Dithiolene-like Palladium Complexes of Methyl 3-Phenyldithiocarbazate and related Derivatives. Crystal Structure of $[Pd\{N[C_6H_3(OMe\text{-}4)NC_6H_4(OMe\text{-}4)]NC(S)SMe\}(SCN)]\cdot 0.5C_6H_6$†

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The salt $K_2[PdCl_4]$ reacted with NHRNHC(S)SMe (R = Ph, C_6H_4OMe-4 or $C_6H_4NO_2$-4) in strongly basic aqueous alcoholic media in the air to give deep coloured, diamagnetic, dithiolene-like complexes $[Pd\{NRNC(S)SMe\}_2]$. The ligands are N,S-chelated through the non-methylated sulfur and the terminal nitrogen. The anionic complex $[AsPh_4][Pd\{N(C_6H_4NO_2\text{-}4)NC(S)SMe\}_2]$ was also isolated. Heating $[Pd\{NPhNC(S)SMe\}_2]$ and $[Pd\{N(C_6H_4OMe\text{-}4)NC(S)SMe\}_2]$ led to the new complexes $[Pd\{N(C_6H_4NPh\text{-}2)NC(S)SMe\}(NCS)]\cdot 0.5C_6H_6$ and $[Pd\{N[C_6H_3(OMe\text{-}4)NC_6H_4(OMe\text{-}4)]NC(S)SMe\}(SCN)]\cdot 0.5C_6H_6$, respectively. The crystal structure of the latter was determined.

We have previously reported on complexes of platinum,[1] nickel[2] and copper[3] with methyl dithiocarbazate $NH_2NHC(S)SMe$ and its 3-substituted derivatives. The ligands are generally chelated through the thione sulfur and 3-nitrogen atoms, in neutral or anionic form. Complexes containing the doubly deprotonated ligands are dithiolene-like and show electron-transfer properties. Reports on palladium complexes of these ligands are rare and, to our knowledge, none have been made on those containing the doubly deprotonated ligands. We report here on dithiolene-like complexes of palladium with doubly deprotonated dithiocarbazic esters and on the peculiar reactivity of some of them. The compounds considered are NHRNHC(S)SMe (R = Ph, 4-$MeOC_6H_4$ or 4-$O_2NC_6H_4$). Preliminary results have been presented.[4]

Experimental

Materials.—The chemicals were commercial analytical grade reagents used without further purification, except for the solvents employed for electrochemical measurements which were purified as described in ref. 5. Nitrogen gas was an ultrahigh purity commercial product. All the compounds were dried *in vacuo* (1 Torr, *ca.* 133 Pa) over P_4O_{10}, unless otherwise stated. Deuteriated solvents were from Aldrich Chem. or Merck UVASOL (99.9 atom% D).

Preparation of the Ligands.—The compound NHPhNHC(S)SMe was prepared following the method reported in ref. 2.

$NH(C_6H_4OMe\text{-}4)NHC(S)SMe$. A solution of KOH (132 mmol) in MeOH (150 cm^3) was added to a stirred solution of 4-$MeOC_6H_4NHNH_2\cdot HCl$ (66 mmol) in MeOH (350 cm^3) at 0 °C. After 2.5 h CS_2 (66 mmol) was added followed after 1 h by MeI (66 mmol). After 1 h of stirring at 0 °C the mixture was poured into chilled water (1300 cm^3). After 18 h at 0 °C the crude dark product was filtered off, dried and crystallized from boiling benzene. Yield 30%, m.p. 112 °C. ^1H NMR $[(CD_3)_2SO]$: δ 11.31 [1 H, s, N(2)H], 8.20 [1 H, s, N(3)H], 6.82–6.60 (4 H, m, C_6H_4), 3.67 (3 H, s, OCH_3) and 2.41 (3 H, s, SCH_3).

$NH(C_6H_4NO_2\text{-}4)NHC(S)SMe$. A mixture of 4-$O_2NC_6H_4NHNH_2$ (10 mmol), CS_2 (330 mmol) and water (200 cm^3) was stirred in a closed vessel for 6 d. The solid product was filtered off, washed with water and dried. Yield 76%, m.p. 159 °C. ^1H NMR $[(CD_3)_2SO]$: δ 11.62 [1 H, s, N(2)H], 9.68 [1 H, s, N(3)H], 8.12–6.77 (4 H, m, C_6H_4) and 2.45 (3 H, s, SCH_3).

Preparation of the Complexes.—$[Pd\{NPhNC(S)SMe\}_2]$ **1a**. A solution of $K_2[PdCl_4]$ (1.25 mmol) in water (40 cm^3) was added to a solution of NHPhNHC(S)SMe (2.5 mmol) in EtOH (80 cm^3). Ammonium hydroxide (1 mol dm^{-3}) was added until pH 9. After 24 h of stirring in an open vessel the product was filtered off and dried. Yield 90%.

$[Pd\{N(C_6H_4OMe\text{-}4)NC(S)SMe\}_2]$ **1b**. This complex was prepared as above. Yield 80%.

$[Pd\{N(C_6H_4NO_2\text{-}4)NC(S)SMe\}_2]$ **1c**. The compound $NH(C_6H_4NO_2\text{-}4)NHC(S)SMe$ (1 mmol) was suspended in water (30 cm^3). Addition of 1 mol dm^{-3} NH_4OH (10 cm^3) led to a brown solution, to which was added a solution of $K_2[PdCl_4]$ (0.5 mmol) in water (40 cm^3). After 2 h of stirring the dark violet mixture was filtered and the filtrate left in an open vessel for 24 h. The violet colour disappeared and a dark brown mixture formed. The compound was filtered off, washed with water and dried. Yield 76%.

$[AsPh_4][Pd\{N(C_6H_4NO_2\text{-}4)NC(S)SMe\}_2]$ **2**. The compound $NH_2NH_2\cdot H_2O$ (5 cm^3) was added to a stirred and heated suspension of $[Pd\{N(C_6H_4NO_2\text{-}4)NC(S)SMe\}_2]$ (0.24 mmol) in EtOH (15 cm^3). After formation of a dark violet solution the heating was stopped. At room temperature a solution of $AsPh_4Cl\cdot H_2O$ (1.19 mmol) in water (30 cm^3) was slowly added. After 45 min of stirring the dark brown compound was filtered off, washed with water and dried. Yield 80%.

$[Pd\{N(C_6H_4NPh\text{-}2)NC(S)SMe\}(NCS)]\cdot 0.5C_6H_6$ **3**. A solution of $[Pd\{NPhNC(S)SMe\}_2]$ (1.0 mmol) in benzene (25 cm^3) was boiled for 2 h. A microcrystalline compound separated at room temperature. It was recovered and dried. Yield 45%.

$[Pd\{N[C_6H_3(OMe\text{-}4)NC_6H_4(OMe\text{-}4)]NC(S)SMe\}(SCN)]\cdot 0.5C_6H_6$ **4**. A solution of $[Pd\{N(C_6H_4OMe\text{-}4)NC(S)SMe\}_2]$ (0.9 mmol) in benzene (30 cm^3) was boiled for 2 h. The solution

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical data for the ligands and palladium complexes

Compound	Colour	Analysis (%)*			
		C	H	N	S
NH($C_6H_4NO_2$-4)NHC(S)SMe	Yellow	39.5 (39.5)	3.4 (3.7)	17.0 (17.2)	25.9 (26.3)
NH(C_6H_4OMe-4)NHC(S)SMe	White	47.3 (47.5)	5.3 (5.4)	12.3 (12.3)	28.1 (28.0)
1a [Pd{NPhNC(S)SMe}$_2$]	Dark violet	38.2 (38.5)	3.2 (3.2)	11.2 (11.2)	26.1 (25.8)
1b [Pd{N(C_6H_4OMe-4)NC(S)SMe}$_2$]	Dark violet	38.8 (38.7)	3.5 (3.6)	10.0 (10.0)	22.5 (22.9)
1c [Pd{N($C_6H_4NO_2$-4)NC(S)SMe}$_2$]	Dark brown	32.4 (32.6)	2.3 (2.4)	13.9 (14.3)	21.4 (21.8)
2 [$AsPh_4$][Pd{N($C_6H_4NO_2$-4)NC(S)SMe}$_2$]	Dark brown	49.5 (49.4)	3.5 (3.5)	8.2 (8.6)	12.8 (13.2)
3 [Pd{N(C_6H_4NPh-2)NC(S)SMe}(NCS)]·0.5C_6H_6	Dark brown	43.7 (44.1)	3.3 (3.1)	11.0 (11.4)	19.8 (19.6)
4 [Pd{N[C_6H_3(OMe-4)NC_6H_4(OMe-4)]NC(S)SMe}(SCN)]·0.5C_6H_6	Dark violet	43.8 (43.7)	3.3 (3.5)	9.9 (10.2)	17.5 (17.5)

* Required values are given in parentheses.

Table 2 Details of the structure determination of compound **4**

Empirical formula	$C_{20}H_{19}N_4O_2PdS_3$
M	550.0
Colour, habit	Dark violet, prismatic
Crystal size/mm	0.8 × 0.2 × 0.15
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	8.740(2)
b/Å	9.840(5)
c/Å	13.484(5)
α/°	102.99(4)
β/°	92.87(3)
γ/°	98.56(3)
U/Å^3	1113.2(7)
Z	2
D_c/Mg m^{-3}	1.641
μ/mm^{-1}	1.139
F(000)	554
Diffractometer	Nicolet P21
Radiation	Mo-Kα (λ = 0.710 69 Å)
T/K	293
Monochromator	Highly oriented graphite crystal
2θ Range/°	3.0–55.0
Scan type	2θ–θ
Scan speed/° min^{-1}	Variable, 1.50–29.00 in ω
Scan range, ω/°	2.00 + Kα separation
Reflections collected	5337
Observed reflections	4017 [$I > 3.0\sigma(I)$]
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0043F^2$
No. parameters	281
R	0.036
R'	0.0485
Goodness-of-fit	0.67
Largest and mean Δ/σ	0.399, 0.077
Data-to-parameter ratio	14.3:1
Largest difference peaks/e Å^{-3}	0.32, −0.41

was left at room temperature in an open Erlenmeyer flask. After 2 weeks well formed crystals were filtered off and dried. Yield 38%.

Physical Measurements.—Analytical data for the complexes are given in Table 1. Microanalyses were performed by the Microanalytical Service of the Area della Ricerca di Roma del CNR. The NMR spectra were recorded by the NMR Service of the Area della Ricerca di Roma del CNR. The UV/VIS reflectance spectra of finely powdered solids were obtained on a Cary 5 spectrophotometer fitted with a standard reflectance attachment and MgO in the reference beam. Solution spectra were recorded at room temperature on a Perkin-Elmer 330 spectrophotometer (concentration range 10^{-5}–10^{-3} mol dm^{-3}). Infrared spectra (200–4000 cm^{-1}) were recorded on a Perkin-Elmer 16FPC FT-IR spectrophotometer as Nujol or poly(chlorotrifluoroethylene) mulls. Magnetic measurements were performed on solid samples with a Gouy balance calibrated with Hg[Co(SCN)$_4$].

Electrochemical Measurements.—Direct current polarography and cyclovoltammetry were performed, as reported in ref. 5, with an Amel model 471 three-electrode multifunctional assembly. The working electrode was a standard Amel pulsing or stationary electrode and the counter electrode a platinum wire. The reference electrode was Hg|Hg_2Cl_2, NaCl (saturated, aq)|agar–NaCl (aq)|agar (1.5% w/v)–dmf–water (40% v/v)–NEt_4ClO_4 (saturated)|methyl cellulose (5% w/v)–dmf–NEt_4ClO_4 (saturated) sintered-glass disc (dmf = dimethylformamide). Its potential was 22 mV *vs.* an aqueous saturated calomel electrode (SCE), the liquid junction potential being included. All potentials reported in Tables 6 and 7 are quoted with respect to the reference electrode with an accuracy of ± 5 mV.

Crystal Structure Determination of Complex **4**.—Relevant data are summarized in Table 2. Cell parameters were refined from 2θ values of 25 accurately centred high-angle reflections. No significant variation was observed in the intensities of two standard reflections monitored at regular intervals. The X-ray diffraction intensities were corrected for Lorentz and polarization effects and a semiempirical absorption correction based on a ψ scan of selected reflections was applied (transmission factor range 1.063–0.938). Scattering factors, *f'* and *f''* values, were taken from the usual source.[6] The structure was solved by means of direct methods using the SIR-CAOS programs,[7] and refined by full-matrix least-squares methods. Refinement and geometrical calculation were carried out by using the SHELXTL program set.[8]

Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters, and restrained to ride on their associated atoms. Final fractional atomic coordinates are given in Table 3, bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Preparation and Properties of Palladium Complexes.—The compounds NHRNHC(S)SMe (R = Ph, C_6H_4OMe-4 or $C_6H_4NO_2$-4) react readily with $K_2[PdCl_4]$ in aqueous ethanol. If the medium is made strongly basic, crystalline, intensely coloured, diamagnetic compounds **1a**–**1c**, which contain doubly deprotonated ligands, are formed. We assume that there is a progressive deprotonation, in accord with the reactions of NH_2NHC(S)SMe and its 3-substituted derivatives with $K_2[PtCl_4]$[1] and $NiCl_2$.[2] The complexes are soluble in most organic solvents, showing differences depending on the substituent in the phenyl ring. The NO_2-substituted compound is the least soluble. The complexes can be electrochemically oxidized and reduced giving cationic and anionic complexes. They can easily be reduced by $NH_2NH_2 \cdot H_2O$ to monoanionic complexes. We have isolated and characterized [$AsPh_4$]-

[Pd{N($C_6H_4NO_2$-4)NC(S)SMe}$_2$] **2**. The complexes [Pd{NPhNC(S)SMe}$_2$] and [Pd{N(C_6H_4OMe-4)NC(S)SMe}$_2$] show peculiar behaviour when crystallized from boiling C_6H_6. Each formally loses 1 molecule of MeSH giving the new compounds [Pd{N(C_6H_4NPh-2)NC(S)SMe}(NCS)]·0.5C_6H_6 **3** and [Pd{N[C_6H_3(OMe-4)NC_6H_4(OMe-4)]NC(S)SMe}(SCN)]·0.5C_6H_6 **4**, respectively. We previously observed similar behaviour for the complex [Ni{NPhNC(S)SMe}$_2$].[2]

Crystal Structure of Complex **4**.—Figs. 1 and 2 show the structure of the complex labelled in the same way as that of the analogous nickel complex[2] in order to point out similarities and differences. On the whole the electronic distribution and related interatomic distances within the tridentate ligand are again consistent with a system of alternating single and double bonds without any appreciable degree of conjugation (see Table 4). The Pd–N co-ordination bond lengths, 1.961 and 2.073 Å, are almost 0.13 Å longer than the corresponding Ni–N values of 1.833 and 1.934 Å, which is also the difference between the covalent radii of the two metals; they fall however in the range 1.95–2.08 Å reported in the literature.[9–14]

The most noticeable difference between the two complexes is the thiocyanate bonding mode, here sulfur bonded at a distance of 2.30 Å, in close agreement with the value found in other thiocyanate palladium derivatives.[9–11] Since steric hindrance cannot be invoked, nor, on the basis of the above-mentioned similarity of the interatomic distances to those found in the nickel complex, does the methoxy substituent seem to have any electronic effect upon the ligand and donor atoms, such an S-bonding mode should be attributed mainly to the major affinity of palladium for sulfur. The Pd–S(1) distance of 2.260 Å, only 0.085 Å longer than the corresponding Ni–S, confirms this proposition. It remains however one of the shortest Pd–S distances found in this type of compound, where they usually lie in the range 2.29–2.34 Å.[9]

The square-planar arrangement around the palladium slightly suffers from both in-plane (trapezoidal) and out-of-

Table 3 Atomic coordinates (× 10^4) for compound **4**

Atom	*x*	*y*	*z*
Pd	310.3(3)	4 799.8(2)	6 908.2(2)
S(1)	2 472(1)	4 574.4(9)	6 074.6(7)
S(2)	3 954(1)	6 449(1)	4 892.1(7)
S(3)	199(1)	2 819(1)	7 553.9(7)
O(1)	−4 706(4)	9 080(3)	7 138(3)
O(2)	−5 002(4)	2 803(3)	10 122(2)
N(1)	1 345(3)	6 875(3)	5 703(2)
N(2)	273(3)	6 449(3)	6 324(2)
N(3)	−1 618(3)	5 524(3)	7 537(2)
N(4)	2 216(6)	1 136(5)	6 518(4)
C(1)	2 413(4)	6 061(3)	5 588(2)
C(2)	−926(4)	7 110(3)	6 487(3)
C(3)	−1 215(5)	8 264(4)	6 066(3)
C(4)	−2 475(5)	8 845(4)	6 317(3)
C(5)	−3 514(5)	8 350(4)	6 992(3)
C(6)	−3 307(4)	7 262(4)	7 412(3)
C(7)	−2 003(4)	6 571(3)	7 175(2)
C(8)	−2 553(3)	4 871(3)	8 194(2)
C(9)	−4 071(4)	4 225(4)	7 894(3)
C(10)	−4 918(4)	3 518(4)	8 517(3)
C(11)	−4 263(4)	3 469(4)	9 456(3)
C(12)	−2 749(4)	4 141(5)	9 774(3)
C(13)	−1 897(4)	4 815(4)	9 138(3)
C(14)	1 408(5)	1 844(4)	6 916(3)
C(15)	3 624(5)	8 063(4)	4 570(3)
C(16)	−5 869(5)	8 672(6)	7 767(4)
C(17)	−6 498(6)	2 023(5)	9 789(4)
C(18)	675(7)	−907(6)	436(4)
C(19)	624(7)	−1 031(6)	−608(4)
C(20)	−64(7)	−127(6)	−1 030(4)

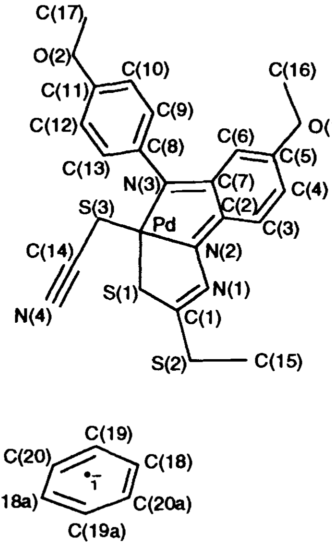

Fig. 1 Schematic view of complex **4** showing the atom labelling and the centrosymmetrical benzene solvent molecule

Table 4 Bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses

Pd–S(1)	2.260(1)	Pd–S(3)	2.298(2)	C(2)–C(3)	1.427(6)	C(2)–C(7)	1.479(5)
Pd–N(2)	1.961(3)	Pd–N(3)	2.073(3)	C(3)–C(4)	1.339(6)	C(4)–C(5)	1.428(6)
S(1)–C(1)	1.739(4)	S(2)–C(1)	1.725(4)	C(5)–C(6)	1.349(6)	C(6)–C(7)	1.425(5)
S(2)–C(15)	1.796(5)	S(3)–C(14)	1.673(5)	C(8)–C(9)	1.381(4)	C(8)–C(13)	1.386(5)
O(1)–C(5)	1.349(5)	O(1)–C(16)	1.426(6)	C(9)–C(10)	1.382(6)	C(10)–C(11)	1.377(5)
O(2)–C(11)	1.361(5)	O(2)–C(17)	1.410(5)	C(11)–C(12)	1.388(5)	C(12)–C(13)	1.379(6)
N(1)–N(2)	1.369(4)	N(1)–C(1)	1.311(5)	C(18)–C(19)	1.383(9)	C(18)–C(20a)	1.341(8)
N(2)–C(2)	1.315(5)	N(3)–C(7)	1.315(5)	C(19)–C(20)	1.353(9)		
N(3)–C(8)	1.426(5)	N(4)–C(14)	1.134(7)				
S(1)–Pd–S(3)	98.0(1)	S(1)–Pd–N(2)	84.2(1)	C(2)–C(3)–C(4)	118.2(4)	C(3)–C(4)–C(5)	122.0(4)
S(3)–Pd–N(2)	176.5(1)	S(1)–Pd–N(3)	164.1(1)	O(1)–C(5)–C(4)	112.2(4)	O(1)–C(5)–C(6)	125.2(4)
S(3)–Pd–N(3)	97.9(1)	N(2)–Pd–N(3)	80.0(1)	C(4)–C(5)–C(6)	122.6(4)	C(5)–C(6)–C(7)	119.0(4)
Pd–S(1)–C(1)	94.4(1)	C(1)–S(2)–C(15)	103.2(2)	N(3)–C(7)–C(2)	115.8(3)	N(3)–C(7)–C(6)	126.5(3)
Pd–S(3)–C(14)	106.2(2)	C(5)–O(1)–C(16)	118.5(4)	C(2)–C(7)–C(6)	117.7(3)	N(3)–C(8)–C(9)	121.9(3)
C(11)–O(2)–C(17)	117.1(3)	N(2)–N(1)–C(1)	110.7(3)	N(3)–C(8)–C(13)	119.2(3)	C(9)–C(8)–C(13)	118.8(3)
Pd–N(2)–N(1)	124.0(2)	Pd–N(2)–C(2)	116.9(2)	C(8)–C(9)–C(10)	120.7(3)	C(9)–C(10)–C(11)	120.2(3)
N(1)–N(2)–C(2)	118.9(3)	Pd–N(3)–C(7)	112.3(2)	O(2)–C(11)–C(10)	124.5(3)	O(2)–C(11)–C(12)	115.9(3)
Pd–N(3)–C(8)	124.7(2)	C(7)–N(3)–C(8)	122.5(3)	C(10)–C(11)–C(12)	119.6(4)	C(11)–C(12)–C(13)	120.0(4)
S(1)–C(1)–S(2)	114.0(2)	S(1)–C(1)–N(1)	126.7(3)	C(8)–C(13)–C(12)	120.7(3)	S(3)–C(14)–N(4)	176.3(5)
S(2)–C(1)–N(1)	119.2(3)	N(2)–C(2)–C(3)	125.1(3)	C(19)–C(18)–C(20a)	119.8(6)	C(18)–C(19)–C(20)	120.1(5)
N(2)–C(2)–C(7)	114.4(3)	C(3)–C(2)–C(7)	120.5(3)	C(19)–C(20)–C(18a)	120.1(5)		

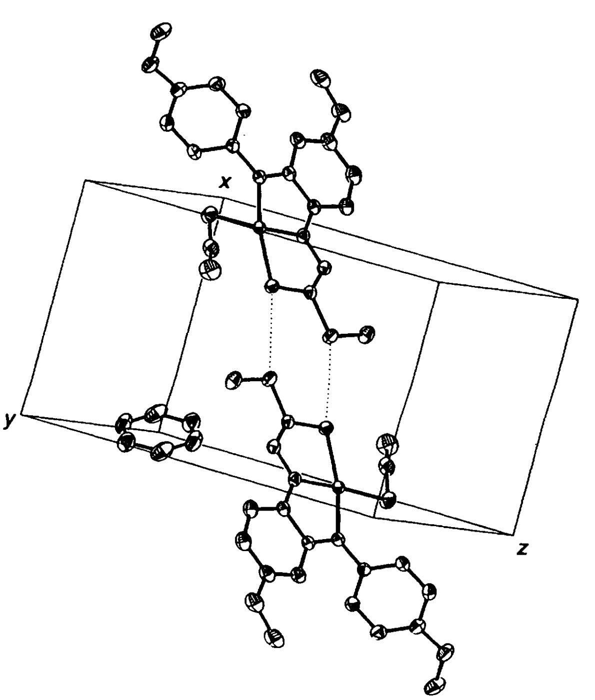

Fig. 2 Perspective view of the unit-cell contents for complex **4**. Only van der Waals contacts among crystallographically equivalent complex molecules are present. The sulfur–sulfur interactions at 3.64 Å between two centrosymmetrical units are shown (dotted lines). Ellipsoids are at the 30% probability level

Table 5 Electronic solution (CH_2Cl_2) (above) and reflectance spectra (below) of the palladium complexes

Compound	$10^{-3}\tilde{\nu}^{a}/cm^{-1}$
1a	11.9 (4.20), [20.3] (3.75), 22.1 (3.86), 28.3 (4.11), [32.7] (4.25), 40.0 (4.45) 11.9, 20.8, [27.0], [34.4], [38.8]
1b	11.6 (4.21), 18.0 (4.12), [19.8] (4.03), 27.4 (4.17), 40.4 (4.52), 11.6, 17.8, 20.4, [27.0], [32.0], 39.1
1c	11.4(3.02),[b] [17.3](2.42),[b] 25.0(2.30),[b] [36.7](3.14),[b] 39.6 (3.17)[b] 11.8, [16.2], 23.6, [32.0], 37.6
2	19.2 (4.47), [23.8] (4.29), [34.7] (4.41), [36.8] (4.42), [37.7] (4.45) [14.7], 17.8, [31.6], 37.6
3	12.4(3.33), [18.9](3.84), 21.6(3.95), [32.05](4.16), [37.0] (4.33), 40.0 (4.38) 11.8, 20.9, 23.1, 37.6
4[c]	11.6 (3.73), [18.5] (3.86), 22.5 (4.17), [30.7] (4.08), 40.0 (4.43) 11.9, 17.8 [27.3], 38.2

[a] log (ε/dm^3 mol^{-1} cm^{-1}) in parentheses, shoulders in square brackets. [b] Very dilute solution (10^{-7} mol dm^{-3}). [c] Chromophore PdN_2S_2, see text.

plane (tetrahedral) distortion. Deviations from the best plane defined by the PdS_2N_2 chromophore are 0.049 and 0.033 Å for N(2) and S(3) and −0.038 and −0.034 Å for N(3) and S(1) respectively. In addition apart from the rotation of the $MeOC_6H_4$ group by 66° around the N(3)–C(8) bond, a 'saddle' distortion can be noted for the complex unit as a whole, the out-of-plane displacements gradually increasing on going from palladium to the peripheral atoms.

Infrared Spectra.—The spectra of the ligands show absorption bands attributable to ν(N–H) (assigned by deuteriation) at 3191 and 3044 cm^{-1} for R = Ph, 3199 and 3103 cm^{-1} for R = C_6H_4OMe-4 and 3281 and 3115 cm^{-1} for R = $C_6H_4NO_2$-4. The bands are not present in the spectra of the corresponding complexes [Pd{NRNC(S)SMe}$_2$] confirming that both N atoms of the ligands are deprotonated. Moreover the spectra show bands attributable to ν(Pd–N) and ν(Pd–S) in the ranges 480–405 and 380–303 cm^{-1}, respectively, in support of N, S chelation. In the spectrum of [Pd{N[(C_6H_3(OMe-4)-NC_6H_4(OMe-4)]NC(S)SMe}(SCN)]·0.5C_6H_6 **4** a sharp absorption at 2112 cm^{-1} is assigned to ν(C≡N) of the thiocyanate group (see text). The presence of a medium band at 2100 cm^{-1} in the spectrum of [Pd{N(C_6H_4NPh-2)NC(S)SMe}(NCS)]·0.5C_6H_6 **3** strongly suggests the assignment to ν(C=N) of isothiocyanate, as found in the nickel complex with the same ligand.[2]

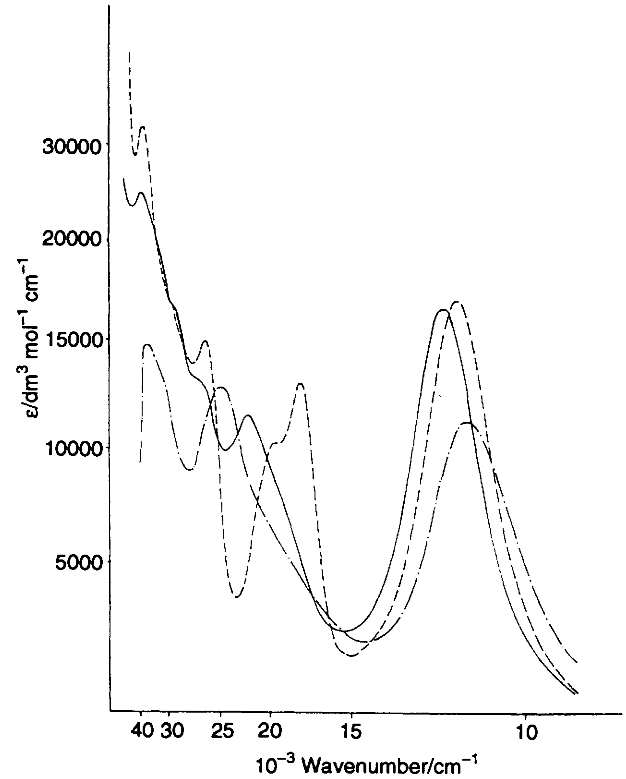

Fig. 3 Electronic spectra in CH_2Cl_2 of [Pd{NRNC(S)SMe}$_2$], where R = Ph **1a** (——), C_6H_4OMe-4 **1b** (– – –) or $C_6H_4NO_2$-4 **1c** (— · — ·)

Electronic Spectra.—Data are given in Table 5. The electronic spectra of the complexes [Pd{NRNC(S)SMe}$_2$] **1a**–**1c** are very similar and show features common to dithiolene-like complexes with electron-transfer properties (see Fig. 3). The prominent strong bands in the range 11 000–12 000 cm^{-1} are assigned to ligand-to-metal charge-transfer (c.t.) absorptions in accord with our previous reports on similar complexes of platinum,[1] nickel[2] and copper.[3] The spectra of **3** and **4** (see Fig. 4) show very similar features to that of [Ni{N(C_6H_4NPh-2)NC(S)SMe}(NCS)].[2]

Electrochemical Measurements.—Cyclovoltammetric and polarographic data are reported in Tables 6 and 7. The voltage range 0–1.5 V was explored in oxidation mode and 0 to −1.5 V in reduction mode. The data for the compounds with doubly deprotonated ligands show that the palladium complexes belong to an electron-transfer series as is usual for dithiolene and dithiolene-like complexes with five-membered delocalized chelate rings (Scheme 1). Both complexes [Pd{NPhNC(S)Me}$_2$] **1a** and [Pd{N(C_6H_4OMe-4)NC(S)-SMe}$_2$] **1b** show well defined oxidation and reduction waves corresponding to one-electron reversible processes leading to the formation of cations **I** and **II** and anions **IV** and **V**. The salt

Table 6 Electrochemical data for the oxidation of palladium complexes in CH_2Cl_2 solution (1×10^{-3} mol dm^{-3})[a]

Cyclic voltammetry[b]

Compound	$E^{\mathrm{I}}_{\mathrm{pa}}$/V	$E^{\mathrm{II}}_{\mathrm{pa}}$/V	$E^{\mathrm{III}}_{\mathrm{pa}}$/V	$\Delta E^{\mathrm{I}}_{\mathrm{p}}$[c]/V	$\Delta E^{\mathrm{II}}_{\mathrm{p}}$[c]/V	$\Delta E^{\mathrm{III}}_{\mathrm{p}}$[c]/V	$i^{\mathrm{I}}_{\mathrm{a}}/i^{\mathrm{I}}_{\mathrm{c}}$	$i^{\mathrm{II}}_{\mathrm{a}}/i^{\mathrm{II}}_{\mathrm{c}}$	$i^{\mathrm{III}}_{\mathrm{a}}/i^{\mathrm{III}}_{\mathrm{c}}$
1a	1.230	0.980		0.110	0.100		1.6	1.0	
1b	1.060	0.840		0.100	0.100		1.5	0.8	
2			0.250			0.100			0.9

D.c. voltammetry at a pulsing platinum electrode[d]

							Slope[e]/V		
	$E^{\mathrm{I}}_{\frac{1}{2}}$/V	$E^{\mathrm{II}}_{\frac{1}{2}}$/V	$E^{\mathrm{III}}_{\frac{1}{2}}$/V	i^{I}/μA	i^{II}/μA	i^{III}/μA	I	II	III
1a	1.220	0.950		0.100	0.100		0.060	0.070	
1b	0.990	0.760		2.96	2.64		0.070	0.070	
2			0.230			0.60			0.080

[a] Containing 0.1 mol dm^{-3} NBu_4BF_4, 20 °C, all potentials *vs.* SCE. [b] Scan rate 200 mV s^{-1}. [c] Anodic (a)-to-cathodic (c) peak potential separation. [d] Pulsing time $t_p = 2$ s. [e] Calculated using $E_{\frac{3}{4}} - E_{\frac{1}{4}}$.

Table 7 Electrochemical data for the reduction of palladium complexes in CH_2Cl_2 solution (1×10^{-3} mol dm^{-3})[a]

Cyclic voltammetry[b]

Compd.	$E^{\mathrm{IV}}_{\mathrm{pc}}$/ V	$E^{\mathrm{V}}_{\mathrm{pc}}$/ V	$\Delta E^{\mathrm{IV}}_{\mathrm{p}}$[c]/ V	$\Delta E^{\mathrm{V}}_{\mathrm{p}}$[c]/ V	$i^{\mathrm{IV}}_{\mathrm{c}}/i^{\mathrm{IV}}_{\mathrm{a}}$	$i^{\mathrm{V}}_{\mathrm{c}}/i^{\mathrm{V}}_{\mathrm{a}}$
1a	−0.225	−0.745	0.090	0.100	1.1	0.9
1b	−0.320	−0.870	0.100	0.110	1.0	1.0
2		−0.110		0.090		1.2
3	−0.080	−0.750	0.140	0.120	1.1	1.2
4	−0.240	−0.870	0.110	0.130	1.1	1.2

D.c. voltammetry at a pulsing platinum electrode[d]

					Slope[e]/V	
	$E_{\frac{1}{2}}^{\mathrm{IV}}$/V	$E_{\frac{1}{2}}^{\mathrm{V}}$/V	i^{IV}/μV	i^{V}/μV	IV	V
1a	−0.185	−0.800	0.70	0.90	0.080	0.090
1b	−0.300	−0.860	2.96	2.96	0.070	0.070
2		−0.080		0.48		0.080
3	−0.055	−0.750	2.40	2.60	0.080	0.090
4	−0.215	−0.850	2.32	2.20	0.090	0.090

[a] Containing 0.1 mol dm^{-3} NBu_4BF_4, 20 °C, all potentials *vs.* SCE. [b] Scan rate 200 mV s^{-1}. [c] Cathodic-to-anodic peak potential separation. [d] Pulsing time $t_p = 2$ s. [e] Calculated using $E_{\frac{3}{4}} - E_{\frac{1}{4}}$.

$$\underset{\mathbf{I}}{[Pd(N_2S_2)]^{2+}} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{\mathbf{II}}{[Pd(N_2S_2)]^{+}} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{\mathbf{III}}{[Pd(N_2S_2)]} \underset{-e}{\overset{+e}{\rightleftharpoons}}$$

$$\underset{\mathbf{IV}}{[Pd(N_2S_2)]^{-}} \underset{-e}{\overset{+e}{\rightleftharpoons}} \underset{\mathbf{V}}{[Pd(N_2S_2)]^{2-}}$$

Scheme 1

$[AsPh_4][Pd\{N(C_6H_4NO_2\text{-}4)NC(S)SMe\}_2]$, corresponding to the anion **IV**, was studied instead of neutral $[Pd\{N(C_6H_4NO_2\text{-}4)NC(S)SMe\}_2]$ **1c** because the low solubility of the latter prevented electrochemical measurements. The salt shows an oxidation wave corresponding to the formation of the neutral complex **III** and a reduction wave corresponding to the formation of the anion **V**. Both complexes containing thiocyanate anion show reduction waves corresponding to processes leading to mono-and di-anionic forms. They lack solid-state electronic delocalization in the ligands,[2] but electrochemical measurements suggest some delocalization in solution. We note that the reduction potentials of the complexes containing a NO_2 group are lower than those of the other complexes considered, owing to the strong electron-attracting effect of the group.

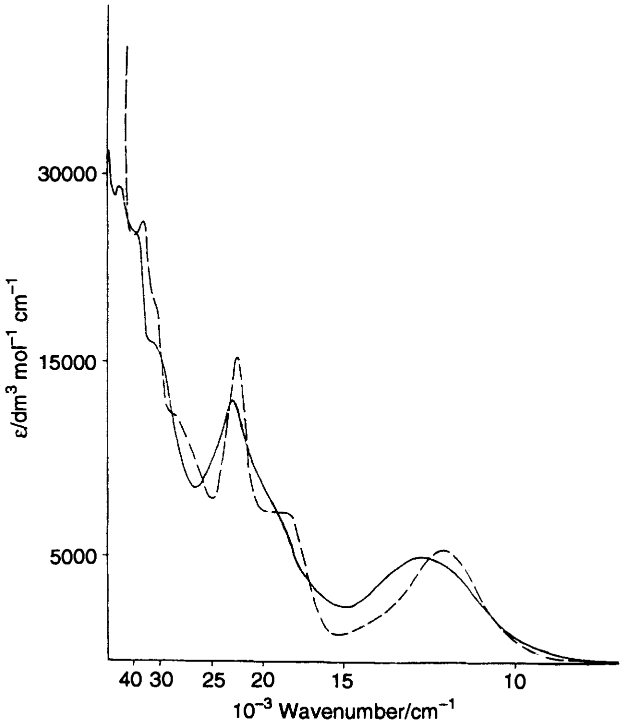

Fig. 4 Electronic spectra in CH_2Cl_2 of complexes **3** (——) and **4** (- - -)

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