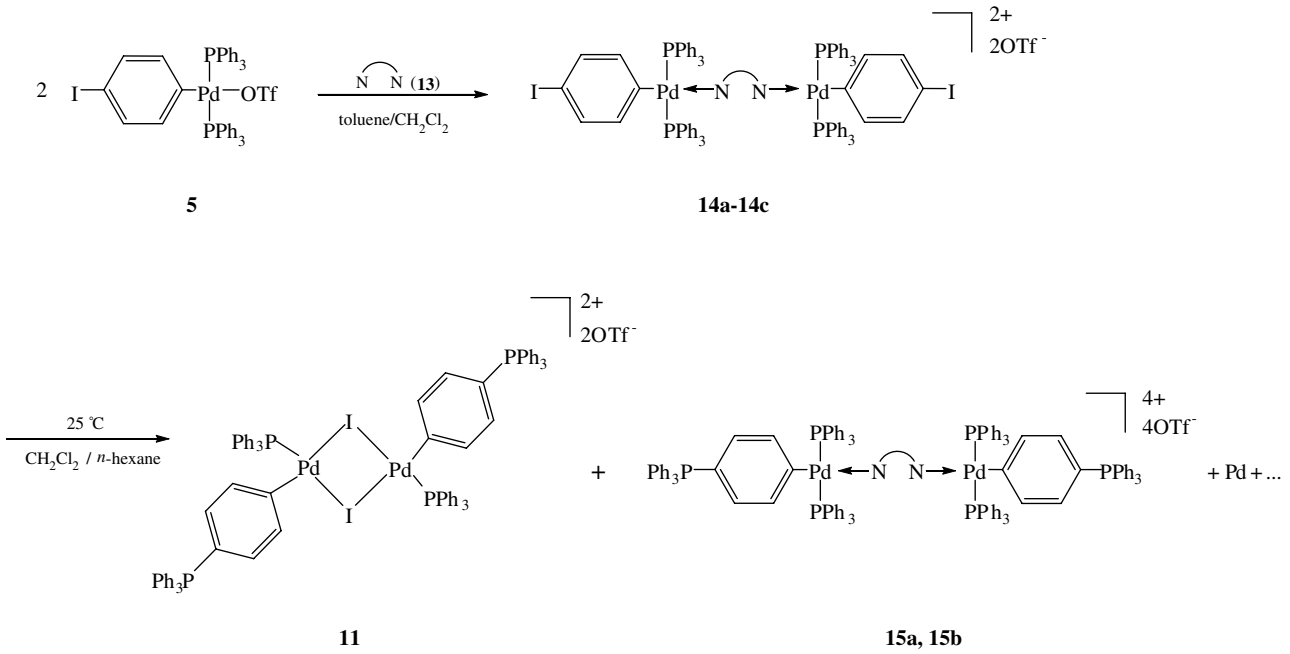
Fig. 4. ORTEP plot (50% probability level) of **11** with the atom numbering scheme (the hydrogen atoms, four chloroform molecules and the two OTf^- ions are omitted for clarity). Selected bond distances (Å) and angles (°): Pd(1)–I(1) 2.6566(3), Pd(1)–I(1A) 2.7088(3), Pd(1)–C(19) 2.005(3), Pd(1)–P(1) 2.2748(7), P(2)–C(22) 1.796(3); and I(1)–Pd(1)–I(1A) 86.367(8), I(1)–Pd(1)–P(1) 176.15(2), I(1A)–Pd(1)–P(1) 97.48(2), I(1)–Pd(1)–C(19) 87.56(8), I(1A)–Pd(1)–C(19) 173.22(8), C(19)–Pd(1)–P(1) 88.60(8), Pd(1)–I(1)–Pd(1A) 93.633(8).

analysis is depicted in Fig. 4; selected bond lengths and angles are presented in the legend to Fig. 4.

The molecule sits on a crystallographic center of symmetry with the asymmetric unit containing one-half of the dimer in *anti*-configuration (Fig. 4). As expected, [*trans*-$(C_6H_4$-4-$PPh_3)(PPh_3)Pd(\mu\text{-}I]_2(OTf)_2$ (**11**) displays almost a ideal square-planar geometry around Pd1. The Pd–I bonds are different, the one *trans* to the carbon C19 (Pd1–I1A 2.7088(3) Å) being longer than the Pd1–I distance *trans* to the phosphine ligand (Pd1–I1 2.6566(3) Å) (Fig. 4). Therefore, the $C_6H_4PPh_3$ group exerts a stronger *trans*-influence than PPh_3. A similar trend has been observed previously for, e.g. [*trans*-$(PPh_3)(Ph)Pd(\mu\text{-}I)]_2$ and [*trans*-(PPh_3)(PhCO)-$Pd(\mu\text{-}I)]_2$ [17–19]. All other bond lengths and angles of **11** are similar to those values found elsewhere [18–20].

The $^{31}P\{^1H\}$ NMR spectrum of **11** shows two resonance signals at 21 and 27 ppm (vide supra) [17,18].

The palladium triflate complex **5** can also be applied in the synthesis of homobimetallic rigid-rod structured [*trans*-$(C_6H_4$-4-I$)(Ph_3P)_2Pd \leftarrow N^{\frown}N \rightarrow Pd(PPh_3)_2(C_6H_4$-4-I$)]^{2+}$ (**14a**, $N^{\frown}N = C_6H_4$-1,4-$(C{\equiv}N)_2$; **14b**, $N^{\frown}N = (C_6H_4$-4-$C{\equiv}N)_2$; **14c**, $N^{\frown}N$ = 4,4′-bipyridine (=bipy) (Scheme 2, Table 1).



Scheme 2. Synthesis of **14a**–**14c** and their conversion to **11**, **15a** and **15b**, respectively.

Table 1
Synthesis of **14** and **15**

Compound	N ⌒ N	Yield[a] (%)
14a	N≡C–C≡N	69
14b	N≡C–C≡N	80
14c	N, N	80
15a	N≡C–C≡N	25
15b	N≡C–C≡N	27

[a] Based on **5**.

Subsequently, 0.5 equiv. of the Lewis-bases N⌒N (**13a**, N⌒N = C_6H_4-1,4-($C{\equiv}N)_2$; **13b**, N⌒N = (C_6H_4-4-$C{\equiv}N)_2$; **13c**, N⌒N = bipy) were added to **5**, whereupon the bridged bis-palladium complexes **14a**–**14c** are formed (Scheme 2). The latter species were identified by multinuclear NMR spectroscopy and elemental analysis (Section 3). In comparison with **5**, the resonance signals for the C_6H_4-I aromatic protons in the ^{1}H NMR spectra of **14a**–**14c** (*d*-chloroform) are shifted upfield, both with retention of the characteristic coupling pattern. Moreover, new resonance signals were observed for the connecting units (1,4-dicyano benzene: singlet at 7.03 ppm; 4,4′-dicyano biphenyl: two doublets at 6.73 and 7.68 ppm with $J_{HH} = 7.9$ Hz; 4,4′-bipyridine: two doublets at 7.03 and 8.13 ppm with $J_{HH} = 6.5$ Hz).

The $^{31}P\{^1H\}$ NMR spectra of **14a**–**14c** (*d*-chloroform) show a singlet at ca. 20 ppm (Section 3).

In the IR spectra of **14a**–**14c** one very characteristic absorption at 1265 cm^{-1} is found, which is consistent with the non-coordinating character of OTf^-. A similar behavior is observed for all other cationic organometallic species discussed earlier. Furthermore, the C≡N stretching vibration of **14a** and **14b** is a most informative spectroscopic tool for monitoring the progress of the reaction of **5** with **13a** and **13b**, respectively. The $\nu_{C\equiv N}$ band is thereby shifted to higher wavenumbers (**14a**: 2269, **14b**: 2260 cm^{-1}) as compared to free **13a** (2234 cm^{-1}) and **13b** (2228 cm^{-1}). This corresponds with the coordination of the cyano unit to a transition metal atom, i.e. {[(dppp)Pd][C_6H_4-1,4-($C{\equiv}N)_2$]$_2$($OTf)_2$}$_4$ [20,21].

However, it appeared that **14a** and **14b**, which are much better soluble than **14c**, rearrange in dichloromethane–hexane mixtures of ratio 2:3 to produce [*trans*-(Ph_3P-4-C_6H_4)($Ph_3P)_2$Pd ← N⌒N → Pd($PPh_3)_2$(C_6H_4-4-PPh_3)]$^{4+}$ (**15a**, N⌒N = C_6H_4-1,4-($C{\equiv}N)_2$; **15b**, N⌒N = (C_6H_4-4-$C{\equiv}N)_2$) along with {[(Ph_3P-4-C_6H_4)($Ph_3P)_2$Pd(μ-I)]$_2$}$^{2+}$ (**11**) (Scheme 2). The formation of **11** and **15** from **14** is similar to that already discussed earlier for **7**/**10** and **9**/**12** (Eqs. (2) and (3)). The characterization of **15a** and **15b** is based on IR and multinuclear NMR studies, whereby the same analytical behavior is found as for **10** and **12** (vide supra and Section 3).

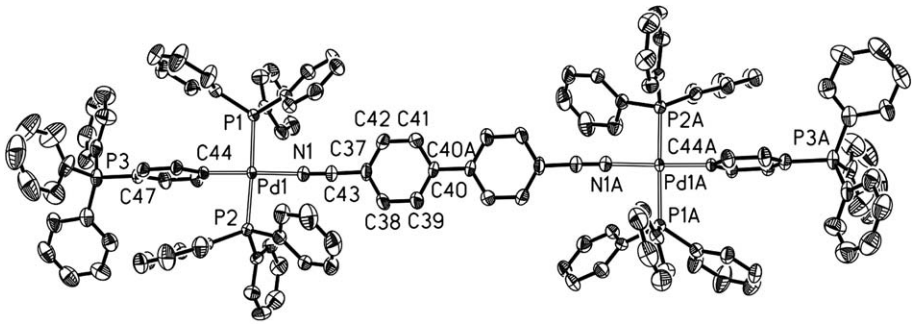


Fig. 5. ORTEP plot (50% probability level) of **15b** with the atom numbering scheme (the hydrogen atoms, two toluene molecules and the four OTf^- ions are omitted for clarity; crystallographic C_2 symmetry with symmetry operation $-x+1, y+1, -z+2$). Symmetry generated atoms are indicated with the suffix A. Selected bond distances (Å) and angles (°): Pd(1)–N(1) 2.082(5), Pd(1)–P(1) 2.334(2), Pd(1)–P(2) 2.338(2), Pd(1)–C(44) 1.993(5), N(1)–C(43) 1.142(8), C(62)–P(3) 1.802(8); and P(1)–Pd(1)–P(2) 173.03(6), N(1)–Pd(1)–C(44) 173.5(3), Pd(1)–N(1)–C(43) 174.1(7), N(1)–C(43)–C(37) 176.1(9).

Single crystals of **15b** could be grown from diffusion of toluene into a dichloromethane solution containing **15b** at 25 °C. The asymmetric unit of **15b** contains half of the cationic part, two non-coordinated triflate ions and a solvent molecule of toluene. In between the two phenylene groups of the connecting 4,4′-dicyanobiphenyl unit is a center of inversion. The molecular structure of **15b** is given in Fig. 5 together with selected bond distances and angles.

The palladium atoms Pd1 and Pd1A display a distorted square-planar coordination mode. As suggested from NMR studies (Section 3) the triphenyl phosphine ligands are positioned *trans* to each other, which automatically positions the nitrogen donor atom of the bridging 4,4′-dicyanobiphenyl *trans* to the C_6H_4 aryl ring of the $C_6H_4PPh_3$ entity (Fig. 5). The phenylene moiety of the $C_6H_4PPh_3^+$ group is perpendicular oriented to the transition metal coordination plane (87.1(2)°), while the biphenyl moiety is in-plane bound (12.8(3)°). The Pd–N, Pd–P and Pd–C separations are in the typical range as for other palladium organometallic complexes [15].

3. Experimental part

3.1. 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). FT-IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer as KBr pellets. NMR spectra were recorded with a Bruker Avance 250 spectrometer, operating in the Fourier transform mode. ^1H NMR spectra were recorded at 250.123 MHz (internal standard, relative to $CDCl_3$, δ 7.26 and CD_2Cl_2, δ 5.32); $^{13}C\{^1H\}$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to $CDCl_3$, δ 77.16 and CD_2Cl_2, δ 53.50). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane (δ 0.00) 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). 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, University of Technology and the Institute of Organic Chemistry at the University of Heidelberg.

3.2. General remarks

Complex **2** [21] was prepared by a published procedure. All other chemicals were purchased from commercial suppliers and were used as received. For complexes **3**, **7**, **9**–**11**, **12**, **14** and **15** no $^{13}C\{^1H\}$ NMR data could be obtained, since these species are less soluble in common NMR solvents.

3.3. Synthesis of 3

To 1,4-diiodobenzene (**1**) (900 mg, 2.73 mmol) dissolved in 50 mL of toluene one equivalent of $Pd(PPh_3)_4$ (**2**) (3.15 g, 2.73 mmol) was added in one portion at 25 °C. During 2 h of stirring at this temperature a white precipitate formed. The supernatant layer was decanted and the residue was washed twice with *n*-hexane (2×20 mL) to gave *trans*-$(Ph_3P)_2Pd(I)(C_6H_4\text{-}4\text{-}I)$ (**3**) as a colorless solid (2.4 g, 2.50 mmol, 92% based on **1**).

M.p.: 188 °C (dec.). Anal. Calc. for $C_{42}H_{34}I_2P_2Pd$ (960.91): C, 52.50; H, 3.57. Found: C, 52.64; H, 3.80%. IR (KBr): 3047 (m), 2961 (m), 1479 (s), 1461 (s), 1433 (vs), 1401 (sh), 1364 (m), 1262 (m), 1182 (s), 1093 (vs), 1067 (s), 998 (vs), 784 (s), 740 (s), 691 (vs), 511 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.2$ (dd, 2H, $J_{HH} = 8.2$ Hz, $^4J_{HP} = 3.8$ Hz, ^{o}H, C_6H_4), 6.4 (d, 2H, $J_{HH} = 8.2$ Hz, ^{m}H, C_6H_4), 7.2–7.3 (m, 18H, $^{o/p}$H, PPh_3), 7.4–7.5 (m, 12H, ^{m}H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.9$.

3.4. Synthesis of 7

[AgOTf] (**4**) (50.0 mg, 0.195 mmol) was added in one portion to **3** (186.9 mg, 0.195 mmol) which was dissolved in a toluene–dichloromethane mixture of ratio 5:2 (40 mL) at 25 °C. After 30 min of stirring, the reaction mixture was filtered through a pad of Celite. Pyrazine (**6**) (15.6 mg, 0.195 mmol) was added in one portion to the reaction solution, and the resulting suspension was stirred for additional 30 min. After addition of 50 mL of *n*-hexane a colorless precipitate formed. The solvents were removed by filtration through Celite and the solid was dried in *oil-pump vacuum*. Yield: 144.8 mg (0.136 mmol, 70% based on **3**).

M.p.: 121 °C (dec.). Anal. Calc. for $C_{47}H_{38}F_3IN_2O_3P_2PdS$ (1063.16): C, 53.10; H, 3.60; N, 2.63. Found: C, 53.55; H, 4.00; N, 2.54%. IR (KBr): 3052 (m), 2286 (w), 1480 (s), 1463 (s), 1435 (s), 1264 (vs) [$\nu_{s(SO)}$], 1223 (sh), 1156 (s), 1097 (s), 1065 (s), 1029 (s) [ν_{C-F}], 993 (s), 820 (m), 797 (s), 748 (s), 694 (s), 636 (s), 573 (m), 518 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.3$ (m, 2H, ^oH, C_6H_4), 6.7 (m, 2H, ^mH, C_6H_4), 7.0 (m, 2H, ^oH, $C_4H_4N_2$), 7.3–7.4 (m, 30H, PPh_3), 8.2 (m, 2H, ^mH, $C_4H_4N_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.2$.

3.5. Synthesis of 9a/9b

To **3** (222.5 mg, 0.23 mmol) dissolved in 40 mL of toluene–dichloromethane (ratio 5:2) one equivalent of [AgOTf] (**4**) (59 mg, 0.23 mmol) was added in one portion at 25 °C. After 30 min of stirring, the reaction mixture was filtered through a pad of Celite. *iso*-Nicotinonitrile (**8**) (23 mg, 0.095 mmol) was added at 25 °C, and the resulting suspension was stirred for 30 min. After appropriate work-up (see synthesis of **7**), **9a/9b** were obtained as colorless solids. Yield: 200 mg (0.184 mmol, 80% based on **3**).

M.p.: 145 °C (dec.). Anal. Calc. for $C_{49}H_{38}F_3IN_2O_3P_2PdS$ (1087.18): C, 54.13; H, 3.52; N, 2.58. Found: C, 53.76; H, 3.87; N, 2.50%. IR (KBr): 3053 (s), 2375 (w), 2276 (w) [$\nu_{C\equiv N}$], 2244 [$\nu_{C\equiv N}$], 1972 (w), 1899 (w), 1822 (w), 1607 (m), 1479 (s), 1434 (s), 1367(w), 1264 (vs) [$\nu_{s(SO)}$], 1154 (s), 1097 (s), 1066 (m), 1029 (vs) [ν_{C-F}], 993 (vs), 839 (w), 796 (m), 747 (vs), 696 (vs), 637 (vs), 515 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.3$ (d, 2H, $J_{HH} = 8.1$ Hz, ^oH, C_6H_4), 6.6 (m, 4H, ^mH, $C_6H_4/^oH$, C_5H_4NCN), 7.2–7.4 (m, 30H, PPh_3), 8.5 (d, 2H, $J_{HH} = 6.2$ Hz, ^mH, C_5H_4NCN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.2$, 21.2.

3.6. Synthesis of 10

Compound **7** (150 mg, 0.141 mmol) was dissolved in 5 mL of dichloromethane at 25 °C and 30 mL of benzene were added as a second layer. On slow diffusion of the two layers during three days, complex **10** crystallized. The supernatant solution was decanted, the remaining colorless crystals were hand-picked and dried in *oil-pump vacuum*. Yield: 60 mg (0.044 mmol, 32% based on **7**).

M.p.: 135 °C (dec.). Anal. Calc. for $C_{66}H_{53}F_6N_2O_6P_3PdS_2 \cdot C_6H_6$ (1332.81): C, 59.48; H, 4.01; N, 2.10. Found: C, 59.71; H, 4.04; N, 1.75%. IR (KBr): 3057 (s), 1552 (m), 1436 (s), 1268 (vs) [$\nu_{s(SO)}$], 1152 (s), 1108 (s), 1030 (s) [ν_{C-F}], 1001 (m), 804 (m), 729 (s), 692 (s), 637 (s), 528 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta = 6.6$ (m, 2H, ^oH, $C_6H_4PPh_3$), 6.7 (m, 2H, ^mH, $C_6H_4PPh_3$), 6.8 (m, 2H, ^oH, $C_6H_4N_2$), 7.3–7.4 (m, 45H, PPh_3), 7.8 (m, 2H, ^mH, $C_6H_4N_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.4$, 27.3.

3.7. Synthesis of 11

Filtration of the supernatant solutions of **10**, **9a/9b**, **15a** or **15b** through Celite and concentration in *oil-pump vacuum* gave colorless **11** (for example, 12 mg, 0.005 mmol, 5% based on **7**; vide supra).

M.p.: 152–153 °C (dec.). Anal. Calc. for $C_{86}H_{68}F_6I_2O_6P_4Pd_2S_2 \cdot 0.5CH_2Cl_2$ (2008.61): C, 51.43; H, 3.41. Found: C, 51.38; H, 3.83%. IR (KBr): 2919 (m), 1627 (m), 1549 (m), 1483 (m), 1439 (s), 1400 (s), 1265 (vs) [$\nu_{s(SO)}$], 1150 (s), 1107 (m), 1030 (s) [ν_{C-F}], 850 (m), 729 (s), 691 (s), 636, 529 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): $\delta = 6.8$ (m, 4H, ^oH, $C_6H_4PPh_3$), 7.3–7.7 (m, 64H, ^mH, $C_6H_4PPh_3$ and PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 21.5$, 27.1.

3.8. Synthesis of 12a/12b

Complexes **9a/9b** were dissolved in 5 mL of dichloromethane and 30 mL of toluene were added as a second layer. After three days crystals of **12a/12b** were obtained. The supernatant solution was decanted and the colorless crystals were hand-picked and dried in *oil-pump vacuum*. Yield: 80 mg (0.031 mmol, 27% based on **9a/9b**).

M.p.: 88 °C (dec.). Anal. Calc. for $C_{68}H_{53}F_6N_2O_6P_3PdS_2.CH_2Cl_2$ (1371.64): C, 59.55; H, 3.90; N, 2.04. Found: C, 59.69; H, 4.13; N, 1.77%. IR (KBr): 3052 (m), 2276 (w), 2188 (w), 1970 (w), 1893 (w), 1606 (m), 1542 (m), 1481 (s), 1464 (s), 1435 (s), 1265 (vs) [$\nu_{s(SO)}$], 1259 (vs), 1223 (s), 1152 (vs), 1097 (vs), 1066 (s), 1029 (s) [ν_{C-F}], 993 (vs), 836 (m), 795 (s), 749 (vs), 693 (vs), 637 (vs), 571 (m), 521 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.3$ (m, 2H, ^oH, $C_6H_4PPh_3$), 6.6 (m, 2H, ^mH, C_6H_4CN), 6.7 (d, 2H, $J_{HH} = 7.5$ Hz, ^mH, $C_6H_4PPh_3$), 7.3–7.7 (m, 45H, PPh_3), 7.7 (d, 2H, $J_{HH} = 7.3$ Hz, ^oH, C_6H_4CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.8$, 27.9.

3.9. Synthesis of 14a

Complex **3** (156 mg, 0.162 mmol) was dissolved in a mixture of toluene–dichloromethane (ratio 5:2) (40 mL). One equivalent of [AgOTf] (**4**) (41.7 mg, 0.162 mmol) was added at 25 °C. After stirring the reaction mixture for 30 min, it was filtered through a pad of Celite. To the eluate, terephthalonitrile (**13a**) (10.4 mg, 0.081 mmol) was added and the resulting suspension was stirred for additional 30 min. On addition of 50 mL of *n*-hexane a colorless precipitate formed. The supernatant solution was decanted

and the residue was dried in *oil-pump vacuum*. Yield: 117.3 mg (0.056 mmol, 69% based on **3**).

M.p.: 120 °C (dec.). Anal. Calc. for $C_{94}H_{72}F_6I_2N_2O_6P_4Pd_2S_2$ (2094.28): C, 53.91; H, 3.47; N, 1.34. Found: C, 54.37; H, 3.34; N, 1.33%. IR (KBr): 2926 (w), 2269 (m) [$\nu_{C\equiv N}$], 1623 (m), 1480 (w), 1435 (s), 1401 (sh), 1265 (vs) [$\nu_{s(SO)}$], 1151 (s), 1096 (m), 1067 (w), 1029 (s) [ν_{C-F}], 994 (m), 797 (s), 749 (s), 693 (s), 636 (s), 519 (s) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.3$ (dd, 4H, $J_{HH} = 8.1$ Hz, $^4J_{HP} = 3.6$ Hz, ^{o}H, C_6H_4), 6.7 (d, 4H, $J_{HH} = 8.1$ Hz, ^{m}H, C_6H_4), 7.0 (s, 4H, C_6H_4CN), 7.3–7.4 (m, 60H, PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.0$.

3.10. Synthesis of *14b*

[AgOTf] (**4**) (59 mg, 0.23 mmol) was added in one portion to **3** (222.5 mg, 0.23 mmol) which was 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 mixture was filtered through a pad of Celite. To the eluate was added 4,4′-biphenyldicarbonitrile (**13b**) (23 mg, 0.095 mmol), and stirring was continued for 30 min. Addition of 50 mL of *n*-hexane afforded a colorless precipitate. The supernatant solution was removed by filtration and the residue was dried in *oil-pump vacuum*. Yield: 200 mg (0.089 mmol, 80% based on **3**).

M.p.: 127 °C (dec.). Anal. Calc. for $C_{100}H_{76}F_6I_2N_2O_6P_4Pd_2S_2 \cdot CH_2Cl_2$ (2255.31): C, 53.23; H, 3.40; N, 1.24. Found: C, 54.30; H, 3.86; N, 1.60%. IR (KBr): 3057 (s), 2260 (m) [$\nu_{C\equiv N}$], 1602 (m), 1482 (s), 1436 (s), 1364 (w), 1399(m), 1268 (vs) [$\nu_{s(SO)}$], 1224 (sh), 1154 (s), s 1096 (s), 1067 (m), 1030 (vs) [ν_{C-F}], 994 (vs), 826 (s), 796 (s), 749 (vs), 694 (vs), 637 (vs), 518 (vs) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.3$ (bd, 4H, $J_{HH} = 7.5$ Hz, ^{o}H, C_6H_4), 6.6 (d, 4H, $J_{HH} = 7.5$ Hz, ^{m}H, C_6H_4), 6.7 (d, 4H, $J_{HH} = 7.9$ Hz, ^{m}H, C_6H_4CN), 7.3–7.9 (m, 60H, PPh_3), 8.8 (d, 4H, $J_{HH} = 7.9$ Hz, ^{o}H, C_6H_4CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.1$.

3.11. Synthesis of *14c*

To **3** (201.2 mg, 0.21 mmol) dissolved in 40 mL of toluene–dichloromethane (ratio 5:2) one equivalent of **4** (53.8 mg, 0.21 mmol) was added at 25 °C. After 30 min of stirring at this temperature, the reaction mixture was filtered through a pad of Celite. To the eluate 4,4′-bipyridine (**13c**) (16.3 mg, 0.105 mmol) was added in one portion and the resulting suspension was stirred for 30 min. After appropriate work-up (see synthesis of **14a**), complex **14c** was obtained as a colorless solid. Yield: 200 mg (0.094 mmol, 80% based on **3**).

M.p.: 158 °C (dec.). Anal. Calc. for $C_{96}H_{76}F_6I_2N_2O_6P_4Pd_2S_2$ (2122.33): C, 54.33; H, 3.61; N, 1.32. Found: C, 53.85; H, 4.03; N, 1.40%. IR (KBr): 2963 (s), 2929 (m), 2858 (m), 1654 (m), 1478 (m) 1432 (s), 1400(s), 1261 (vs) [$\nu_{s(SO)}$], 1094 (sh), 1026 (vs) [ν_{C-F}], 801 (vs), 740 (s), 691 (vs), 637 (m) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.5$ (dd, 4H, $J_{HH} = 8.0$ Hz, $^4J_{HP} = 3.2$ Hz, ^{o}H, C_6H_4), 6.8 (d, 4H, $J_{HH} = 8.0$ Hz, ^{m}H, C_6H_4), 7.0 (d, 4H, $J_{HH} = 6.5$ Hz, ^{m}H, C_6H_5N), 7.2–7.4 (m, 60H, PPh_3), 8.1 (d, 4H, $J_{HH} = 6.5$ Hz, ^{o}H, C_6H_5N). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.9$.

3.12. Synthesis of *15a*

Compound **14a** (200 mg, 0.095 mmol) was dissolved in 5 mL of dichloromethane at 25 °C and 30 mL of benzene were added as a second layer. Single crystals of **15a** grow during five days. The supernatant solution was decanted and the colorless crystals were hand-picked and dried in *oil-pump vacuum*. Yield: 70 mg (0.026 mmol, 28% based on **14a**).

M.p.: 165 °C (dec.). Anal. Calc. for $C_{132}H_{102}F_{12}N_2O_{12}P_6Pd_2S_4$ (2663.19): C, 59.53; H, 3.86; N, 1.05. Found: C, 59.44; H, 4.19; N, 0.96%. IR (KBr): 2997 (s), 2290 (m) [$\nu_{C\equiv N}$], 1637 (m), 1586 (m), 1552 (s), 1481 (s), 1437 (s), 1378 (m), 1267 (vs) [$\nu_{s(SO)}$], 1223 (s), 1191 (m), 1151 (s), 1109 (s), 1049 (m), 1031 (s) [ν_{C-F}], 998 (m), 804 (m), 731 (s), 692 (s), 637 (s), 547 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.8$ (m, 8H, $C_6H_4PPh_3$), 7.3–7.9 (m, 90H, PPh_3), 7.8 (m, 4H, C_6H_4-1,4-$(CN)_2$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.4$, 27.3.

3.13. Synthesis of *15b*

Compound **14b** (200 mg, 0.094 mmol) was dissolved in 5 mL of dichloromethane at 25 °C and 30 mL of benzene were added as a second layer. During 5 days single crystals of **15b** formed. After decanting the supernatant solution, the crystals were hand-picked and dried in *oil-pump vacuum*. Yield: 80 mg (0.028 mmol, 30% based on **14b**).

M.p.: 146 °C (dec.). Anal. Calc. for $C_{145}H_{122}F_{12}N_2O_{12}P_6Pd_2S_4$ (2839.49): C, 61.51; H, 4.06; N, 0.99. Found: C, 60.77; H, 4.18; N, 1.35%. IR (KBr): 3056 (m), 2907 (s), 2280 (m) [$\nu_{C\equiv N}$], 1553 (m), 1432 (s), 1269 (vs) [$\nu_{s(SO)}$], 1223 (s), 1145 (s), 1030 (s) [ν_{C-F}], 801 (s), 796 (s), 695 (s) cm^{-1}. ^1H NMR ($CDCl_3$): $\delta = 6.3$ (dd, 4H, $J_{HH} = 7.5$ Hz, $^4J_{HP} = 3.7$ Hz, ^{o}H, $C_6H_4PPh_3$), 6.6 (d, 4H, $J_{HH} = 7.5$ Hz, ^{m}H, C_6H_4CN), 6.7 (d, 4H, $J_{HH} = 7.6$ Hz, ^{m}H, $C_6H_4PPh_3$), 7.3–7.7 (m, 90H, PPh_3), 7.7 (d, 4H, $J_{HH} = 7.6$ Hz, ^{o}H, C_6H_4CN). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 21.8$, 21.9.

4. X-ray structure determination

The solid-state structures of **3**, **9a**, **10**, **11** and **15b** were determined by 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 are given in Table 2. For protection against oxygen and moisture the preparation of single crystals was performed in perfluoro alkyl ether (ABCR GmbH & Co KG; viscosity 1600 cSt). Data collection and cell determination has been done with the program SMART [22,23]. For data integration and refinement of the unit cell the program SAINT was used [23]. The space group was determined using the program XPREP [23]

Table 2
Summary of crystallographic data for **3**, **9a**, **10**, **11**, and **15b**

	3	**9a**	**10**	**11**	**15b**
Formula	$C_{42}H_{34}I_2P_2Pd$	$C_{50}H_{39}Cl_3N_2F_3IP_2O_3PdS$	$C_{69}H_{56}F_6N_2P_3O_6PdS_2$	$C_{90}H_{72}Cl_{12}F_6I_2P_4O_6Pd_2S_2$	$C_{152}H_{122}F_{12}N_2P_6O_{12}Pd_2S_4$
Formula weight	960.83	1206.48	1386.59	2443.48	2923.38
Space group	*I*2/*a*	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic
Z	4	2	4	1	2
a (Å)	11.431(6)	11.0850(13)	11.1031(5)	13.2529(4)	17.630(2)
b (Å)	13.423(7)	14.5885(17)	18.5170(8)	13.5826(5)	21.776(2)
c (Å)	23.570(15)	16.876(2)	31.2694(13)	15.2062(5)	18.791(3)
α (°)	90	85.705(2)	90	85.8510(10)	90
β (°)	95.131(9)	85.651(2)	98.0750(10)	75.9520(10)	103.760(2)
γ (°)	90	73.064(2)	90	66.6700(10)	90
Volume (Å^3)	3600(1)	2599.2(5)	6365.1(5)	2437.41(14)	7007.1(16)
d_{calc} (g cm^{-1})	1.772	1.542	1.447	1.665	1.386
Temperature (K)	203(2)	298(2)	103(2)	193(2)	203(2)
F(000)	1872	1200	2836	1208	2996
μ (Mo Kα) (mm^{-1})	2.348	1.259	0.504	1.502	0.462
Crystal size (mm)	0.3 × 0.2 × 0.2	0.4 × 0.2 × 0.2	0.52 × 0.03 × 0.03	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.2
θ^{min}, θ^{max} (°)	1.73, 26.37	1.85, 25.35	1.88, 28.28	1.38, 28.38	1.51, 26.47
h,*k*,*l* (min, max)	−14, 0, 0; 14, 16, 29	−13, −17, 0; 13, 17, 20	−14,0,0; 14,24,41	−16,−18,0; 17,18,20	−22,0,0; 21,27,23
No. of total, unique reflections (R_{av})	22516, 3840 (0.1147)	19795, 10527 (0.0605)	48973, 15781 (0.0683)	19060, 11995 (0.0247)	47795, 14794 (0.0827)
N_{ref}, N_{par}	3676, 215	9397, 708	15781, 1030	11995, 559	14362, 898
R_1[a] (*I* > 2σ*I*, all)	0.0769, 0.1004	0.0685, 0.1082	0.0533, 0.0984	0.0368, 0.0520	0.0847, 0.1351
wR_2[b] (I > 2σI, all)	0.1901, 0.2047	0.1656, 0.1951	0.1224, 0.1469	0.0870, 0.0931	0.1993, 0.2254
S	0.970	1.031	1.038	1.042	1.049
Residual density (e/Å^3)	−2.271, 4.058	−1.279, 1.360	−0.836, 1.706	−0707, 0.905	−0.711, 2.058

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

[b] $wR2 = \sqrt{\frac{\sum w(F_o^2-F_c^2)^2}{\sum w(F_o^2)^2}}$ with $w = \frac{1}{\sigma^2(F_o^2)+(g_1P)^2+g_2P}$; $P = \frac{(\max(F_o^2,0)+2F_c^2)}{3}$.

and the absorption has been corrected empirically with SADABS [24]. The structure was solved by direct methods with the program SHELX 97 and structure refinement was based on least-square based F^2 using SHELX 97 [25].

All non-hydrogen atoms were fully refined anisotropically in their local positions. The positions of the hydrogen atoms in **3**, **9a**, **11** and **15b** have been refined with a riding model. In **10** the hydrogen atom positions of the main molecule have been taken from the difference Fourier map and refined freely. Others have been refined with a riding model.

In **9a** the chloroform and the triflate counter anion are disordered and have been refined to split occupancies of 0.52/0.16/0.32 ($HCCl_3$), 0.75/0.25 (SO_3) and 0.33/0.67 (CF_3), respectively. In **15b** the toluene solvent molecule is disordered and has been refined to a split occupancy of 0.42/0.58.

5. Supplementary material

Crystallographic data for the structural analyses of **3**, **9a**, **10**, **11** and **15b** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 611486 for **3**, CCDC No. 611487 for **9a**, CCDC No. 611488 for **10**, CCDC No. 611489 for **11** and CCDC No. 253279 for **15b**. 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; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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