Cyclopalladated compounds with a bidentate [C, N]/terdentate [C, N, S] benzylidenethiophene imine ligand. Crystal and molecular structures of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(μ-OAc)]$_2$, [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}–(Cl)·(PPh$_3$)] and [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)]

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Abstract

Reaction of the Schiff base ligand 2,3-(MeO)$_2$C$_6$H$_3$C(H)=NCH$_2$(C$_4$H$_3$S) (1), with palladium(II) acetate in toluene gave the dinuclear cyclometallated complex [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(μ-OAc)]$_2$ (2), with the ligand bonded to the palladium atom through the imine nitrogen and the C6 carbon atom. The X-ray crystal structure of complex 2 is described. The reaction of 2 with aqueous sodium chloride gave the chloro-bridged complex [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(μ-Cl)]$_2$ (3), after a metathesis reaction. Reaction of 3 with PPh$_3$ in acetone gave the mononuclear cyclometallated complex [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(Cl)(PPh$_3$)] (4), in a bridge-splitting reaction. Treatment of 4 with silver triflate gave the cyclometallated complex [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(PPh$_3$)][CF$_3$SO$_3$] (7), with the palladium atom bonded to four different atoms C, N, S and P. Reaction of 3 with the diphosphines dppp and dppb in a 1:1 molar ratio gave the dinuclear cyclometallated complexes [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$)] (5: $n=3$; 6: $n=4$), with the diphosphine bridging the two palladium atoms. The X-ray crystal structures of complexes 4 and 6 are reported. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: C–H activation; Cyclometallation; Phosphorus ligands; Schiff bases; Palladium

1. Introduction

Cyclometallated compounds [1–5] involve σM–C bond formation and additional coordination of the metal atom to a suitable ligand donor atom. Currently they show a wide range of applications in organic and organometallic chemistry [6]. We have studied the synthesis and reactivity of cyclometallated complexes derived from ligands bearing more than one donor atom, i.e. [C, N, O] [7,8] and [C, N, N] [9–12] terdentate ligands; more recently we have dealt with potentially [C, N, S] terdentate ligands and we have shown that reaction of palladium(II) and platinum(II) salts with thiosemicarbazones yields cyclometallated complexes with an unusual tetranuclear structure (Scheme 1, I) [13,14]. However, treatment of the related Schiff base ligands with palladium(II) acetate gave complexes with a mononuclear structure (Scheme 1, II) [15].

In both cases, the ligand was coordinated through the carbon, nitrogen and sulfur atoms. In the present paper we report the chemistry of the Schiff base 2,3-

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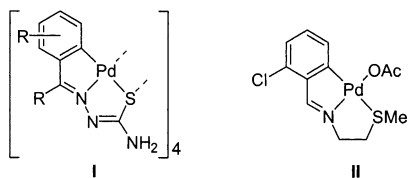
Scheme 1.

$(MeO)_2C_6H_3C(H)=NCH_2(C_4H_3S)$ (1), a potentially bidentate [C, N]/terdentate [C, N, S] ligand. The reaction of 1 with palladium(II) acetate yielded the dinuclear cyclometallated complex showing the characteristic folded structure with acetato-bridging ligands, 2, in which 1 is only [C, N] bonded and the sulfur atom is not prone to bind directly to the palladium atom in contrast to other sulfur-bearing ligands; however, this may be achieved by creating a vacant coordination site by treatment of the corresponding complex with a Ag(I) salt, as is shown for the chloro-bridged derivative. We also report the reactivity of the chloro-bridged complex 3 with tertiary mono- and diphosphines and the crystal structures of two of these compounds are described.

2. Results and discussion

2.1. Preparation of the cyclometallated complexes

The compounds and reactions are shown in Scheme 2. The compounds described in this paper were characterized by elemental analysis (C, H, N) and by IR spectroscopy and by ^1H, $^{31}P\{^1H\}$ and, in part, $^{13}C\{^1H\}$-NMR spectroscopy and FAB mass spectrometry (data in Section 3).

Reaction of the Schiff base ligand 2,3-$(MeO)_2C_6H_3C(H)=NCH_2(C_4H_3S)$ (1), with palladium(II) acetate in toluene gave the dinuclear cyclometallated complex $[Pd\{2,3-(MeO)_2C_6H_2C(H)=NCH_2(C_4H_3S)\}(\mu-OAc)]_2$ (2), which was fully characterized. The IR spectrum of 2 showed the $v(C=N)$ stretch at 1609 cm^{-1}, shifted to lower wavenumbers (as compared to the free ligand) due to N-coordination of the imine [16,17]. The IR spectrum also showed strong bands assigned to the symmetric and asymmetric $v(COO)$ vibrations, in agreement with those expected for bridging acetate ligands [18] (see Section 3). The ^1H-NMR spectrum showed the resonance corresponding to the HC=N proton at δ 7.55, shifted to lower frequency, confirming coordination of the ligand through the lone pair of the nitrogen atom [19]. The absence of the signal due to the H^6 proton showed that metallation had occurred at the C6 carbon. The signals assigned to the diastereotopic CH$_2$ protons, consequent on the folded arrangement of the acetato-bridged dimmers, appeared at δ 4.10 and 4.71 [$J_{(HH)} = 16.6$ Hz]. The low-field shift of the signals assigned to the C1, C6 and CH=N carbon

atoms in the $^{13}C\{^1H\}$ spectrum confirmed metallation [9,15]. The FAB mass spectrum of 2 showed a cluster of peaks, centered at 852 amu which corresponded to [M]$^+$. The isotopic pattern is in good agreement with the expected dinuclear structure.

Treatment of 2 with aqueous sodium chloride gave the chloro-bridged complex $[Pd\{2,3-(MeO)_2C_6H_2C(H)=NCH_2(C_4H_3S)\}(\mu-Cl)]_2$ (3), which was fully characterized (see Section 3). The IR spectrum showed the absence of the $v(COO)$ bands. A singlet resonance in the ^1H-NMR spectra at δ 8.08 was assigned to the HC=N proton. The signals corresponding to the H^4 and H^5 protons appeared as doublets at δ 6.98 and 6.70. The FAB mass spectra showed a peak at 765 amu assigned to the [M−Cl]$^+$ fragment.

2.2. Molecular structure of $[Pd\{2,3-(MeO)_2C_6H_2C(H)=NCH_2(C_4H_3S)\}(\mu-OAc)]_2$ (2)

Suitable crystals were grown by slowly evaporating a chloroform/*n*-hexane solution of the complex. The molecular structure is illustrated in Fig. 1. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 2.

The structure consists of dimeric molecules separated by van der Waals distances. In each monomeric unit the palladium atom is bonded to a phenyl carbon atom, the imine nitrogen of the Schiff base ligand and to two oxygen atoms of the acetato bridging ligands. The Pd(1)–Pd(2) distance of 2.877(1) Å, similar to values found earlier [20], precluded any interaction between the metal atoms. The geometry about the palladium atom can be regarded as slightly distorted square-planar. The sum of angles at the palladium atoms is approximately 360°. The angles between adjacent atoms in the coordination sphere are close to the expected value of 90°; the most noticeable distortion corresponds to the C(1)–Pd(1)–N(1) and C(19)–Pd(2)–N(2) angles of 81.5(1) and 81.3(1)°, respectively, consequent upon chelation. The Pd(1)–C(1) and Pd(2)–C(19) bond distances of 1.967(3) and 1.964(3) Å, respectively, are somewhat shorter than the values predicted from their covalent radii [21] but similar to values found earlier [20,22]. However, the Pd(1)–N(1) and Pd(2)–N(2) bond lengths of 2.023(2) and 2.014(2) Å, respectively, are in agreement with the value based on the sum of covalent radii for nitrogen and palladium [21] and similar to values reported previously [20,22]. The differing Pd(1)–O(3) and Pd(1)–O(5) [2.051(2) and 2.132(2) Å, respectively] and Pd(2)–O(6) and Pd(2)–O(4) [2.029(2) and 2.146(2) Å, respectively] bond distances reflect the higher *trans* influence of the aryl carbon as compared to the imine nitrogen atom.
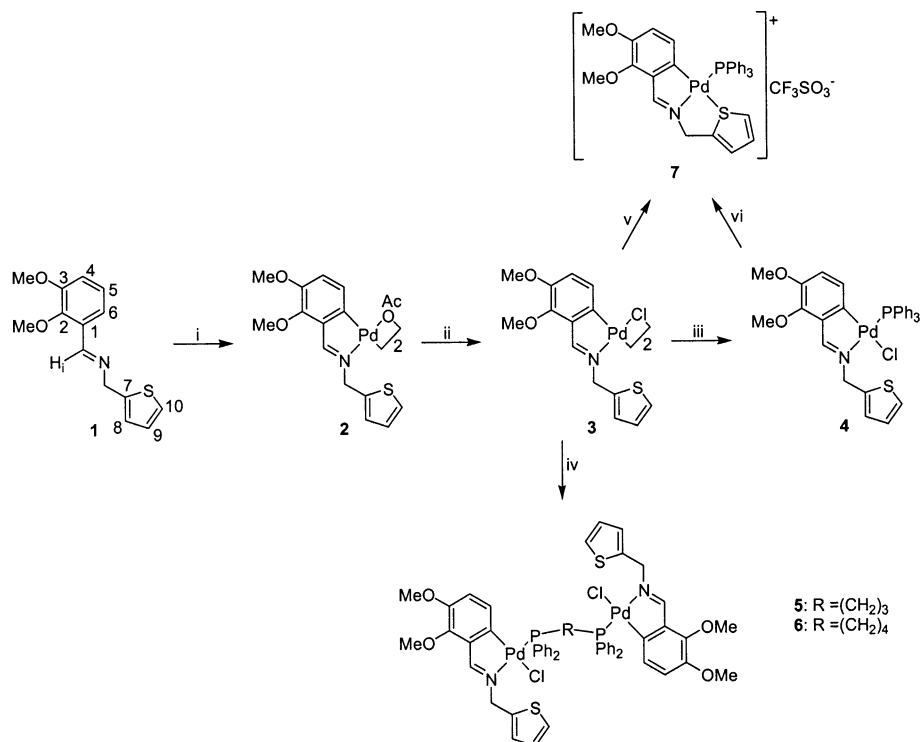
Scheme 2. (i) Pd(AcO)$_2$ (toluene); (ii) NaCl (acetone/water); (iii) PPh$_3$ (acetone); (iv) dppp or dppb (acetone, 1:1 molar ratio); (v) (1) AgCF$_3$SO$_3$; (2) PPh$_3$ (acetone); (vi) AgCF$_3$SO$_3$ (acetone)

2.3. Reactivity of the cyclometallated complexes

Reaction of the chloro-bridged compound **3** with triphenylphosphine yielded the mononuclear complex [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(Cl)(PPh$_3$)] (**4**), which was fully characterized (see Section 3). The IR spectrum showed the low-wavenumbers shift of the v(C=N) stretch due to N-coordination of the ligand [16,17]. The HC=N and H^5 resonances appeared in the ^{1}H-NMR spectrum as a doublet an a doublet of

doublets, respectively, showing coupling to the ^{31}P nucleus [δ 8.43 ($J_{PH} = 8.4$) and δ 5.96 ($J_{PH} = 5.9$ Hz), respectively]. The ^{31}P{^{1}H} spectrum showed the phosphorus resonance at δ 42.9. These findings and the low-frequency shift of the C4–OMe resonance (due to shielding by a phosphine phenyl ring) were in agreement with a phosphorus *trans* to nitrogen arrangement [23–26]. The FAB mass spectrum showed peaks centered at 665 and 628 amu assignable to the [M]$^+$ and [M−Cl]$^+$ fragments.

Treatment of **4** with silver triflate and triphenylphosphine in acetone gave the mononuclear complex [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)}(PPh$_3$)][CF$_3$SO$_3$], (**7**), after AgCl removal with the palladium atom bonded to four different atoms: C, N, P and S. The most noteworthy difference in the ^{1}H-NMR spectrum of **7** as compared to **4**, was the CH$_2$ proton resonance which appeared at δ 5.23 (5.42 in **4**). Unfortunately, the H^{10} signal was occluded by the phosphine phenyl protons in both cases. The ^{13}C{^{1}H} NMR spectra showed the high-frequency shift (2.4 ppm) of the CH$_2$ signal which appeared at δ 57.5. The conductivity measurements carried out in dry acetonitrile have shown the complex to be a 1:1 electrolyte. Complex **7** could also be prepared by reaction of complex **3** with silver triflate and subsequent treatment with triphenylphosphine.

Reaction of **3** with the tertiary diphosphines Ph$_2$P(CH$_2$)$_3$PPh$_2$ (dppp) and Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb)
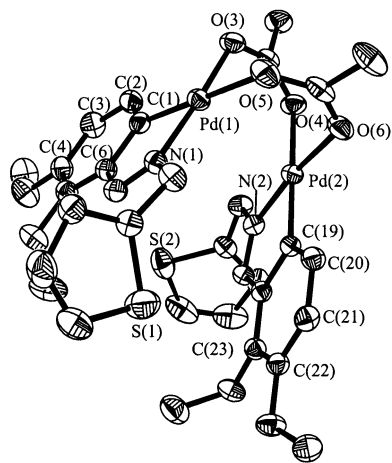
Fig. 1. Molecular structure of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)}(μ-OAc)]$_2$ (**2**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 1
Crystallographic data for complexes **2**, **4** and **6**

	2	**4**	**6**
Chemical formula	$C_{32}H_{34}N_2O_8$ Pd_2S_2	$C_{32}H_{29}ClNO_2$ PPdS	$C_{58}H_{60}Cl_6N_2O_4$ $P_2Pd_2S_2$
Formula weight	851.53	664.44	1400.64
T (°C)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.184(1)	8.798(2)	10.668(1)
b (Å)	14.259(1)	15.871(4)	12.124(1)
c (Å)	18.139(1)	21.401(6)	13.123(1)
α (°)		89.970(4)	74.865(2)
β (°)	99.371(1)	89.888(5)	74.475(2)
γ (°)		78.526(4)	70.299(2)
V (Å^3)	3364.8(3)	2928.4(13)	1512.3(3)
Z	4	4	1
μ (mm^{-1})	1.245	0.881	1.028
Reflections collected	22 847	18 321	10 335
Reflections Unique	8285 [$R_{int}=0.031$]	13 071 [$R_{int}=0.015$]	7276 [$R_{int}=0.054$]
R_1 [a]	0.0320	0.0296	0.0588
wR_2 [b]	0.0836	0.0714	0.1305

[a] $R_1 = \Sigma \, ||F_o|-|F_c||/\Sigma \, |F_o|$, $[F > 4\sigma(F)]$.
[b] $wR_2 = \Sigma \, [w(F_o^2 - F_o^2)^2/\Sigma \, w(F_o^2)^2]^{1/2}$, all data.

in a 1:1 molar ratio gave the dinuclear cyclometallated complexes [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)]-(Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_n$PPh$_2$)] (**5**; $n=3$; **6**: $n=4$) which were fully characterized (see Section 3). The symmetric nature of the complexes was established by the presence of only one singlet signal in the ^{31}P{^{1}H} spectra ca. δ 34.

2.4. Molecular structure of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(Cl)(PPh$_3$)] (**4**) and [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] (**6**)

Suitable crystals were grown by slowly evaporating dichloromethane/n-hexane solutions of the complexes. The molecular structures are illustrated in Figs. 2 and 3. Crystal data are given in Table 1 and selected bond distances and angles with estimated standard deviations are shown in Table 3.

The crystal of complex **4** consists of discrete molecules separated by van der Waals distances (two molecules per asymmetric unit).

The crystal structure of **6** comprises a centrosymmetric dinuclear molecule of [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] (half of the molecule per asymmetric unit) and a dichloromethane solvent molecule.

Table 2
Selected bond lengths (Å) and angles (°) for complex **2**

Bond lengths			
Pd(1)–C(1)	1.967(3)	Pd(2)–C(19)	1.964(3)
Pd(1)–N(1)	2.023(2)	Pd(2)–N(2)	2.014(2)
Pd(1)–O(3)	2.051(2)	Pd(2)–O(4)	2.146(2)
Pd(1)–O(5)	2.132(2)	Pd(2)–O(6)	2.029(2)
Bond angles			
C(1)–Pd(1)–N(1)	81.5(1)	C(19)–Pd(2)–N(2)	81.4(1)
C(1)–Pd(1)–O(3)	91.4(1)	C(19)–Pd(2)–O(6)	92.2(1)
N(1)–Pd(1)–O(3)	172.92(9)	N(2)–Pd(2)–O(6)	172.99(9)
C(1)–Pd(1)–O(5)	177.7(1)	C(19)–Pd(2)–O(4)	175.2(1)
N(1)–Pd(1)–O(5)	96.41(9)	N(2)–Pd(2)–O(4)	94.24(9)
O(3)–Pd(1)–O(5)	90.67(9)	O(6)–Pd(2)–O(4)	91.02(9)

In both compounds the four coordinated Pd atom is bonded to the phenyl carbon atom and the imine nitrogen of the Schiff base ligand, one chloro ligand and to the phosphorus atom of the phosphine ligand. The coordination sphere of the palladium may be described as slightly distorted square-planar. The angles between adjacent atoms in the coordination sphere of palladium are close to the expected value of 90° with the most noticeable distortions corresponding to the bite angles C(1)–Pd(1)–N(1) and C(33)–Pd(2)–N(2) of 81.08(9) and 81.20(9)°, respectively for complex **4** and C(1)–Pd(1)–N(1) of 81.2(2)° for compound **6**. The sum of the angles about palladium is approximately 360°. The Pd–C [2.033(2) and 2.034(2) Å for complex **4** and 2.025(5) Å for complex **6**] and Pd–N bond distances [2.098(2) Å for complex **4** and 2.115(4) Å for complex **6**] are similar to values reported earlier [8,24]. The Pd–N bond length shows the high *trans* influence of the phosphine phosphorus as compared to oxygen [Pd–N
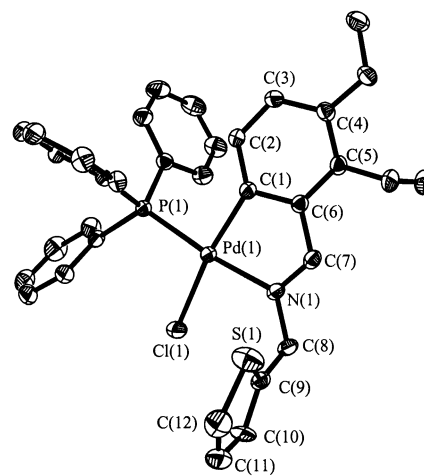

Fig. 2. Molecular structure of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)=NCH$_2$(C$_4$H$_3$S)}(Cl)(PPh$_3$)] (**4**), with labelling scheme. Hydrogen atoms have been omitted for clarity.
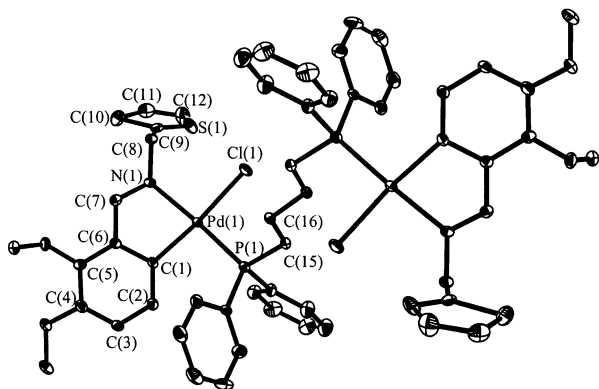
Fig. 3. Molecular structure of [{Pd[2,3-(MeO)₂C₆H₂C(H)= NCH₂(C₄H₃S)](Cl)}₂(μ-Ph₂P(CH₂)₄PPh₂)] (**6**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

distances 2.023(2) and 2.014(2) Å for complex **2**]. The Pd–P and Pd–Cl bond distances are also within the expected values [24].

No intra or intermolecular interactions were observed for the thiophene sulfur.

3. Experimental

3.1. General procedures

Solvents were purified by standard methods [27]. Chemicals were reagent grade. The phosphines PPh₃, Ph₂P(CH₂)₃PPh₂ (dppp) and Ph₂P(CH₂)₄PPh₂ (dppb) were purchased from Aldrich-Chemie. Microanalyses were carried out using a Carlo Erba Elemental Analyzer, Model 1108. IR spectra were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 1330 and on a Mattson spectrophotometers. NMR spectra were obtained as CDCl₃ solutions and referenced to SiMe₄ (^{1}H, ^{13}C{^{1}H}) or 85% H₃PO₄ (^{31}P{^{1}H}) and were recorded on a Bruker AC-200F spectrometer. All chemical shifts were reported downfield from standards. The FAB mass spectra were recorded using a Quatro mass spectrometer with a Cs ion gun; 3-nitrobenzyl alcohol was used as the matrix. Conductivity measurements were made on a CRISON GLP 32 conductivimeter using 10^{-3} M solutions in dry acetonitrile.

3.1.1. Preparation of 2,3-(MeO)₂C₆H₃C(H)= NCH₂(C₄H₃S) (**1**)

2,3-Dimethoxybenzaldehyde (2.00 g, 12.05 mmol) was added to a solution of 2-thiophenemethylamine (1.36 g, 12.02 mmol) in 50 cm³ of dry CHCl₃. The solution was heated under reflux in a Dean–Stark apparatus for 4 h. After cooling to room temperature (r.t.) the CHCl₃ was removed to give a yellow oil. Yield: 2.84 g, 90%. Anal. Found: C, 64.3; H, 5.7; N, 5.5. Calc. for C₁₄H₁₅SO₂N: C, 64.3; H, 5.8; N, 5.4%. IR: ν(C=N), 1637 s cm^{-1}. ^{1}H-NMR (200 MHz, CDCl₃, δ ppm, J Hz): 8.79 [s, 1H, Hi], 7.65 [dd, 1H, H⁶, J(H⁶H⁵) = 7.8, J(H⁶H⁴) = 1.7], 7.25 [dd, 1H, H⁹, J(H⁹H¹⁰) = 3.6, J(H⁹H⁸) = 2.7], 7.10 (t, 1H, H⁵), 6.98 (m, 3H, H⁴, H⁸, H¹⁰), 5.01 (s, 2H, CH₂), 3.90 (s, 3H, MeO), 3.88 (s, 3H, MeO). ^{13}C{^{1}H}-NMR (50.28 MHz, CDCl₃, δ ppm): 158.3 (C=N); 152.7, 149.5, 142.3, 129.6 (C1, C2, C3, C7); 126.8, 124.8, 124.6, 124.2 (C4, C8, C9, C10); 119.0 (C6); 114.6 (C5) 59.7 (CH₂); 61.8, 55.8 (MeO).

3.1.2. Preparation of [Pd{2,3-(MeO)₂C₆H₂C(H)= NCH₂(C₄H₃S)}(μ-OAc)]₂ (**2**)

A pressure tube containing 2,3-(MeOC₆H₃)₂C(H)= NCH₂(C₄H₃S) (**1**), (142 mg, 0.54 mmol), palladium(II) acetate (120 mg, 0.54 mmol) and 20 cm³ of dry C₆H₅CH₃ was sealed under Ar. The resulting mixture was heated at 60 °C for 12 h. After cooling to r.t. the solution was filtered through celite to remove the black palladium formed. The solvent was removed under vacuum to give a brown oil, which was chromato-

Table 3
Selected bond lengths (Å) and angles (°) for complexes **4** and **6**

4				**6**	
Bond lengths					
Pd(1)–C(1)	2.033(2)	Pd(2)–C(33)	2.034(2)	Pd(1)–C(1)	2.025(5)
Pd(1)–N(1)	2.098(2)	Pd(2)–N(2)	2.098(2)	Pd(1)–N(1)	2.115(4)
Pd(1)–P(1)	2.2430(7)	Pd(2)–P(2)	2.2446(7)	Pd(1)–P(1)	2.263(1)
Pd(1)–Cl(1)	2.3640(8)	Pd(2)–Cl(2)	2.3656(8)	Pd(1)–Cl(1)	2.387(1)
Bond angles					
C(1)–Pd(1)–N(1)	81.20(9)	C(33)–Pd(2)–N(2)	81.08(9)	C(1)–Pd(1)–N(1)	81.2(2)
C(1)–Pd(1)–P(1)	92.51(7)	C(33)–Pd(2)–P(2)	92.65(7)	C(1)–Pd(1)–P(1)	92.2(1)
N(1)–Pd(1)–P(1)	173.69(6)	N(2)–Pd(2)–P(2)	173.70(6)	N(1)–Pd(1)–P(1)	173.0(1)
C(1)–Pd(1)–Cl(1)	170.78(7)	C(33)–Pd(2)–Cl(2)	170.80(7)	C(1)–Pd(1)–Cl(1)	171.0(1)
N(1)–Pd(1)–Cl(1)	92.22(6)	N(2)–Pd(2)–Cl(2)	92.29(6)	N(1)–Pd(1)–Cl(1)	92.3(1)
P(1)–Pd(1)–Cl(1)	93.97(3)	P(2)–Pd(2)–Cl(2)	98.89(3)	P(1)–Pd(1)–Cl(1)	91.16(5)

graphed on a column packed with silica gel. Elution with CH_2Cl_2–EtOH (1.2%) afforded the final product after concentration, as a yellow crystalline solid. Yield: 0.11 g, 25%. Anal. Found: C, 45.2; H, 4.1; N, 3.4. Calc. for $C_{32}H_{34}N_2O_8Pd_2S_2$: C, 45.1; H, 4.0; N, 3.3%. IR: $\nu(C=N)$, 1609 s cm^{-1}; $\nu_{as}(COO)$, 1583 m cm^{-1}; $\nu_s(COO)$, 1416 s cm^{-1}. ^1H-NMR (200 MHz, CDCl$_3$, δ ppm, J Hz): 7.55 [t, 1H, Hi, $J(H1CH_2) = 1.5$], 7.27, 6.75 (m, H^4, H^5, H^8, H^{10}), 6.96 [dd, 1H, H^9, $J(H^9H^{10}) = 4.9$, $J(H^9H^8) = 3.4$], 4.10 [dd, 2H, CH_2, $J(CHH) = 16.6$], 4.71 (dd, 2H, CH_2), 3.82 (s, 3H, MeO), 3.75 (s, 3H, MeO), 2.17 (s, 3H, OAc). $^{13}C\{^1H\}$ NMR (50.28 MHz, CDCl$_3$, δ ppm): 181.2 (OC(CH$_3$)O); 168.6 (C=N); 149.2, 147.8, 144.5 (C2, C3, C7); 138.7, 136.2 (C1, C6); 115.1 (C4); 128.7 (C5); 127.3, 126.7, 126.6 (C8, C9, C10); 55.1 (CH_2); 61.9, 56.2(MeO); δ 24.4 (OC(CH_3)O). FAB-MS: $m/z = 852$ [M]$^+$; 366 [(L–H)Pd]$^+$.

3.1.3. Preparation of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)}(μ-Cl)]$_2$ (3)

An aq. solution of NaCl (ca. 10^{-2} M) was added dropwise to a solution of **2** (68 mg, 0.08 mmol) in 15 cm^3 of C$_3$H$_6$O. The resulting mixture was stirred for 24 h. The yellow precipitate formed was filtered of, washed with water and dried under vacuum to give complex **3** as a yellow solid. Yield: 0.054 g, 85%. Anal. Found: C, 41.4; H, 3.7; N, 3.4. Calc. for $C_{28}H_{28}Cl_2N_2O_4Pd_2S_2$: C, 41.8; H, 3.5; N, 3.5%. IR: $\nu(C=N)$, 1603 cm^{-1}. ^1H-NMR (200 MHz, CDCl$_3$, δ ppm, J Hz): 8.08 (s, 1H, Hi), 7.32 [dd, 1H, H^{10}, $J(H^9H^{10}) = 5.4$, $J(H^8H^{10}) = 0.9$)], 7.17 [d, 1H, H^8, $J(H^8H^9) = 2.9$], 7.03 (dd, 1H, H^9), 6.98 [d, 1H, $J(H^4H^5) = 8.3$], 6.70 (d, 1H) (H^4,H^5), 5.03 (s, 2H, CH_2), 3.83 (s, 3H, MeO), 3.80 (s, 3H, MeO). FAB-MS: $m/z = 765$ [M–Cl]$^+$; 366 [(L–H)Pd]$^+$.

3.1.4. Preparation of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)}(Cl)(PPh$_3$)] (4)

PPh$_3$ (6.0 mg, 0.022 mmol) was added to a suspension of **3** (10.0 mg, 0.012 mmol) in C$_3$H$_6$O (15 cm^3). The mixture was stirred for 12 h and the solvent removed to give a yellow solid which was recrystallized from C$_3$H$_6$O–C$_6$H$_{14}$. Yield: 0.012 g, 80%. Anal. Found: C, 57.9; H, 4.5; N, 1.9. Calc. for $C_{32}H_{29}NSO_2Pd_2ClP$: C, 57.8; H, 4.4; N, 2.1%. IR: $\nu(C=N)$, 1617 cm^{-1}. ^1H-NMR (200 MHz, CDCl$_3$, δ ppm, J Hz): 8.43 [d, 1H, Hi $J(HiP) = 8.4$], 7.18 [d, 1H, H^8, $J(H^8H^9) = 2.4$], 7.03 [dd, 1H, H^9, $J(H^9H^{10}) = 4.9$], 6.19 [d, 1H, H^4, $J(H^4H^5) = 8.3$], 5.96 [dd, 1H, H^5, $J(H^5P) = 5.9$], 5.42 (s, 2H, CH_2), 3.80 (s, 3H, MeO), 3.63 (s, 3H, MeO). $^{31}P\{^1H\}$-NMR (80.96 MHz, CDCl$_3$, δ ppm): 42.9 s. $^{13}C\{^1H\}$-NMR (50.28 MHz, CDCl$_3$, δ ppm, J Hz): 172.4d, $J(PC) = 4.3$ Hz (C=N); 148.7, 148.2, 147.8 (C2, C3, C7); 141.12, 138.9 (C1, C6); 115.1d, $J(PC) = 6.4$ Hz (C4); 133.1d, $J(PC) = 10.6$ Hz (C5); 128.3, 127.2, 126.1 (C8, C9, C10); 55.1 (CH_2); 61.9, 55.6 (OMe). P-phenyl: C$_i$ 131.1d, $J(PC) = 49.7$ Hz; C$_o$ 135.4d, $J(PC) = 12.0$ Hz; C$_m$

127.6d, $J(PC) = 10.6$ Hz; C$_p$ 130.6d, $J(PC) = 2.84$ Hz. FAB-MS: $m/z = 665$ [M]$^+$; 628 [M–Cl]$^+$; 366 [(L–H)Pd]$^+$.

Compounds **5–6** were obtained following a similar procedure as yellows solids but using a complex **3**–diphosphine 2:1 molar ratio.

3.1.5. [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_3$PPh$_2$)] (5)

Yield: 0.07 g, 58%. Anal. Found: C, 54.7; H, 4.5; N, 2.5. Calc. for $C_{55}H_{54}Cl_2N_2O_4P_2Pd_2S_2$: C, 54.3; H, 4.5; N, 2.3%. IR: $\nu(C=N)$, 1617 s cm^{-1}. ^1H-NMR (200 MHz, CDCl$_3$, δ ppm, J Hz): 8.36 [d, 1H, Hi $J(HiP) = 7.3$], 7.18 [d, 1H, H^8, $J(H^8H^9) = 2.4$], 7.01 [dd, 1H, H^9, $J(H^9H^{10}) = 4.9$], 6.20 [d, 1H, H^4, $J(H^4H^5) = 8.3$], 5.96 [dd, 1H, H^5, $J(H^5P) = 5.9$], 5.37 (s, 2H, CH_2), 3.77 (s, 3H, MeO), 3.62 (s, 3H, MeO). $^{31}P\{^1H\}$-NMR (80.96 MHz, CDCl$_3$, δ ppm) 33.5 s. $^{13}C\{^1H\}$-NMR (50.28 MHz, CDCl$_3$, δ ppm, J Hz): 171.9d, $J(PC) = 3.5$ Hz (C=N); 148.7, 148.2, 147.6 (C2, C3, C7); 140.1, 139.0 (C1, C6); 115.2d, $J(PC) = 5.6$ Hz (C4); 132.5d, $J(PC) = 11.4$ Hz (C5); 127.9, 127.0, 126.1 (C8, C9, C10); 54.9 (CH_2); 61.9, 55.6 (OMe). P-phenyl: C$_i$ 130.4d, $J(PC) = 35.4$ Hz; C$_o$ 134.0d, $J(PC) = 12.1$ Hz; C$_m$ 128.4d, $J(PC) = 10.6$ Hz; C$_p$ 130.7d, $J(PC) = 2.13$ Hz.

3.1.6. [{Pd[2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)](Cl)}$_2$(μ-Ph$_2$P(CH$_2$)$_4$PPh$_2$)] (6)

Yield: 0.010 g, 68%. Anal. Found: C, 54.2; H, 4.7; N, 2.1. Calc. for $C_{56}H_{56}Cl_2N_2O_4P_2Pd_2S_2$: C, 54.6; H, 4.6; N, 2.3%. IR: $\nu(C=N)$, 1613 s cm^{-1}. ^1H-NMR (200 MHz, CDCl$_3$, δ ppm, J Hz): 8.38 [d, 1H, Hi $J(HiP) = 7.8$], 7.17 [d, 1H, H^8, $J(H^8H^9) = 3.4$], 7.01 [dd, 1H, H^9, $J(H^9H^{10}) = 4.9$], 6.22 [d, 1H, H^4, $J(H^4H^5) = 8.3$], 5.97 [dd, 1H, H^5, $J(H^5P) = 5.9$], 5.39 (s, 2H, CH_2), 3.77 (s, 3H, MeO), 3.63 (s, 3H, MeO). $^{31}P\{^1H\}$-NMR (80.96 MHz, CDCl$_3$, δ ppm): 34.5 s. $^{13}C\{^1H\}$-NMR (50.28 MHz, CDCl$_3$, δ ppm, J Hz): 171.8d, $J(PC) = 2.5$ Hz (C=N); 148.7, 148.2, 147.4 (C2, C3, C7); 140.1, 139.0 (C1, C6); 115.1, $J(PC) = 5.9$ Hz (C4); 132.4d, $J(PC) = 11.3$ Hz (C5); 128.1, 127.1, 126.1 (C8, C9, C10); 54.8 (CH_2); 61.8, 55.7 (OMe). P-phenyl: C$_i$ 130.3d, $J(PC) = 46.7$ Hz; C$_o$ 134.3d, $J(PC) = 11.3$ Hz; C$_m$ 128.4d, $J(PC) = 9.9$ Hz; C$_p$ 130.6d, $J(PC) = 1.42$ Hz.

3.1.7. Preparation of [Pd{2,3-(MeO)$_2$C$_6$H$_2$C(H)= NCH$_2$(C$_4$H$_3$S)}(PPh$_3$)][CF$_3$SO$_3$] (7)

Silver trifluoromethanesulfonate (4.1 mg, 0.029 mmol) was added to a solution of **4** (10.5 mg, 0.029 mmol) in C$_3$H$_6$O (15 cm^3). The resulting mixture was stirred for 2 h, filtered through celite to remove the AgCl precipitate and the solvent removed to give a yellow solid which was recrystallized from CH_2Cl_2–C$_6$H$_{14}$. Yield: 0.090 g, 72%. Anal. Found: C, 50.4; H, 3.7; N, 2.1. Calc. for $C_{33}H_{29}F_3NO_5PPdS_2$: C, 50.1; H, 3.8; N, 1.8%. IR: $\nu(C=N)$, 1619 s cm^{-1}. ^1H-NMR (200 MHz,

CDCl$_3$, δ ppm, J Hz, J Hz): 8.46 [d, 1H, Hi J(HiP) = 6.8], 7.14 [d, 1H, H^8, J(H^{8}H^9) = 3.4], 7.05 [dd, 1H, H^9, J(H^{9}H^{10}) = 4.9], 6.22 [d, 1H, H^4, J(H^{4}H^5) = 8.8], 5.94 [dd, 1H, H^5, J(H^{5}P) = 5.9], 5.23 (s, 2H, CH$_2$), 3.88 (s, 3H, MeO), 3.66 (s, 3H, MeO). ^{31}P{^{1}H}-NMR (80.96 MHz, CDCl$_3$, δ ppm): 41.2 s. ^{13}C{^{1}H}-NMR (50.28 MHz, CDCl$_3$, δ ppm): 173.1 (C=N); 149.7, 149.0 (C2, C3); 141.8 (C7); 140.7, 138.5 (C1, C6); 115.3d, J(PC) = 6.4 Hz (C4); 133.2d, J(PC) = 7.1 Hz (C5); 127.7, 127.2, 125.8 (C8, C9, C10); 57.5 (CH$_2$); 62.0, 55.6 (OMe). P-phenyl: C$_i$ 130.4d, J(PC) = 46.8 Hz; C$_o$ 134.0d, J(PC) = 11.3 Hz; C$_m$ 128.3d, J(PC) = 9.9 Hz; C$_p$ 130.6. FAB-MS: m/z = 628 [M$-$SO$_3$CF$_3$]$^+$. Specific molar conductivity, Λ_m = 145.1 ohm^{-1} cm^2 mol^{-1} (in MeCN).

3.1.8. X-ray crystallographic study

Three-dimensional, r.t. X-ray data were collected on a Siemens Smart CCD diffractometer by the ω scan method using graphite-monochromated Mo$-$K$_\alpha$ radiation. All the measured reflections were corrected for Lp effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least squares on F^2. The S2 and C28 (complex **2**) and S1, C10, S2 and C42 (complex **4**) atoms of the thiophene ring were found to be disordered over two positions. The occupancies of the two pairs of positions were tied to give an overall value of 1.0 and then refined taking into account the minor components. Hydrogen atoms were included in calculated positions and refined in riding mode. Refinement converged at a final R = 0.0320, 0.0296 and 0.0588 (for complexes **2**, **4** and **6**, respectively, observed data, F) and wR_2 = 0.0836, 0.0714 and 0.1305 (for complexes **2**, **4** and **6**, respectively, unique data, F^2), with allowance for thermal anisotropy of all non-hydrogen atoms. The structure solution and refinement were carried out using the program SHELX-97 [28].

4. Supplementary material

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 179032–179034 for compounds **2**, **4**, and **6**. Copies of these data may be obtained free of charge on application to 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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