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Synthesis of heteroleptic nickel(II) and palladium(II) dithiolenes

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Abstract

Deprotection of 4-(*p*-cyanophenyl)-1,3-dithiole-2-thione, 4-(2-thienyl)-1,3-dithiole-2-one (**1**) and 4-(3-thienyl)-1,3-dithiole-2-one (**2**) with a base in MeOH or KOH and the posterior addition of nickel(II) and palladium(II) complexes give the formation of heteroleptic dithiolenes with 1,2-bis(diphenylphosphino)ethane, dppe, as an additional ligand. The X-ray analyses of two Pd-dithiolenes show a planar five-membered ring involving the metallic center and the dithiolene unit.

Keywords: Heteroleptic dithiolenes; Nickel; Palladium

1. Introduction

Considerable research has focused on the synthesis, reactivity and physical and photophysical properties of dithiolene complexes bearing transition metals [1,2]. The uniqueness of the dithiolenes stems from their ability to exits in several clearly define oxidation states due to the high degree of electron delocalisation [3–6] observed in the metalladithiolene ring (consisting of the metal, the two sulfur and two unsaturated carbons), which also manifests itself in intense electronic transitions at unusually low energies. As a consequence of this, transition metal complexes with dithiolene ligands have interesting and versatile properties [7–10] such as electrical conductivity, molecular magnetism (favoured for their planar geometry) and catalytic behavior. The most outstanding property with more potential applications is based on their intense electronic transition in the near-IR region. Thus, dithiolenes have been used for Q-switching near infrared (NIR) laser, which allows the generation of short and very intense pulses, since the 1970s [11–14].

By contrast with the number of homoleptic dithiolene complexes prepared, particularly the square-planar complexes of d^8 metal anions (Ni, Pt and Pd) [2]; only a few heteroleptic complexes are known [15–17], which involve one or more dithiolate ligands together with other ligands (2,2′-bipyridine, 1,2-bis(diphenylphosphino)ethane, cyclopentadienyl, CN) in the metal coordination sphere.

Following our previous work on the synthesis of dithiolene complexes with aromatic substituents [18,19], in this paper we report on the synthesis of heteroleptic dithiolene complexes of the type of $[M\{S_2C_2H\text{-}R\}(dppe)]$ (dppe = 1,2-bis(diphenyldiphosphino)ethane, M = Ni, Pd and R = *p*-cyanophenyl, 2-thienyl, 3-thienyl) and the X-ray characterisation of two of them with palladium as the metallic center.

2. Experimental

2.1. General comments

All reactions and product manipulations were performed under an argon atmosphere using standard Schlenck techniques. THF was dried over and distilled from Na. NMR spectra were recorded on a Varian Gemini 300 MHz or a Bruker ARX 400 MHz spectrometer, IR spectra were measured with a Perkin–Elmer 883 or

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Perkin–Elmer FT-IR Espectrum One, as KBr pellets. UV spectra of 0.1 mM solutions were obtained with a UNICAM UV 300 and mass spectra were obtained with a VG Autospec mass spectrometer operating in the electron Impact (EI) mode and liquid secondary iron mass spectrometry (LSIMS) mode. Elemental compositions were analysed with a Perkin–Elmer 2400B. 4-(2-Thienyl)-1,3-dithiol-2-thione [20], 4-(3-thienyl)-1,3-dithiol-2-thione [20] and 4-(*p*-cyanophenyl)-1,3-dithiole-2-thione [18,20] were prepared by published methods. Electrochemical measurements were recorded on a EG&G 273 model and carried out in dry CH_2Cl_2 under argon using $[n\text{-}NBu_4]PF_6$ (0.1 M) as a background electrolyte, with a Pt disk electrode versus SCE (values in V).

*2.2. 4-(2-Thienyl)-1,3-dithiole-2-one (**1**)*

To a solution of 4-(2-thienyl)-1,3-dithiol-2-thione (216 mg, 1 mmol) in MeCN (10 ml) was added $Hg(OAc)_2$ (414 mg, 1.3 mmol). The mixture was refluxed for 6 h and after cooling the solvent was completely removed in vacuo. Purification was carried out by column chromatography (silica, CH_2Cl_2). The resulting solution was carefully washed with sat. Na_2CO_3 and water. After drying (Na_2SO_4) the solvent was evaporated in vacuo to afford a yellow solid. Yield: 85%. *Anal.* Calc. for [$C_7H_4OS_3$]: C, 41.93; H, 2.01; S, 47.92. Found: C, 41.95; H, 2.42; S, 47.52%. IR (KBr, cm^{-1}): ν(C=O) 1638. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.30–7.28 (m, 1H, *H_5-thienyl*), 7.07–7.03 (m, 2H, *$H_{3,4}$-thienyl*), 6.73 (s, 1H, *H_5-dithiole*) ppm. *m/z* (EI^+): 200 ($[M]^+$, 16%), 136 (100%).

*2.3. 4-(3-Thienyl)-1,3-dithiole-2-one (**2**)*

This compound was prepared as described for **1** using 4-(3-thienyl)-1,3-dithiol-2-thione (216 mg, 1 mmol). Yellow solid. Yield: 80%. *Anal.* Calc. for [$C_7H_4OS_3$]: C, 41.93; H, 2.01; S, 47.92. Found: C, 41.54; H, 2.40; S, 47.49%. IR (KBr, cm^{-1}): ν(C=O) 1628. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.42–7.18 (m, 1H, *H_2-thienyl*), 7.30–7.23 (m, 2H, *$H_{4,5}$-thienyl*), 6.77 (s, 1H, *H_5-dithiole*) ppm. *m/z* (EI^+): 200 ($[M]^+$, 100%), 172 ($[M–C–O]^+$, 52%), 140 ($[M–C–O–S]^+$, 12%).

*2.4. [M{S_2C_2H-(p-CN-C_6H_4)}(dppe)], M = Ni (**3**), Pd (**4**)*

4-(*p*-Cyanophenyl)-1,3-dithiole-2-thione (47 mg, 0.2 mmol) was suspended in MeOH (20 ml) under argon atmosphere. KOH (0.5 ml, 1 M in MeOH) was added and the reaction mixture was refluxed until the thione was dissolved (3 h). After cooling [$NiCl_2$(dppe)] (106 mg, 0.2 mmol) or [$PdCl_2$(dppe)] (115 mg, 0.2 mmol) was added. The reaction mixture was stirred for 24 h and the precipitate was subsequently collected by filtration and washed with diethyl ether. M = Ni (**3**), green solid. Yield: 45%. *Anal.* Calc. for [$C_{35}H_{29}NNiP_2S_2$]: C, 64.90; H, 4.51; N, 2.16; S, 9.90. Found: C, 64.68; H, 4.86; N, 2.09; S, 10.01%. IR (KBr, cm^{-1}): $\nu(C\equiv N)$ 2218, ν(C=C) 1597. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.80–7.66 (m, 10H), 7.46–7.36 (m, 14H), 7.30 (s, 1H), 2.38 (d, 4H, $J = 17.4$ Hz) ppm. $^{31}P\{^1H\}$ NMR: AB system $\delta_A = 58.6$, $\delta_B = 57.9$ ppm ($J_{AB} = 46.5$ Hz). *m/z* ($LSIMS^+$): 647 ($[M]^+$, 100%). M = Pd (**4**), orange solid. Yield: 65%. *Anal.* Calc. for [$C_{35}H_{29}NP_2PdS_2$]: C, 60.39; H, 4.20; N, 2.01; S, 9.21. Found: C, 59.99; H, 4.15; N, 1.96; S, 9.21%. IR (KBr, cm^{-1}): $\nu(C\equiv N)$ 2213, ν(C=C) 1599. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.84–7.73 (m, 10H), 7.52–7.40 (m, 14H), 7.20 (d, 1H, $J = 3.6$ Hz), 2.53 (d, 4H, $J = 20.7$ Hz) ppm. $^{31}P\{^1H\}$ NMR: AB system $\delta_A = 51.7$, $\delta_B = 51.6$ ppm (J_{AB}=36.1 Hz). *m/z* ($LSIMS^+$): 695 ($[M]^+$, 100%).

*2.5. [M{S_2C_2H-(2-C_4H_3S)}(dppe)], M = Ni (**5**), Pd (**6**)*

4-(2-Thienyl)-1,3-dithiole-2-one (**1**) (50 mg, 0.25 mmol) was suspended in EtOH (10 ml) under argon atmosphere, for M = Pd in THF (10 ml). NaOEt (2 ml, 0.4 M in EtOH) was added and the reaction mixture was refluxed until the ketone was dissolved (1.5 h). After cooling [$NiCl_2$(dppe)] (132 mg, 0.25 mmol) or [$PdCl_2$(dppe)] (144 mg, 0.25 mmol) was added. The reaction mixture was stirred for 24 h and then the solvent was reduced in vacuo to 5 ml. Hexane or diethyl ether (20 ml) was added to precipitate the corresponding compound which was filtered off. Purification was carried out by column chromatography. M = Ni (**5**), (silica, 60 ethyl acetate/40 hexane), green solid. Yield: 15%. *Anal.* Calc. for [$C_{32}H_{28}NiP_2S_3$]: C, 61.05; H, 4.45; S, 15.26. Found: C, 60.68; H, 4.06; S, 14.88%. IR (KBr, cm^{-1}): ν(C=C) 1633. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.77–7.70 (m, 8H), 7.45–7.19 (m, 12H), 6.92 (m, 2H), 6.84 (m, 1H), 6.72 (m, 1H), 2.35–2.27 (m, 4H) ppm. $^{31}P\{^1H\}$ NMR: AB system $\delta_A = 58.0$, $\delta_B = 57.5$ ppm ($J_{AB} = 34.8$ Hz). *m/z* ($LSIMS^+$): 628 ($[M]^+$, 100%), 431 ($[S(dppe)^+]$, 72%). M = Pd (**6**), (silica, dichloromethane), purple solid. Yield: 49%. *Anal.* Calc. for [$C_{32}H_{28}P_2PdS_3$]: C, 56.71; H, 4.13; S, 14.18. Found: C, 56.40; H, 4.43; S, 13.68%. IR (KBr, cm^{-1}): ν(C=C) 1634. ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.77–7.68 (m, 9H), 7.37–7.33 (m, 11H), 6.99 (m, 1H), 6.89–6.83 (m, 2H), 6.72 (m, 1H), 2.42 (d, 4H, $J = 15.3$ Hz) ppm. $^{31}P\{^1H\}$ NMR: AB system $\delta_A = 50.9$, $\delta_B = 50.7$ ppm ($J_{AB} = 26.7$ Hz). *m/z* ($LSIMS^+$): 676 ($[M]^+$, 100%), 506 ([Pd(dppe)], 18%), 429 ([S(dppe)], 32%).

*2.6. [M{S_2C_2H-(3-C_4H_3S)}(dppe)], M = Ni (**7**), Pd (**8**)*

4-(3-Thienyl)-1,3-dithiole-2-one (**2**) (50 mg, 0.25 mmol) was suspended in THF (15 ml). NaOEt (2 ml, 0.4 M in EtOH) was added and the reaction mixture was refluxed until the ketone was dissolved (1.5 h). After cooling [$NiCl_2$(dppe)] (132 mg, 0.25 mmol) or [$PdCl_2$(dppe)] (144 mg, 0.25 mmol) was added. The reaction mixture was stirred for 24 h and then the solvent was reduced in vacuo to 5 ml. Hexane (20 ml) was added to precipitate the corresponding compound which was filtered off. M = Ni (**7**), green solid. Yield: 44%. *Anal.* Calc. for [$C_{32}H_{28}NiP_2S_3$]: C, 61.05; H, 4.45; S, 15.26. Found: C, 60.67; H, 4.48; S, 14.84%. IR (KBr, cm^{-1}): ν(C═C) 1629. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.77–7.61 (m, 10H), 7.44–7.37 (m, 10H), 7.19–7.13 (m, 2H), 7.00 (m, 1H), 6.93 (s, 1H), 2.30 (d, 4H, $J = 13.2$ Hz) ppm. $^{31}P\{^1H\}$ NMR: AB system $\delta_A = 57.8$, $\delta_B = 57.6$ ppm ($J_{AB} = 34.1$ Hz). *m*/*z* (LSIMS$^+$): 628 ([M]$^+$, 100%), 431 ([S(dppe)$^+$], 25%). M = Pd (**8**), brown solid. Yield: 90%. *Anal.* Calc. for [$C_{32}H_{28}P_2PdS_3$]: C, 56.71; H, 4.13; S, 14.18. Found: C, 56.40; H, 4.21; S, 13.76%. IR (KBr, cm^{-1}): ν(C═C) 1638. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 7.80–7.71 (m, 8H), 7.43–7.35 (m, 12H), 7.21 (m, 2H), 7.03 (m, 1H), 6.85 (m, 1H), 2.43 (d, 4H, $J = 15.3$ Hz) ppm. $^{31}P\{^1H\}$ NMR: δ 50.5 (s) ppm. *m*/*z* (LSIMS$^+$): 676 ([M]$^+$, 100%), 476 (52%), 291 (72%).

2.7. Crystallographic studies

Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into dichloromethane solutions. A summary of the fundamental crystal and refinement data of compounds **4** and **6** is given in Table 3. The crystals were mounted on a glass fiber with inert oil and centered on a Bruker Nonius Kappa CCD diffractometer in the case of **4** and on a Bruker-Siemens Smart CCD diffractometer in **6** using monochromated Mo Kα radiation ($\lambda = 0.7107$ Å), scan type θ–2θ. The diffraction frames were integrated using the SAINT [21] package and corrected for absorption with SORTAV [22,23] or SADABS [24] programs. The structures were solved by direct methods using SHELXS [25]. Full-matrix least squares refinement was carried out using SHELXTL [26] minimising $\omega(F_o^2 - F_c^2)^2$. Hydrogen atoms were included using a riding model. Weighted *R* factors (R_w) and all goodness-of-fit *S* values are based on F^2; conventional *R* factors (*R*) are based on *F*.

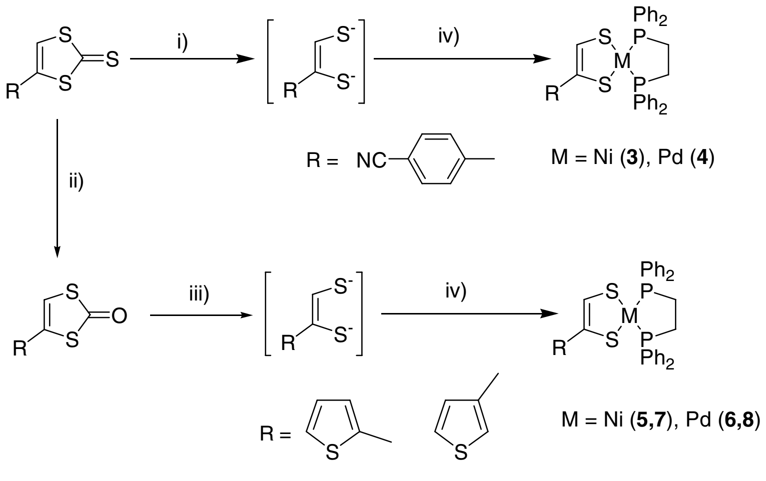
3. Results and discussion

Deprotection of 4-(*p*-cyanophenyl)-1,3-dithiole-2-thione [18,20], 4-(2-thienyl)-1,3-dithiole-2-one (**1**) and 4-(3-thienyl)-1,3-dithiole-2-one (**2**) with a base in MeOH or in THF (to improve the solubility) leads to the formation in situ of the corresponding dithiolate salts. Curiously the formation of the dithiolates takes place starting from the thione (Scheme 1, (i)) in the case of *p*-cyanophenyl, though in the case of 2- and 3-thienyl the transformation is on the corresponding ketone, in order to improve the electrophilicity around the C atom in the 2 position, necessary as a previous reaction. Subsequent addition of [$NiCl_2$(dppe)] and [$PdCl_2$(dppe)] followed by purification work-up afforded the heteroleptic complexes as shown in Scheme 1.

The spectroscopic data of all the dithiolenes are in agreement with their formulation. In the ^{1}H NMR spectra, the proton of the S_2C_2H unit appears as a doublet or multiplet, possibly due to the coupling of this proton with the P atom in the *trans* position. More illustrative are the $^{31}P\{^1H\}$ NMR spectra, most of them show an AB system around 58 ppm for Ni complexes and 51 ppm for Pd complexes. This AB system is due to the closed resonances of the two inequivalent phosphorous atoms because of the lack of symmetry of the dithiolene ligand used in this work. The LSIMS$^+$ mass spectra exhibit the molecular peaks in all cases.

Crystals of the palladium complexes [Pd{S_2C_2H-(*p*-CN-C_6H_4)}(dppe)] (**4**) and [Pd{S_2C_2H-(2-C_4H_3S)}(dppe)] (**6**) were grown by slow diffusion of diethyl ether into a dichloromethane solution of each complex. Perspective drawings of the structures are shown in Figs. 1 and 2 respectively. Bond distances and angles are collected in Tables 1 and 2 and crystallographic data are collected in Table 3.

The crystalline structure of the two compounds is similar to that of other group 10 metallo-1,2-enedithiolate complexes [8,27–33]. Compound **6** crystallises as the water



i) KOH/MeOH, ii) Hg(OAc)2, iii) NaOEt/ THF, iv) [MCl2(dppe)]

Scheme 1. Synthesis of heteroleptic dithiolene complexes.

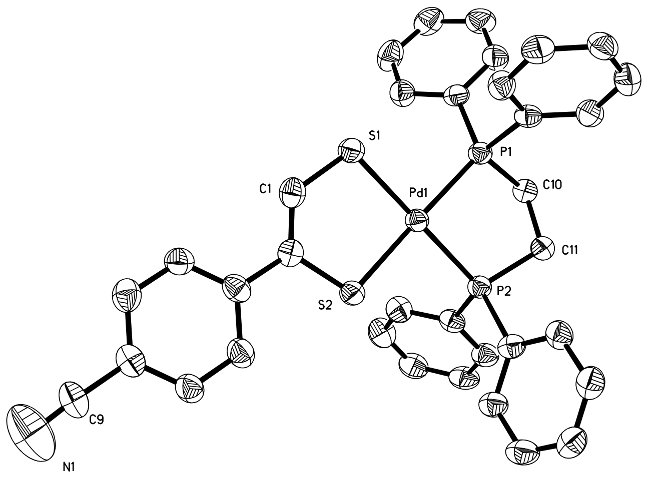


Fig. 1. Crystal structure of [Pd{S_2C_2H-(*p*-CN-C_6H_4)}(dppe)] (**4**). Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

solvate with two independent molecules per unit cell. The P–Pd–P angles are very similar in both complexes, [P(1)–Pd(1)–P(2) = 86.09(5)° in **4** and P(1)–Pd(1)–P(2) = 85.00(6)°, P(4)–Pd(2)–P(3) = 84.71(6)° in **6**] as occurs with the S–Pd–S angles [S(1)–Pd(1)–S(2) = 88.34(5)° in **4** and S(1)–Pd(1)–S(2) = 89.31(5)°; S(5)–Pd(2)–S(4) = 88.48(6)° in **6**]. The metallo-1,2-enedithiolate consists of a planar five-membered ring in the two cases with the palladium atom deviating slightly from the least squares planes, 0.0143(6) Å in **4** and 0.0387(7), 0.0571(14) Å in the two independent molecules of **6**. The substituents *p*-cyanophenyl in **4** and 2-thienyl in **6** are also coplanar with the metallo-1,2-dithiolene unit with smaller torsion angles in the case of the two molecules of complex **6** [C(33)–C(34)–

Table 1
Bond lengths (Å) and angles (°) for [Pd{S_2C_2H-(*p*-CNC_6H_4)}(dppe)] (**4**)

Pd(1)–P(1)	2.2808(13)	Pd(1)–S(2)	2.2980(13)
Pd(1)–P(2)	2.2869(12)	N(1)–C(9)	1.094(8)
Pd(1)–S(1)	2.2893(12)		
P(1)–Pd(1)–P(2)	86.09(5)	P(2)–Pd(1)–S(1)	179.12(4)
P(1)–Pd(1)–S(1)	93.66(5)	P(1)–Pd(1)–S(2)	177.77(4)
P(2)–Pd(1)–S(2)	91.90(5)	C(21)–P(2)–Pd(1)	114.31(15)
S(1)–Pd(1)–S(2)	88.34(5)	C(31)–P(2)–Pd(1)	120.45(14)
C(51)–P(1)–Pd(1)	114.48(15)	C(11)–P(2)–Pd(1)	107.51(15)
C(41)–P(1)–Pd(1)	122.48(15)	C(1)–S(1)–Pd(1)	103.28(17)
C(10)–P(1)–Pd(1)	106.74(15)	C(2)–S(2)–Pd(1)	103.73(16)

Table 2
Bond lengths (Å) and angles (°) for [Pd{S_2C_2H-(2-C_4H_3S)}(dppe)] (**6**)

Pd(1)–P(1)	2.2716(16)	Pd(2)–S(5)	2.2969(17)
Pd(1)–P(2)	2.2778(15)	Pd(2)–S(4)	2.3068(17)
Pd(1)–S(1)	2.2935(14)	C(1)–C(2)	1.341(8)
Pd(1)–S(2)	2.3114(16)	C(5)–C(6)	1.312(12)
Pd(2)–P(4)	2.2721(17)	C(33)–C(34)	1.338(10)
Pd(2)–P(3)	2.2903(16)	C(39)–C(40)	1.531(9)
P(1)–Pd(1)–P(2)	85.00(6)	C(34)–S(4)–Pd(2)	103.5(2)
P(1)–Pd(1)–S(1)	90.84(5)	C(33)–S(5)–Pd(2)	102.9(2)
P(2)–Pd(1)–S(1)	167.89(6)	C(9)–P(1)–Pd(1)	118.9(2)
P(1)–Pd(1)–S(2)	175.92(6)	C(15)–P(1)–Pd(1)	112.81(18)
P(2)–Pd(1)–S(2)	95.65(6)	C(7)–P(1)–Pd(1)	108.1(2)
S(1)–Pd(1)–S(2)	89.31(6)	C(21)–P(2)–Pd(1)	124.4(2)
P(4)–Pd(2)–P(3)	84.71(6)	C(27)–P(2)–Pd(1)	109.45(19)
P(4)–Pd(2)–S(5)	89.91(6)	C(8)–P(2)–Pd(1)	108.1(2)
P(3)–Pd(2)–S(5)	171.91(6)	C(41)–P(3)–Pd(2)	113.4(2)
P(4)–Pd(2)–S(4)	177.97(6)	C(47)–P(3)–Pd(2)	123.85(19)
P(3)–Pd(2)–S(4)	97.01(6)	C(40)–P(3)–Pd(2)	107.7(2)
S(5)–Pd(2)–S(4)	88.48(6)	C(59)–P(4)–Pd(2)	117.3(2)
C(1)–S(1)–Pd(1)	102.4(2)	C(53)–P(4)–Pd(2)	113.7(2)
C(2)–S(2)–Pd(1)	102.5(2)	C(39)–P(4)–Pd(2)	107.3(2)

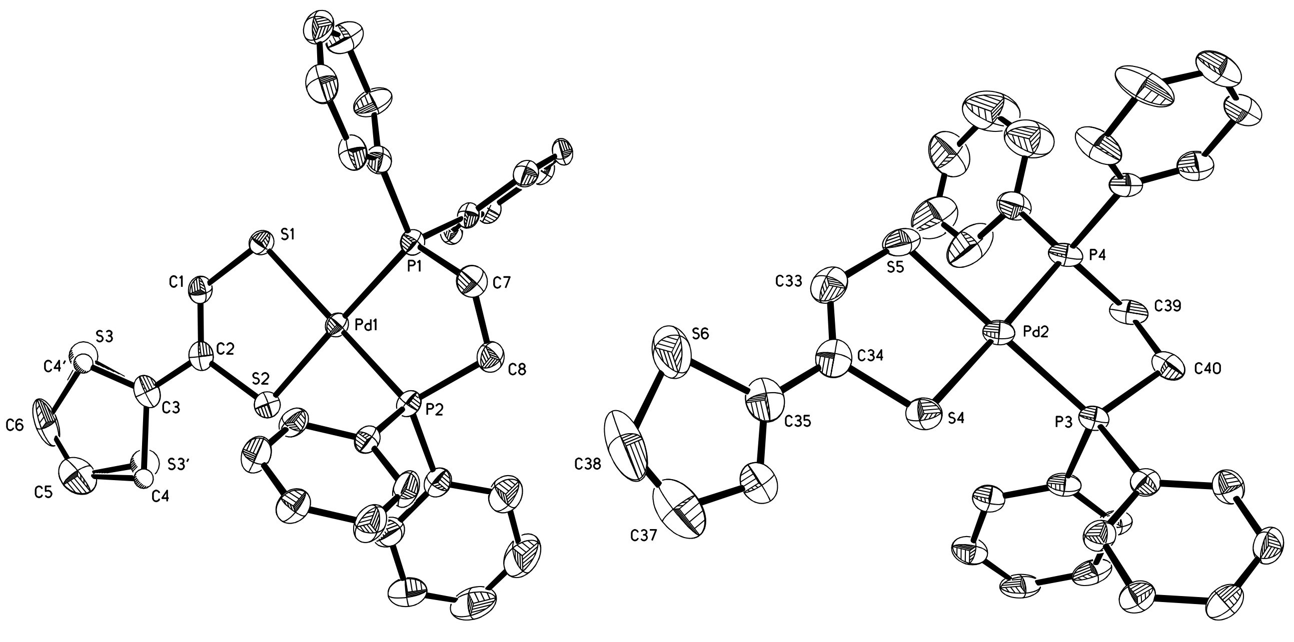


Fig. 2. Crystal structure of the two independent molecules of [Pd{S_2C_2H-(2-C_4H_3S)}(dppe)] (**6**). Thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity.

Table 3
Summary of the crystallographic data for complexes [Pd{S_2C_2H-(*p*-CNC_6H_4)}(dppe)] (**4**) and [Pd{S_2C_2H-(2-C_4H_3S)}(dppe)] (**6**)

	4	**6**
Empirical formula	$C_{35}H_{29}NP_2PdS_2$	$C_{64}H_{53}OP_4Pd_6$
Formula weight	696.05	1367.10
Temperature (K)	150(2)	100(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pbcn*
a (Å)	11.453(2)	49.977(5)
b (Å)	19.734(4)	15.397(5)
c (Å)	14.318(3)	16.191(5)
α (°)	90	90
β (°)	105.81(3)	90
γ (°)	90	90
V (Å^3)	3113.8(11)	112459(6)
Z	4	8
D_c (Mg/m^3)	1.485	1.460
μ (mm^{-1})	0.859	0.922
Crystal size (mm)	0.25 × 0.24 × 0.04	0.55 × 0.16 × 0.08
θ Range for data collection (°)	2.96–30.48	1.63–27.09
Number of data collected	20982	75856
Number of unique data [R_{int}]	7877 [0.0773]	13666 [0.0717]
R_1[a]($F^2 > 2\sigma(F^2)$)	0.0568	0.0647
ϖR_2[b] (all data)	0.1638	0.1679
S[c] (all data)	1.026	1.099
Residual ρ (e Å^3)	1.789, –1.539	1.736, –1.088

[a] $R_1(F) = \sum\|F_o| - |F_c\|/\sum|F_o|$.

[b] $\varpi R_2(F^2) = [\sum[\varpi(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (\alpha P)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

[c] $S = [\sum[\varpi(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where *n* is the number of reflections and *p* the number of refined parameters.

C(35)–S(6) = 9.1° and C(1)–C(2)–C(3)–S(2) = 9.5° in **6** and C(2)–C(3)–C(8)–S(2) = 13° in **4**]. The Pd–S bond lengths are in the range of other Pd-dithiolene complexes [31,34–37]. The C–C bonds in the dithiolene unit are best described as double bonds [C(1)–C(2) = 1.329(6) Å in **4** and C(1)–C(2) = 1.341(8), C(33)–C(34) = 1.338(10) Å in **6**] while the C–C bonds in the bisphosphine dppe are single bonds. One of the molecules in compound **6** shows some disorder in the thiophene ring between *syn* and *anti* conformers with respect to the proton of the dithiolene unit (S_2C_2H), in an equal distribution, while the thiophene in the other molecule displays a *syn* conformation.

*Electrochemical properties of complexes **3**–**8***. Cyclic voltammetry experiments display in all the new complexes one reversible one-electron oxidation due to the dithiolene unit, except in the case of the palladium complex **4** which shows an irreversible oxidation (Table 4). In the case of complexes **3** and **6** an additional irreversible oxidation process is observed at $E_{(ox)}$ = 1.07 V (**4**) and 0.59 V (**6**), which can be assigned to a second oxidation of the dithiolenes (see Table 4).

Table 4
Cyclic voltammetric data for complexes **3**–**8** (V vs. SCE, Pt disk electrode in 0.1 M of NBu_4PF_6)

Compound	3	4	5	6	7	8
$E^1_{1/2}$	+0.39v	+0.52v(i)	+0.42v	+0.39v	+0.408v	+0.38v
$E^2_{1/2}$	+1.16v(i)			+1.11v(i)		

4. Concluding remarks

We have presented the synthesis and complete characterisation of heteroleptic nickel and palladium dithiolenes via deprotection of the corresponding starting thiones and subsequent addition of the metallic derivatives with 1,2-bis(diphenylphosphino)ethane as an ancillary ligand. The X-ray analyses of two Pd-dithiolenes show a planar five-membered ring involving the metallic center and the dithiolene unit.

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Appendix A. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 600597 for compound **4** and CCDC No. 600598 for compound **6**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.04.010.

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