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Thioethercarboxylates in palladium chemistry: First proof of hemilabile properties of S–O ligands [1]

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Abstract

The reaction of *trans*-[PdCl(Ph)(PPh_3)$_2$] with the thallium salts 2-RS-C_6H_4-COOTl (R = Me, Et, *i*-Pr or *t*-Bu) yields the compounds *trans*-[Pd(OOC-C_6H_4-2-SR-κ^1-O)Ph(PPh_3)$_2$] (**1a–d**). The solid state structure of the compound with R = Et has been confirmed by X-ray analysis. In solution, however, an equilibrium is established between certain complexes in which one PPh_3 ligand is replaced by the sulphur atom of the S–O ligand to afford chelates. The position of the equilibrium depends on both the electron density on the sulphur and the polarity of the solvent used. The standard free energy and activation energy of the mentioned equilibrium are $\Delta G^0 = 22$ kJ/mol and $E_A = 25$–30 kJ/mol for the complex with R = *i*-Pr (**1c**). © 1998 Elsevier Science S.A.

Keywords: Palladium; Arylpalladium complexes; Hemilability; Sulphur–oxygen ligands

1. Introduction

Activity, selectivity and stability are the most important features of an organometallic catalyst precursor. The search for a balance between high activity on the one hand and sufficient stability on the other leads to the concept of ‘hemilability’. According to the generally accepted belief, a hemilabile bidentate chelating ligand liberates one coordination site of the metal center only ‘on demand’ of a competing substrate like an olefin.

P–O ligands [1–15] are well investigated and their hemilabile behaviour has been proven by spectroscopic methods [1,14]. Under catalytic conditions a number of P–O compounds function as monodentate ligands [5,11,15]. Potentially hemilabile P–N [16–19], P–S [5,20–22], N–O [23–25], O–O [24] and S–O ligands [24] have been examined to a much lesser extent.

In this paper we describe the synthesis and characterisation of phenylpalladium compounds bearing alkylthioethercarboxylate S–O ligands. The molecular structure of one such a complex showed that the potentially bidentate ligand is only oxygen-bonded. In others, hemilabile behaviour of S–O ligands with respect to PPh_3 substitution in solution, was observed.

2. Results and discussion

2.1. Syntheses of trans-2-alkylthiobenzoatobis (triphenylphosphine) phenylpalladium (II) complexes (1a–d)

The new phenylpalladium compounds **1a–d** (Scheme 1) were prepared by stirring *trans*-[PdCl(Ph)(PPh_3)$_2$] with 2-RS-C_6H_4-COOTl in tetrahydrofuran for three days at room temperature. The precipitation of TlCl, which was filtered off, drove the reaction. The complexes were finally obtained in moderate yields by crystallisation from THF/pentane.

The crystal and molecular structures of **1a** and **1b** were determined by X-ray diffraction, but only results for the latter are reported here. [2] The molecular struc-

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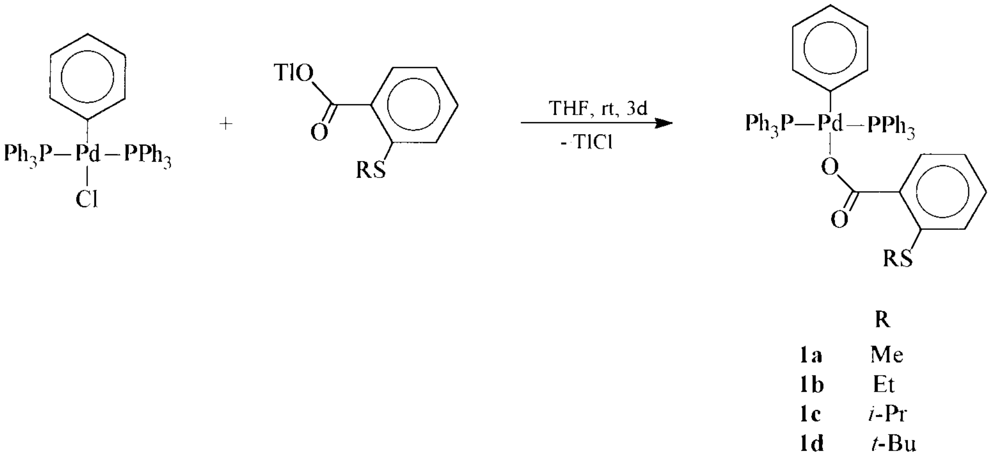
[1] Dedicated to Professor Wolfgang Beck, on the occasion of his 65th birthday.

[2] G.J. Kruger, C. Thompson, W.H. Meyer, R. Brüll, H.G. Raubenheimer, unpublished results.



Scheme 1. Preparation of phenylpalladium compounds **1a–d**.

ture of **1b** clearly shows that the sulphur atom is non-coordinating in the solid state under the chosen reaction conditions (Fig. 1).

2.2. *Infrared spectroscopic characterisation of complexes **1a–d***

The asymmetric and symmetric υ(CO) stretching vibrations for the carboxyl group of the S–O ligands in complexes **1a–d** are found between 1595–1608 cm^{-1} and 1328–1371 cm^{-1}, respectively. The values for the asymmetric stretching vibration correspond to that of a dimeric allyl palladium compound containing two bridging diphenylphosphino butyrate groups (1617 cm^{-1}, nujol), the symmetric vibration of this compound (1289 cm^{-1}, nujol) being at lower energy than those of the complexes **1a–d** [26]. All the frequencies of **1a–d** differ considerably from those of arylnickel compounds with a bidentake κ^2-bonded pyridine carboxylate ligand (1662–1668 cm^{-1}) [23].

2.3. *^{31}P NMR spectroscopic characterisation of complexes **1a–d***

Our original intention with the substitution of chloride in *trans*-[PdCl(Ph)$(PPh_3)_2$] by the negatively charged oxygen atom in potentially bidentate ligands, was to establish whether the neutral sulphur atoms of these ligands would also subsequently replace one PPh_3 group in the reactant complex (Scheme 2). Such a reaction should become thermodynamically more likely with increasing basicity of the sulphur atom. Therefore, a complete series of ligands was used in which an increasing inductive effect of the substituents, R, on the sulphur causes an increased electron density and thus an increased basic strength in the order Me < Et < *i*-Pr < *t*-Bu.

In the solid state Pd–S bond formation was absent. In solution, however, the equilibrium in Scheme 2 was established for compounds **1c** (chloroform) and **1d** (benzene and chloroform) and was clearly recognizable in their ^{31}P NMR spectra (Table 1, Fig. 2).

Complexes **1a** and **1b** formed neither in benzene-d_6 nor in chloroform-d_1 complexes of type **2** containing Pd–S bonds. In compound **1c**, one PPh_3 ligand was substituted only in chloroform-d_1 solution and this process is indicated by the appearance of a new signal at δ 26.6 and by the consequent presence of the signal for free PPh_3 at $\delta - 4.7$ in the ^{31}P NMR spectrum. Even at 70°C no trace of **2c** was found in benzene-d_6. For complex **1d**, with the highest expected electron density on the sulphur, the chelate complex **2d** was observed in both deuterated benzene and chloroform. Thus, the position of the equilibrium depends on both the electron density on the sulphur and the polarity of the solvent used: the higher the electron density and the more polar the solvent the more the equilibrium is shifted to the right side of the equation (Scheme 2). This behaviour holds the promise of good catalytic activity of the complexes **1c** and **1d** in C–C bond formation reactions according to the concept of hemilability. An investigation utilizing the new complexes as catalyst precursors in olefin oligomerisation and co-oligomerisation is presently underway.

The ^{31}P resonances of **1c** and **1d** (Fig. 2) consist of three and two peaks, respectively, and can be attributed to the existence of additional geometric isomers. Indeed, for complex **1a** two such isomers were crystallised and structurally identified by X-ray analysis hinting at a sterically hindered rotation within the S–O ligand in compounds **1a–d**. [1]

2.4. *Determination of thermodynamic parameters for **1c** and **2c***

By using ^{31}P NMR spectral data of **1c** at different temperatures, the values for the equilibrium constant, *K*, and for the rate constant, *k*, applicable to the equa-

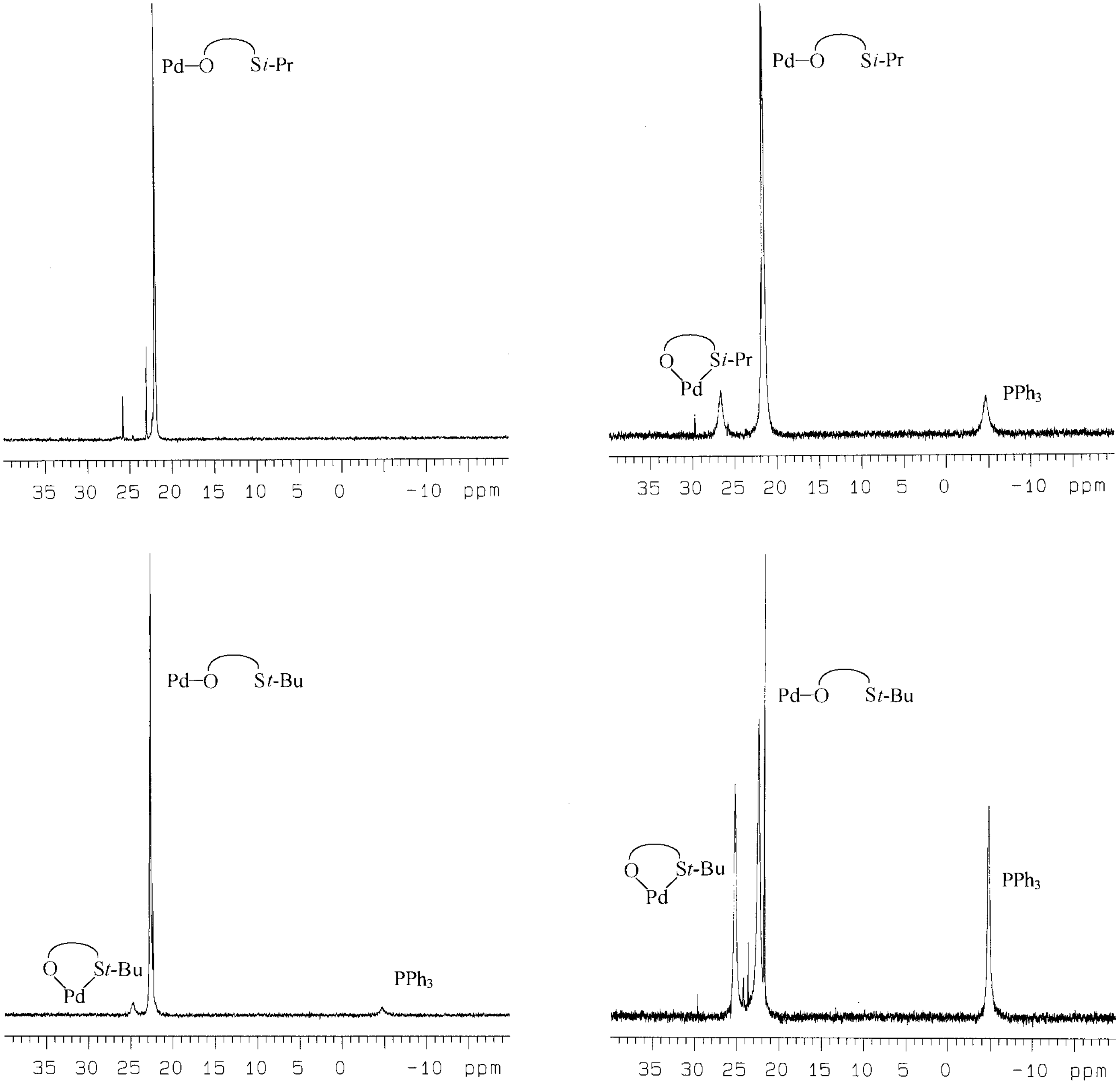
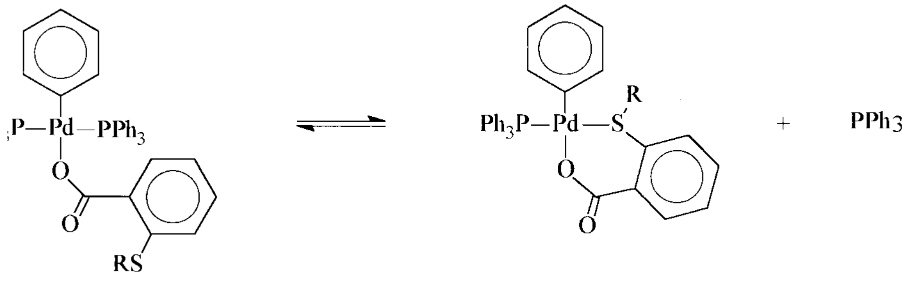


Fig. 1. Schakal drawing of **1b** showing the numbering scheme adopted.



1 **2**

Scheme 2. Possible equilibrium between Pd complexes with a non-chelating and a chelating ligand.

Table 1
Equilibria between type **1** and type **2** complexes. ^{31}P NMR chemical shifts in ppm

Solvent	Complex type	a	b	c	d
C_6D_6	**1**	22.2	22.1	22.0	22.4 22.7
	2	–	–	–	24.8
$CDCl_3$	**1**	21.5	21.4	21.5 21.7 21.9	21.7 22.4
	2	–	–	26.6	25.2

tion in Scheme 2 were determined in chloroform-d_1 solution. The latter was calculated by determining the half widths, h, of the signals for **1c, 2c** and PPh_3 and applying the formula $k = \pi(h - h_0)$ for slow exchange reactions [27]. The value h_0 defines the half width with no exchange occurring and was estimated at 1.5 Hz from the spectrum of **1b**. The approximate equilibrium constants, K, were calculated according to $K = $ [**2c**][PPh_3]/[**1c**] starting with a known amount of **1c** and chloroform-d_1. The equilibrium concentrations of the various compounds participating in the reaction were determined by integration, keeping in mind that the signal of **1c** integrates for two P atoms while that of **2c** refers to only one.

The standard free energy of reaction, ΔG^0, was calculated according to $\Delta G^0 = -RT\ln K$ by plotting $\ln K$ against $1/T$. The activation energy, E_A, followed from an Arrhenius plot ($\ln K$ against $1/T$). Table 2 contains the results and Fig. 3 shows the linear Arrhenius plots.

Due to the influence of the entropy term $T\Delta S^0$ (Scheme 2), the equilibrium is shifted to the right at higher temperatures increasing the equilibrium constants. The value for ΔG^0 was determined in the standard way to be 22 kJ/mol. E_A is of the order of 25–30 kJ/mol.

Substitution occurs to a larger extent for **1d** than for **1c**. The constants, K, at room temperature in chloroform-d_1 solution were calculated as 20×10^{-3} and 4×10^{-3} mol/l respectively. In benzene-d_6, K is smaller (1×10^{-3} mol/l) for compound **1d** under the same conditions.

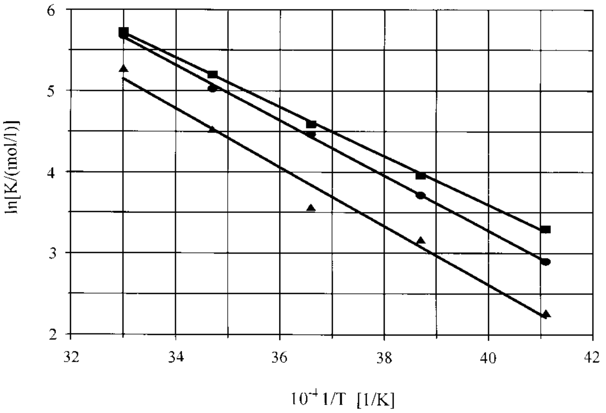


Fig. 2. ^{31}P NMR spectra of **1c** (top) and **1d** (bottom) in C_6D_6 (left) and $CDCl_3$ (right).

2.5. Crystal and molecular structure of 1b

Selected bond lengths and angles are given in Table 3 and fractional atomic coordinates in Table 4. Fig. 1 shows the molecular structure and the adopted numbering scheme. Compound **1b** crystallises in the monoclinic system with unit cell dimensions as given in Table 5 which also contains other crystallographic data. The complex shows a slightly distorted square planar conformation around the central palladium. The deviations of the Pd and the four surrounding ligand atoms which are bonded to the Pd centre, from their least-squares plane (molecular plane) are less than 0.1 Å. The phenyl ring and the carboxylate group of the oxygen-donor ligand are aligned in a plane with deviations of less than 0.07 Å. The phenyl group attached to the central atom is orientated rectangularly to the molecular plane. The ligand plane, however, forms an angle of 63° with the latter.

The 2.3441(2) and 2.3378(2) Å Pd–P and the 2.0024(2) Å Pd–C bond lengths in **1b** compare well with those in *trans*-[PdBr(*o*-tolyl)(PPh_3)$_2$] [2.322(2) Å, 2.319(2) Å, 1.991(8) Å] [28], a compound similar to the starting material. Thus, no major change is introduced by substituting the halide for a carboxylate ligand. Only a few examples of Pd coordinated by one oxygen of a carboxylate moiety are found in the literature. The Pd–O distances in [PdMe(mpyca)(PPh_3)] [25] (mpycaH = 6-methylpyridine-2-carboxylic acid) with a chelating N–O ligand where the oxygen is in *trans* position to the methyl group [2.121(4) Å], and in a dimeric palladium allyl complex with two bridging acetatodiphenylphosphine groups [2.124(6) Å] [26], correspond well to that of **1b** [2.1315(2) Å]. Thus, the complex **1b** does not show unusual structural features. Pd compounds bearing two *trans* [29–31] or *cis* [32] coordinated carboxylate groups have Pd–O bond distances between 2.00 and 2.08 Å. An increased bond

Table 2
Determination of equilibrium and rate constants

T [K]	K [10^{-4} mol/l]	k [l/s]		
		1c	**2c**	PPh_3
243.15	6.7	9.7	18.2	27.0
258.15	10.9	23.9	41.2	52.5
273.15	18.0	35.5	87.3	98.7
288.15	34.3	92.7	153.0	181.3
303.15	54.3	196.3	293.1	309.2
	Results ΔG^0 [kJ/mol]	E_A [kJ/mol]	E_A [kJ/mol]	E_A [kJ/mol]
	21.8 ± 1.2	30.2 ± 2.5	28.3 ± 0.5	25.1 ± 0.5

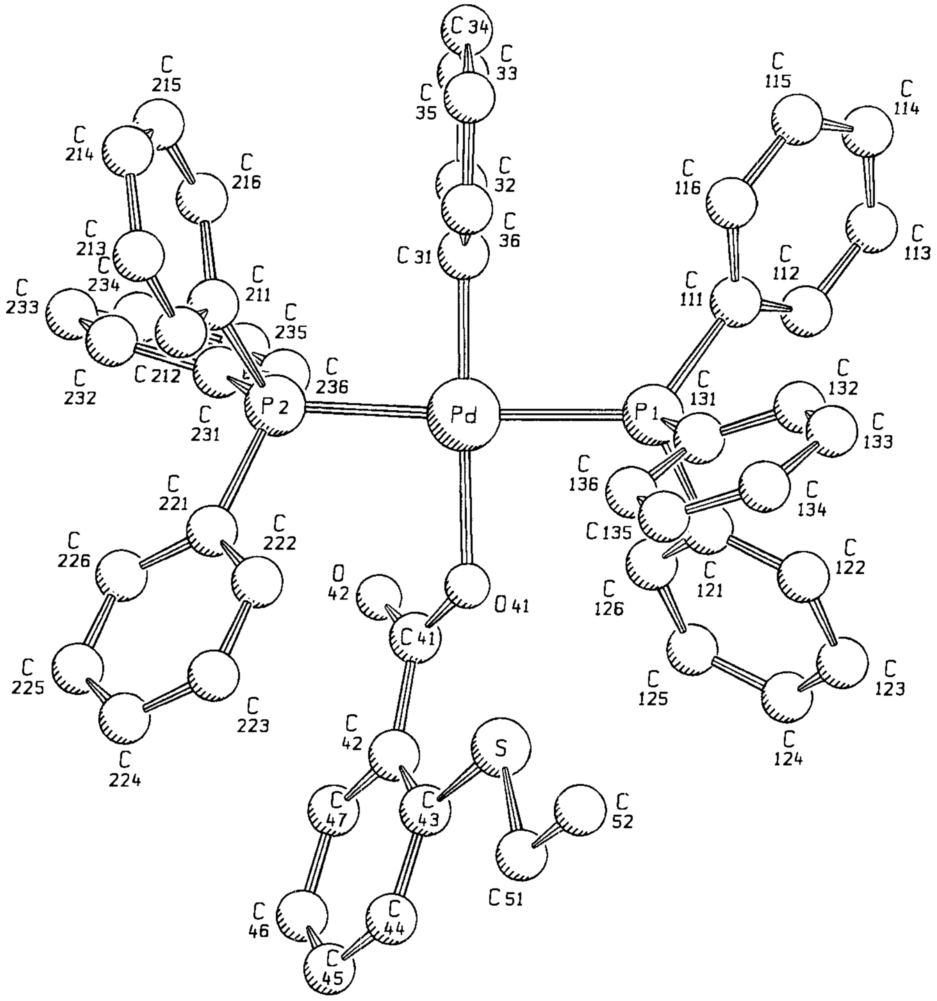


Fig. 3. Arrhenius plots for **1c**; signal basis: **1c**: ■, **2c**: ●, PPh_3: ▲.

length for **1b** is to be expected due to a larger *trans* effect compared to the carboxylate ligand in the *trans*-dicarboxylate Pd complexes.

The geometry of **1b** is similar to that of *trans*-[Ni(*o*-tolyl)(thpca-κ^1-O)$(PPh_3)_2$] (thpcaH = thiophene-2-carboxylic acid) [33] but the bond distances from the Ni metal centre to the adjacent atoms are about 0.1 Å shorter.

Table 3
Selected bond lengths [Å] and angles [°] for **1b**

Pd–P1	2.3441(2)	Pd–O41	2.1315(2)
Pd–P2	2.3378(2)	Pd–C31	2.0024(2)
O41–C41	1.2870(1)	O42–C41	1.2280(1)
P1–Pd–C31	90.36(0)	P1–Pd–O41	88.71(1)
P2–Pd–O41	93.81(1)	P2–Pd–C31	87.14(0)
P2–Pd–P1	177.48(0)	O41–Pd–C31	171.47(0)
Pd–O41–C41	116.28(1)	Pd–C31–C32	123.43(0)
O41–C41–O42	124.45(1)	Pd–C31–C36	118.21(0)
Pd–P1–C111	124.02(0)	Pd–P2–C211	116.75(0)
Pd–P1–C121	111.87(0)	Pd–P2–C221	112.75(0)
Pd–P1–C131	108.25(1)	Pd–P2–C231	113.25(1)

It was found that compound **1a** crystallises in two modifications. They show different molecular structures (to be reported elsewhere) in which the oxygen-donor ligand moiety is turned 180° around the C(carboxyl)–C(phenyl) bond. Compound **1b** shows the same molecular structure as one of these two modifications.

3. Experimental

3.1. General

All reactions and manipulations except the syntheses of ligands and thallium salts were carried out under nitrogen atmosphere using standard Schlenk techniques. Solvents except methanol were dried and purified by standard methods and freshly distilled before use. Other reagents were used without further purification.

The complex *trans*-[PdCl(Ph)$(PPh_3)_2$] [34] and the ligands 2-MeS-C_6H_4-COOH [35] and 2-RS-C_6H_4-COOH (R = Et, *i*-Pr, *t*-Bu) [36,37] were prepared according to literature methods.

Table 4
Fractional coordinates and equivalent isotropic displacement parameters for atoms of **1b**

Atom	x	y	z	U_{eq} /Å^2
Pd	−0.003173(14)	0.48080(2)	0.267937(14)	0.03823(14)
P1	−0.11351(5)	0.53374(6)	0.29400(5)	0.0402(2)
P2	0.10911(5)	0.43457(6)	0.24269(5)	0.0393(2)
O41	−0.05631(14)	0.3474(2)	0.24940(14)	0.0474(6)
O42	0.0567(2)	0.2950(2)	0.3511(2)	0.0685(7)
S	−0.17980(7)	0.24536(7)	0.13754(7)	0.0675(3)
C111	−0.1123(2)	0.6416(2)	0.3459(2)	0.0455(8)
C112	−0.1201(3)	0.6437(3)	0.4182(2)	0.0581(10)
C113	−0.1222(3)	0.7254(3)	0.4557(3)	0.0764(13)
C114	−0.1164(3)	0.8062(3)	0.4210(3)	0.0782(14)
C115	−0.1075(3)	0.8058(3)	0.3497(3)	0.0778(14)
C116	−0.1049(3)	0.7247(3)	0.3127(3)	0.0649(11)
C121	−0.1445(2)	0.4499(2)	0.3504(2)	0.0433(8)
C122	−0.2244(3)	0.4419(3)	0.3410(3)	0.0601(10)
C123	−0.2446(3)	0.3774(4)	0.3867(3)	0.0756(13)
C124	−0.1854(3)	0.3243(3)	0.4408(3)	0.0763(14)
C125	−0.1050(3)	0.3319(3)	0.4525(3)	0.0734(12)
C126	−0.0838(3)	0.3954(3)	0.4070(2)	0.0590(10)
C131	−0.2041(2)	0.5443(2)	0.1976(2)	0.0439(8)
C132	−0.2700(2)	0.6018(3)	0.1856(2)	0.0582(10)
C133	−0.3384(3)	0.6039(3)	0.1121(3)	0.0694(12)
C134	−0.3421(3)	0.5489(3)	0.0499(3)	0.0659(11)
C135	−0.2765(3)	0.4924(3)	0.0609(3)	0.0625(11)
C136	−0.2083(3)	0.4906(3)	0.1332(2)	0.0526(9)
C211	0.1353(2)	0.5073(2)	0.1741(2)	0.0451(8)
C212	0.1037(3)	0.4883(3)	0.0922(2)	0.0548(10)
C213	0.1205(3)	0.5449(4)	0.0404(3)	0.0711(12)
C214	0.1689(3)	0.6205(4)	0.0694(3)	0.0743(14)
C215	0.2003(3)	0.6390(3)	0.1494(4)	0.0765(15)
C216	0.1843(3)	0.5843(3)	0.2032(3)	0.0590(10)
C221	0.0934(2)	0.3222(2)	0.1935(2)	0.0418(8)
C222	0.0166(2)	0.3050(3)	0.1318(2)	0.0497(9)
C223	−0.0003(3)	0.2231(3)	0.0897(3)	0.0613(10)
C224	0.0591(3)	0.1584(3)	0.1092(3)	0.0734(12)
C225	0.1363(3)	0.1744(3)	0.1703(3)	0.0768(14)
C226	0.1534(3)	0.2556(3)	0.2130(2)	0.0580(10)
C231	0.2056(2)	0.4296(2)	0.3336(2)	0.0435(8)
C232	0.2821(2)	0.4223(3)	0.3308(3)	0.0578(10)
C233	0.3543(3)	0.4202(3)	0.4006(3)	0.0704(12)
C234	0.3512(3)	0.4261(3)	0.4740(3)	0.0709(12)
C235	0.2763(3)	0.4332(3)	0.4782(3)	0.0662(11)
C236	0.2044(2)	0.4353(3)	0.4094(2)	0.0507(9)
C31	0.0352(2)	0.6096(2)	0.2681(2)	0.0457(8)
C32	0.0919(3)	0.6533(3)	0.3370(3)	0.0583(10)
C33	0.1140(3)	0.7436(3)	0.3313(4)	0.0803(14)
C34	0.0816(3)	0.7911(3)	0.2605(4)	0.081(2)
C35	0.0257(3)	0.7488(3)	0.1926(4)	0.0724(13)
C36	0.0027(3)	0.6582(3)	0.1961(3)	0.0575(10)
C41	−0.0096(2)	0.2828(3)	0.2928(2)	0.0508(9)
C42	−0.0385(3)	0.1863(2)	0.2661(2)	0.0543(9)
C43	−0.1105(3)	0.1625(3)	0.1980(2)	0.0576(10)
C44	−0.1245(4)	0.0680(3)	0.1792(4)	0.0804(14)
C45	−0.0704(6)	0.0021(4)	0.2239(5)	0.100(2)
C46	−0.0026(6)	0.0259(4)	0.2898(6)	0.101(2)
C47	0.0140(4)	0.1164(3)	0.3116(4)	0.0778(13)
C51	−0.2606(4)	0.1772(4)	0.0636(4)	0.097(2)
C52	−0.3235(5)	0.2408(6)	0.0020(5)	0.116(2)
H112	−0.1278(21)	0.5908(26)	0.4356(20)	0.045(10)
H113	−0.1212(29)	0.7184(32)	0.5097(30)	0.090(15)
H114	−0.1214(27)	0.8579(33)	0.4437(26)	0.077(14)
H115	−0.1089(27)	0.8571(33)	0.3250(26)	0.078(14)
H116	−0.0932(26)	0.7251(30)	0.2697(25)	0.069(13)
H122	−0.2622(32)	0.4804(31)	0.3056(31)	0.082(15)
H123	−0.3028(35)	0.3756(38)	0.3717(31)	0.113(18)
H124	−0.1998(30)	0.2786(37)	0.4675(29)	0.092(15)
H125	−0.0546(36)	0.2982(39)	0.4956(32)	0.118(19)
H126	−0.0293(26)	0.4001(29)	0.4137(23)	0.068(12)
H132	−0.2698(24)	0.6364(27)	0.2276(24)	0.063(11)
H133	−0.3793(25)	0.6404(28)	0.1052(22)	0.056(11)
H134	−0.3867(26)	0.5517(30)	0.0017(26)	0.069(12)
H135	−0.2854(27)	0.4559(31)	0.0153(28)	0.072(13)
H136	−0.1707(25)	0.4548(28)	0.1380(22)	0.052(11)
H212	0.0695(22)	0.4374(26)	0.0720(20)	0.049(10)
H213	0.0995(37)	0.5231(35)	−0.0156(38)	0.111(20)
H214	0.1749(31)	0.6578(37)	0.0354(30)	0.092(16)
H215	0.2285(23)	0.6791(27)	0.1695(21)	0.043(11)
H216	0.2078(23)	0.5966(26)	0.2561(23)	0.055(11)
H222	−0.0219(23)	0.3462(26)	0.1212(21)	0.049(10)
H223	−0.0481(26)	0.2121(26)	0.0519(24)	0.057(11)
H224	0.0456(24)	0.1036(31)	0.0840(23)	0.069(12)
H225	0.1694(27)	0.1303(30)	0.1873(25)	0.071(13)
H226	0.2042(22)	0.2659(22)	0.2554(20)	0.042(9)
H232	0.2833(22)	0.4236(26)	0.2875(22)	0.051(11)
H233	0.3995(32)	0.4087(34)	0.3944(28)	0.090(16)
H234	0.4015(26)	0.4260(29)	0.5201(25)	0.073(12)
H235	0.2789(25)	0.4435(31)	0.5265(26)	0.067(12)
H236	0.1543(22)	0.4418(24)	0.4136(19)	0.043(9)
H32	0.1139(25)	0.6259(28)	0.3900(25)	0.069(12)
H33	0.1571(29)	0.7689(32)	0.3771(28)	0.082(14)
H34	0.0941(28)	0.8496(35)	0.2601(27)	0.084(14)
H35	0.0037(31)	0.7756(35)	0.1400(30)	0.092(16)
H36	−0.0418(24)	0.6302(26)	0.1418(24)	0.064(11)
H44	−0.1715(28)	0.0543(34)	0.1362(27)	0.071(14)
H45	−0.0837(28)	−0.0635(37)	0.2032(28)	0.090(14)
H46	0.0284(42)	−0.0133(41)	0.3254(42)	0.115(22)
H47	0.0572(31)	0.1225(37)	0.3593(30)	0.094(18)
H511	−0.2983(46)	0.1435(51)	0.0901(41)	0.164(28)
H512	−0.2216(34)	0.1283(39)	0.0412(32)	0.119(18)
H521	−0.3759(38)	0.1930(39)	−0.0415(35)	0.125(19)
H522	−0.2951(54)	0.2643(53)	−0.0329(46)	0.164(31)
H523	−0.3578(78)	0.2861(82)	0.0329(72)	0.312(62)

NMR spectra (^{1}H NMR at 300 MHz, ^{13}C {^{1}H} NMR at 75 MHz with Me_4Si as internal standard and ^{31}P {^{1}H} NMR at 121 MHz with 85% H_3PO_4 as external standard) were recorded on a Varian Gemini 2000 NMR spectrometer. For IR spectra (4000 to 600 cm^{-1}, resolution 4 cm^{-1}) a Perkin-Elmer 841 spectrophotometer was used. Elemental analyses were carried out by the Division of Energy Technology, CSIR, Pretoria.

3.2. Crystal structure determinations

Crystals of **1b** suitable for X-ray crystallographic analysis were obtained by crystallisation from THF/pentane. The Siemens SMART CCD system was used for X-ray diffraction data collection at room temperature, using graphite monochromated MoK_α radiation. Empirical absorption corrections were applied by

Table 5
Crystal and refinement data and data collection parameters for 1**b**

Crystal data	
Formula	$C_{51}H_{44}O_2P_2SPd$
Formula weight (g mol^{-1})	889.34
Colour, habit	Light yellow, regular prism
Crystal dimensions (mm^3)	$0.18 \times 0.18 \times 0.25$
μ (mm^{-1})	0.592
Crystal system	Monoclinic
Space group	$P2_1/a$
a(Å)	17.864(1)
b(Å)	14.610(1)
c(Å)	18.228(1)
β(°)	114.849(1)
V(Å^3)	4317.0(5)
Z	4
D(calc.) (g cm^{-3})	1.368
Refinement data	
Refinement method	Full-matrix least-squares on F^2
Number of parameters	690
$R(F)$, observed reflections	0.0331
$wR(F^2)$, all reflections	0.1193
Goodness of fit (S), all	0.991
Δ/σ (max)	< 0.2 (for y of H523)
Δ/σ (mean)	0.009
$\Delta\rho$ (e Å^{-3}), min, max	-0.42, 0.23
Data collection parameters	
Diffractometer	Siemens SMART CCD system (Univ. of the Witwatersrand, Johannesburg)
Radiation	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Monochromator	Graphite
Temperature (K)	293(2)
$F(000)$	1832
Theta range for data collection	1.86° to 23.27°
Index ranges	$-19 \le h \le 15$, $-16 \le k \le 16$, $-20 \le l \le 20$
Reflections collected	15 998
R(internal)	0.022
Independent reflections	6126
Independent observed reflections with $I > 4\sigma(I)$	5417

using the Siemens utility program SADABS for CCD detectors. The structure was solved using SHELXS-86 [38] and refined with SHELXL-93 [39]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were found and refined with isotropic displacement parameters. Final values for the residuals of $R = 0.0331$, $wR = 0.1193$ and $S = 0.991$ were obtained ($wR = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_0^2) + (0.10\ P)^2]$ with $P = (F_0^2 + 2F_c^2)/3$, S = Goodness of fit $= [\Sigma w(F_0^2 - F_c^2)^2/(n-p)]^{1/2}$ with n = number of reflections and p = number of parameters). Important bond lengths and angles of **1b**, the fractional coordinates and equivalent isotropic displacement parameters of all atoms are given in Tables 3 and 4. Table 5 contains crystal data, refinement data and the data collection parameters. All data including anisotropic displacement parameters are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK.

3.3. Preparation of complexes trans-[Pd(OOC-C_6H_4-2-SR-κ^1-O)Ph(PPh_3)$_2$]

2-RS-C_6H_4-COOH (0.63 mmol, R = Me, Et, *i*-Pr, *t*-Bu) was dissolved in 30 ml methanol. The stoichiometric amount of Tl_2CO_3 (148 mg, 0.315 mmol) was added and the mixture refluxed for 30 min. When necessary, water was added (up to 10 ml) during heating until a clear solution was obtained. The solvent was removed in vacuo and the remaining thallium salt dried for another 30 min and subsequently manipulated under nitrogen. A solution of *trans*-[PdCl(Ph)(PPh_3)$_2$] (260 mg, 0.35 mmol) in 15 ml tetrahydrofuran was added to the 80% excess of 2-SR-C_6H_4-COOTl and stirred for three days at room temperature. Precipitated TlCl was filtered off using Celite. The volume of the colourless to orange solutions was reduced in vacuo to approximately 3 ml. The crystallisation of the product at room temperature was initiated by the careful addition of a layer of pentane. Yields were in the range of 40 to 50% without attempting further crystallisation from the mother liquid.

trans-[Pd(OOC-(C_6H_4)-2-SMe-κ^1-O)Ph(PPh_3)$_2$]: colourless crystals, ^{1}H NMR δ (chloroform-d_1, 293 K): 2.10 (s, 3H, SCH_3), 6.3 (m, 2H, Pd-C_6H_5), 6.5 (m, 1H, Pd-C_6H_5 4-H), 6.6 (m, 2H, Pd-C_6H_5), 6.65–7.6 (m, 34H, OOC-(C_6H_4), P(C_6H_5)$_3$). ^{13}C NMR δ (chloroform-d_1, 293 K): 15.9, 121.9, 122.5, 127.1, 127.9, 128.5, 128.6, 129.6, 130.7, 131.1, 132.1, 132.2, 134.5, 137.3, 147.4, 171.1. ^{31}P {^{1}H} NMR δ (chloroform-d_1, 293 K): 21.5. ^{31}P {^{1}H} NMR δ (benzene-d_6, 293 K): 22.2. IR (KBr): υ_{as}(CO): 1608 cm^{-1}, υ_s(CO): 1348 cm^{-1}. Anal. Found: C, 68.4; H, 4.7; S, 3.9. $C_{50}H_{42}O_2P_2SPd$. Calc.:C, 68.6; H, 4.8; S, 3.7%.

trans-[Pd(OOC-(C_6H_4)-2-SEt-κ^1-O)Ph(PPh_3)$_2$]: light-yellow crystals, ^{1}H NMR δ (chloroform-d_1, 293 K): 1.17 (tr, 3H, ^3J = 7.1 Hz, SCH_2CH_3), 2.6 (br, 2H, SCH_2CH_3), 6.2–6.4 (m, 2H, Pd-C_6H_5), 6.4–6.6 (m, 1H, Pd-C_6H_5 4-H), 6.6–6.7 (m, 2H, Pd-C_6H_5), 6.8–7.7 (m, 34H, OOC-(C_6H_4), P(C_6H_5)$_3$). ^{13}C NMR δ (chloroform-d_1, 293 K): 13.2, 26.0, 121.9, 127.1, 127.9, 128.5, 129.6, 130.7, 130.9, 131.2, 134.5, 137.3, 147.3, 171.1. ^{31}P {^{1}H} NMR δ (chloroform-d_1, 293 K): 21.4. ^{31}P {^{1}H} NMR δ (benzene-d_6, 293 K): 22.1. IR (KBr): υ_{as}(CO): 1602 cm^{-1}, υ_s(CO): 1353 cm^{-1}. Anal. Found: C, 68.9; H, 5.1; S, 3.7. $C_{51}H_{44}O_2P_2SPd$. Calc.: C, 68.9; H, 5.0; S, 3.6%.

trans-[Pd(OOC-(C_6H_4)-2-S*i*-Pr-κ^1-O)Ph(PPh_3)$_2$]: colourless crystals, ^{1}H NMR δ (benzene-d_6, 293 K): 1.13 (d, 6H, ^3J = 5.7 Hz, SCH(CH_3)$_2$), 3.16 (m, 1H, SCH(CH$_3$)$_2$), 6.3–6.5 (m, 2H, Pd-C$_6$H$_5$), 6.5–6.6 (m, 1H, Pd-C$_6$H$_5$) 6.6–8.2 (m, 36H, Pd-C$_6$H$_5$, OOC-(C$_6$H$_4$), P(C$_6$H$_5$)$_3$). ^{13}C NMR δ (benzene-d_6, 293 K): 22.8, 33.8, 122.1, 129.8, 130.8, 130.6, 130.9, 131.2, 131.5, 132.1, 132.3, 132.5, 135.1, 138.1, 141.4. ^{31}P {^{1}H} NMR δ (benzene-d_6, 293 K): 22.0. ^{31}P {^{1}H} NMR δ (chloroform-d_1, 293 K): 21.5, 21.7, 21.9. IR (KBr): υ_{as}(CO): 1608 cm^{-1}, υ_s(CO): 1328 cm^{-1}. Anal. Found: C, 68.9; H, 5.0; S, 3.4. $C_{52}H_{46}O_2P_2SPd$. Calc.: C, 69.1; H, 5.1; S, 3.5%.

trans-[Pd(OOC-(C$_6$H$_4$)-2-St-Bu-κ^1-O)Ph(PPh$_3$)$_2$]: light orange crystals, ^{1}H NMR δ (benzene-d_6, 293 K): 1.1 (s, 7.4H, SC(CH$_3$)$_3$, S not coordinated), 1.2–1.3 (m, br, 1.6H, SC(CH$_3$)$_3$, S coordinated), 6.2–7.9 (m, 39H, Pd-C$_6$H$_5$, OOC-(C$_6$H$_4$), P(C$_6$H$_5$)$_3$). ^{13}C NMR δ (benzene-d_6, 293 K): 31.4, 45.0, 121.9, 126.5, 126.8, 127.1, 129.9, 130.6, 130.7, 131.2, 131.5, 131.8, 132.3, 132.4, 135.3, 136.2, 137.8. ^{31}P {^{1}H} NMR δ (benzene-d_6, 293 K): 22.4, 22.7. ^{31}P {^{1}H} NMR δ (chloroform-d_1, 293 K): 21.7, 22.4. IR (KBr): υ_{as}(CO): 1595 cm^{-1}, υ_s(CO): 1371 cm^{-1}. Anal. Found: C, 69.7; H, 5.1; S, 3.2. $C_{53}H_{48}O_2P_2SPd$. Calc.: C, 69.4; H, 5.3; S, 3.5%.

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