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Mononuclear Pt(II) and Pd(II) 1,4-dithiolato complexes. Crystal structures of $[Pt((-)DIOS)(PPh_3)_2]$ and $[Pd(S(CH_2)_4S)(Ph_2P(CH_2)_3PPh_2)]$. Application in styrene hydroformylation

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Abstract

Addition of 1,4-dithiols to dichloromethane solutions of $[PtCl_2(P-P)]$ (P–P = $(PPh_3)_2$, $Ph_2P(CH_2)_3PPh_2$, $Phd_2P(CH_2)_4PPh_2$; 1,4-dithiols = $HS(CH_2)_4SH$, (−)$DIOSH_2$ (2,3-*O*-isopropylidene-1,4-dithiol-L-threitol), $BINASH_2$ (1,1′-dinaphthalene-2,2′-dithiol)) in the presence of NEt_3 yielded the mononuclear complexes [Pt(1,4-dithiolato)(P–P)]. Related palladium(II) complexes [Pd(dithiolato)(P–P)] (P–P = $Ph_2P(CH_2)_3PPh_2$, $Ph_2P(CH_2)_4PPh_2$; dithiolato = $^-S(CH_2)_4S^-$, (−)-DIOS) were prepared by the same method. The structure of $[Pt((-)DIOS)(PPh_3)_2]$ and $[Pd(S(CH_2)_4S)(Ph_2P(CH_2)_3PPh_2)]$ complexes was determined by X-ray diffraction methods. Pt–dithiolato–$SnCl_2$ systems are active in the hydroformylation of styrene. At 100 atm and 125 °C [Pt(dithiolate)(P–P)]/$SnCl_2$ (Pt:Sn = 20) systems provided aldehyde conversion up to 80%.

Keywords: Platinum; Palladium; Thiolate; Hydroformylation

1. Introduction

Metal thiolate complexes have been extensively studied, and several reviews concerning their synthesis and reactivity have been reported [1]. Although to a lesser extent than for phosphorus ligands, their use as catalyst precursors in homogeneous catalytic reactions has also been studied [2–6]. The high catalytic activity shown by dinuclear bridged thiolate rhodium complexes in the hydroformylation of alkenes [2] has rekindled interest in this kind of complex. Several modified thiolato bridge rhodium(I) complexes have been studied in catalysis: with fluorosubstituted monothiolates $[Rh(\mu\text{-}SC_6H_xF_{5-x})(CO)_2]$ ($x = 1, 4$) [4], with aminothiolates $[Rh\{\mu\text{-}S(CH_2)_3NMe_2\}(COD)]_2$ [3], and with dithiolates $[Rh_2(\mu\text{-}S(CH_2)_nS)(COD)_2]$ ($n = 2, 3, 4$) [6,7]. Introducing a chiral centre into the dithiolate [8,9] and adding a chiral phosphorus ligand [10] have enabled them to be used in the asymmetric hydroformylation of styrene. Even though rhodium thiolate complexes have been shown to promote activity in homogeneous catalytic hydroformylation, there are few examples of studies involving metals other than rhodium and processes other than hydroformylation [11–13].

It is known that Pt(II)-chiral-diphosphine complexes give higher enantioselectivities than the corresponding rhodium(I) ones [14]. Only recently have enantiomeric excesses (*ee*) of up to 95% in styrene hydroformylation using Rh(I)-chiral-phosphine–phosphite [15] and Rh(I)-diphosphinite [16] complexes been achieved. The best results using platinum–phosphorus ligand systems were obtained with BPPM [17] and BDPP [18,19] ligands (Fig. 1), and the enantioselectivities achieved were high or excellent (88–96%). However, in the case of platinum systems, the chemical yields in the branched aldehydes are usually unsatisfactory.

We recently reported the preparation of rhodium(I) complexes [8,9] with the chiral dithiolates 2,3-*O*-isopropylidene-1,4-dithiolate-L-threitol ((−)-DIOS) [20] and 1,1′-dinaphthalene-2,2′-dithiolate (BINAS) [21] (Fig. 2). We considered it of interest to extend the study to the

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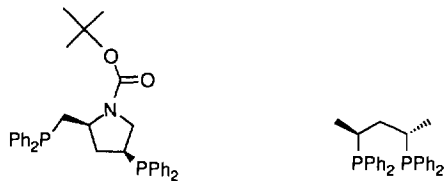
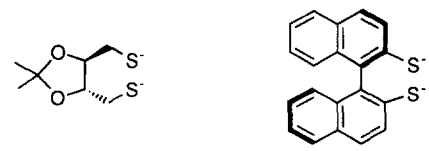


BPPM BDPP

Fig. 1. Chiral diphosphine ligands BPPM and BDPP.



DIOS BINAS

Fig. 2. Chiral dithiolato ligands DIOS and BINAS.

preparation of platinum complexes with the above-mentioned chiral dithiolates DIOS and BINAS in order to study the catalytic activity in asymmetric hydroformylation. These dithiolates have an analogous skeleton to some of the most effective chiral diphosphines DIOP and BINAP, both of C_2 symmetry, used in hydroformylation with Pt complexes [22,23].

There are few examples in the literature of catalytic studies on hydroformylation with platinum thiolate complexes. It has been reported that dinuclear platinum(II) thiolates $[PtCl(PR_3)(\mu\text{-}SR')]_2$, in the presence of $SnCl_2$, behave like active catalysts in styrene hydroformylation [11,12].

Platinum(II) and palladium(II) dithiolate phosphine complexes have mainly been described as containing ligands 1,2- and 1,3-dithiolates and triphenylphosphine or diphosphines $Ph_2P(CH_2)_nPPh_2$ (n = 1, 2, 3) [11,12,24–28]. The 1,4-butanedithiolato complex $[Pt(S(CH_2)_4S)(Ph_2P(CH_2)_2PPh_2)]$ has been prepared in a poor yield (18%) owing to the high tendency of dithiolate complexes to form long chain oligomers [24].

Here we study the preparation and catalytic activity of new mononuclear platinum(II) and palladium(II) complexes [M(1,4-dithiolato)(phosphine)] with the 1,4-dithiolates: 1,4-butanedithiolate (BDT), (−)-DIOS and BINAS. The achiral ligand BDT was chosen as a model for the reactivity and catalytic behaviour of the chiral compounds (−)DIOS and BINAS. The phosphines selected for platinum complexes are triphenylphosphine, $Ph_2P(CH_2)_nPPh_2$ (n = 3 (dppp) and n = 4 (dppb)) and dppp and dppb for palladium complexes.

2. Results and discussion

2.1. Preparation of [Pt(dithiolate)(P–P)] complexes

Complexes [Pt(dithiolate)(P–P)] (dithiolate = $^-S(CH_2)_4S^-$ (BDT), (−)-DIOS, BINAS and P–P =

Table 1
^{1}H data δ (ppm) for platinum and palladium dithiolate complexes **1–13** in $CDCl_3$ [a]

Compound	BDT		(−)-DIOS			BINAS	dppb		dppp	
	$-(CH_2)_2-$	$-S-CH_2$	$-CH_3$	$-CH_2-$	$-CH-$	$-CH-$	$-(CH_2)_2-$	$-P-CH_2-$	$-CH_2-$	$-P-CH_2-$
1	1.70(br)	2.56(m)	—	—	—	—	—	—	—	—
2	—	—	1.35(s)	2.45(m) 2.80(m)	4.05(br)	—	—	—	—	—
3	—	—	—	—	—	6 90(d), 7.00(t) 7.80(d), 7.60(d)	—	—	—	—
4	1.75(br)	2.55(ov)	—				1.60(dr)	2.55(ov)	—	—
5	—	—	1.27(s)	2.53(ov)	3.88(br)	—	1.60(m	2.55(ov)	—	—
6	—	—	—	—	—	6.75(d), 6.93(l) 7.08(d), 7.20(t) 7.50(d), 7.7(d)	1.65(m)	2.55(ov)	—	—
7	1.70(br)	2.77(m)	—	—	—	—	—	—	1.95(m)	2.50(m)
8	—	—	1.35(s)	2.80(br)	3.97(br)	—	—	—	1.95(m)	2.50(br)
9	—	—	—	—	—	6.75(d), 6.05(t) 7.20(d), 7.23(l) 7.50(ov), 7.77(d)	—	—	1.95(m)	2.95(br)
10	1.80(br)	2.48(ov)				—	1.50(br)	2.40(ov)	—	—
11	—	—	1.27(s)	2.45(m)	3.85(br)	—	1.75(m)	2.25(m)	—	—
12	1.70(br)	2.65(br)	—	—	—	—	—	—	1.95(m)	2.40(br)
13	—	—	1.05(s)	2.75(m)	3.95(m)	—	—	—	1.95(m)	2.45(br)

[a] br: wide signal, ov: overlapped. ^{1}H NMR data δ (ppm) signals for free ligands. $BDTH_2$: 1.70 (m, $-(CH_2)_2-$); 2.60 (m, $-S-CH_2-$);. $DIOSH_2$: 1.41 (s. $-CH_3$); 2.79 (m, $-CH_2-$); 3.99 (m, −CH−); 1.60 (m, −SH). $BINASH_2$: 3.26 (s, −SH); 7.00 (d, ^2J = 8.2 Hz, −CH−); 7.28 (m, −CH−); 7.42 (m, −CH−); 7.57 (d, ^2J = 8.8 Hz, −CH−); 7.80 (d, J = 8.8 Hz, −CH−). Dppb: 1.55 (m, $-(CH_2)_2-$); 2.05 (m, $-P-CH_2-$); 7.2–7.5 (Ph). Dppp: 1.65 (m, $-CH_2-$); 2.30 (m, $-P-CH_2-$); 7.2–7.4 (Ph).

Table 2
Comparative ^{31}P NMR data for complexes with different diphosphine and dithiolate member rings

Entry	Complex	P–P ring size	S–S ring size	$\delta^{31}P$ (ppm)	Ref.
1	[Pt(S(CH$_2$)$_2$S)(dppb)]	7	5	12.91	[26]
2	[Pt(S(CH$_2$)$_3$S)(dppb)]	7	6	15.08	[26]
3	**4**	7	7	16.17	—
4	**5**	7	7	15.84	—
5	**6**	7	7	18.12	—
6	[Pt(S(CH$_2$)$_2$S)(dppp)]	6	5	−3.57	[26]
7	[Pt(S(CH$_2$)$_3$S)(dppp)]	6	6	−12.69	[26]
8	**7**	6	7	2.06	—
9	**8**	6	7	1.40	—
10	**9**	6	7	2.64	—

$(PPh_3)_2$, $Ph_2P(CH_2)_4PPh_2$ (dppb) and $Ph_2P(CH_2)_3PPh_2$ (dppp)) were prepared for reaction of the complex *cis*-[$PtCl_2$(P–P)] with the corresponding dithiols in the presence of a small amount of triethylamine (see reaction in Eq. (1)). The reactions took place in dichloromethane solutions at room temperature, except for the triphenylphosphine complexes in which reflux was required.

$$[PtCl_2(P\text{–}P)] + \text{dithiolate} \xrightarrow{NEt_3} [Pt(\text{dithiolate})(P\text{–}P)] + 2Et_3NHCl \quad (1)$$

Complex	P–P	dithiolate
1	$(PPh_3)_2$	BDT
2	$(PPh_3)_2$	(−)DIOS
3	$(PPh_3)_2$	BINAS
4	dppb	BDT
5	dppb	(−)DIOS
6	dppb	BINAS
7	dppp	BDT
8	dppp	(−)DIOS
9	dppp	BINAS

Complexes **1** to **9** were isolated in good yields as relatively air-stable yellow solids and were characterised by the usual techniques. Elemental analyses corresponded to the calculated data. The crystal and molecular structure of complex **2** was determined by X-ray diffraction methods and is discussed below.

The FAB mass spectra of complexes **1** and **3–9** show the peak corresponding to the molecular ion, which is evidence of the mononuclearity of the compound. Partial rupture of the dithiolate ligand was observed through the presence of the corresponding PtS(P–P) fragment. Complete loss of the dithiolate caused the formation of the Pt(P–P) fragments.

^1H NMR spectral data (Table 1) show that the signals corresponding to the coordinated dithiolates are slightly shifted from the free ligands. Diastereotopic methylenic protons are well defined in complex **2**, splitting into two groups of signals at 2.45 and 2.80 ppm, but appear as a single, broad chemical shift for the rest of the chiral complexes. Many of the protons appear as broad signals due probably to conformational exchanges. In the case of complexes containing diphosphines, the signals assigned to the methylenic protons of the coordinated phosphorus ligand appear downfield with respect to the free ligand.

For all the complexes **1** to **9**, the $^{31}P\{^1H\}$ NMR spectra (Section 3) show a single chemical shift with the corresponding pair of ^{195}Pt satellites consistent with a square-planar Pt(II) geometry with cis rearrangement of the phosphorus ligands. In all cases the chemical shift was higher than the one with the corresponding dichloride. The ^{195}Pt–^{31}P coupling constant decreased compared with the corresponding [$PtCl_2$(P–P)] starting materials, indicating that the dithiolates exert a higher *trans* influence than the chloride ligands.

The reported effect of diphosphine ring size on phosphorus signal is observed [27,29]. The effect of the dithiolate ring size on the ^{31}P chemical shift was reported to be less important [27]. In order to establish the scope of this effect, the chemical shifts for different

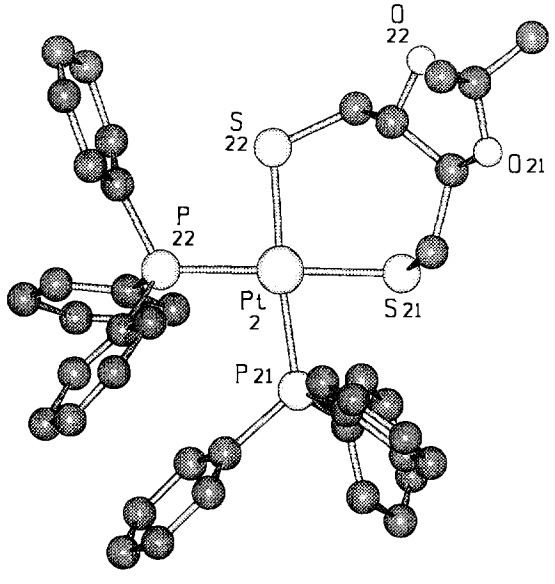


Fig. 3. Molecular structure of compound **2**, *cis*-[Pt((−)-DIOS)$(PPh_3)_2$)].

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex *cis*-[Pt((−)-DIOS)(PPh_3)$_2$]

	x	y	z	U_{eq} [a]
Pt(1)	8731(1)	2(1)	1224(1)	50(1)
S(11)	8957(3)	248(7)	436(4)	80(4)
S(12)	7568(3)	816(7)	608(4)	68(3)
P(12)	8365(3)	−190(5)	1163(4)	50(2)
P(11)	9615(4)	−617(6)	1809(5)	55(3)
C(101)	8455(13)	839(26)	−298(20)	118(17)
C(102)	7859(11)	734(15)	−706(13)	59(7)
C(103)	7565(10)	132(19)	−585(12)	60(8)
C(104)	7333(8)	337(17)	−177(11)	43(7)
O(11)	7786(10)	383(16)	−1360(12)	87(8)
O(12)	7080(9)	−130(16)	−1282(10)	95(8)
C(105)	7318(11)	2(20)	−1683(13)	60(7)
C(106)	6849(16)	370(24)	−2296(20)	100(12)
C(107)	7361(13)	−729(17)	−1884(12)	167(20)
C(111)	9999(7)	−765(14)	1494(9)	59(8)
C(112)	9971(7)	−1515(14)	1229(9)	75(8)
C(113)	10312(13)	−1649(29)	929(17)	93(11)
C(114)	10614(12)	−924(20)	898(15)	7368)
C(115)	10667(14)	−262(23)	1201(17)	85(11)
C(116)	10325(11)	−257(18)	1467(14)	71(9)
C(121)	10148(12)	−62(22)	2638(15)	57(7)
C(122)	10726(10)	−384(17)	3098(12)	48(7)
C(123)	11141(12)	138(23)	3650(15)	71(9)
C(124)	10991(14)	928(23)	3753(18)	88(10)
C(125)	10448(13)	1154(23)	3297(16)	70(10)
C(126)	10040(11)	675(20)	2755(14)	52(7)
C(131)	9518(8)	−1617(11)	2114(10)	69(8)
C(132)	9848(8)	−1914(14)	2767(9)	73(9)
C(133)	9725(10)	−2657(15)	2898(9)	117914)
C(134)	9272(11)	−3102(11)	2377(13)	108(12)
C(135)	8943(8)	−2805(13)	1725(11)	113(14)
C(136)	9066(8)	−2062(14)	1594)(8)	73(9)
C(141)	7666(12)	−718(18)	1341(15)	53(8)
C(142)	7144(13)	−576(21)	1275(16)	73(9)
C(143)	6652(14)	−850(22)	859(17)	89(11)
C(146)	6586(20)	−1457(30)	473(23)	134(16)
C(145)	7131(15)	−1803(28)	551(19)	100(13)
C(146)	7665(14)	−1340(25)	998(18)	85(10)
C(151)	8261(8)	747(9)	2209(9)	60(8)
C(152)	8432(6)	1472(11)	2109(7)	39(6)
C(153)	8367(8)	2154(9)	2379(9)	59(7)
C(154)	8130(9)	2110(11)	2749(10)	113(14)
C(155)	7959(7)	1385(14)	2849(8)	79(10)
C(156)	8024(8)	704(11)	2580(10)	72(9)
C(161)	8721(11)	−788(16)	2622(13)	57(8)
C(162)	8563(11)	−1492(17)	2696(13)	63(7)
C(163)	8855(17)	−1936(28)	3320(21)	118(14)
C(164)	9281(13)	−1696(20)	3826(16)	79(9)
C(165)	9512(17)	−1149(27)	3906(20)	111(12)
C(166)	9246(12)	−424(19)	3265(14)	74(9)
Pt(2)	11234(1)	−6528(1)	3789(1)	48(1)
P(22)	10352(3)	−5842(5)	3107(5)	54(3)
P(21)	11591(3)	−6287(6)	3121(4)	63(3)
S(22)	10967(3)	−6741(6)	4521(4)	60(3)
S(21)	12120(3)	−7261(6)	4404(4)	54(2)
C(201)	12652(11)	−6715(27)	5145(16)	85(13)
C(202)	12643(8)	−7014(18)	5756(12)	58(8)
C(203)	12118(11)	−6742(18)	5738(12)	56(7)
C(204)	11548(9)	−7349(22)	5229(12)	63(9)
O(21)	13090(7)	−6686(14)	6371(10)	78(7)
O(22)	12290(8)	−6868(16)	6378(11)	75(7)
C(205)	12937(10)	−6611(25)	6827(13)	70(10)
C(206)	13233(11)	−7206(21)	7377(14)	91(10)
C(205)	12966(15)	−5699(29)	6978(24)	150(19)
C(211)	11740(11)	−7154(16)	2813(13)	61(8)
C(212)	11520(17)	−7917(27)	2909(21)	117(14)
C(213)	11497(15)	−8594(22)	2640(18)	96(11)
C(214)	11856(12)	−8577(19)	2242(14)	76(10)
C(215)	11988(13)	−7896(22)	2143(15)	86(10)
C(216)	11959(12)	−7144(20)	2415(15)	79(10)
C(221)	12293(12)	−5775(18)	3636(16)	54(8)
C(222)	12327(13)	−5100(23)	4048(16)	74(9)
C(223)	12819(14)	−4698(24)	4407(18)	84(10)
C(224)	13307(12)	−4778(19)	4463(14)	70(8)
C(225)	13298(15)	−5388(22)	4070(17)	93(11)
C(226)	12779(15)	−6063(27)	3670(19)	100(12)
C(231)	11199(8)	−5640(13)	2349(8)	68(9)
C(232)	10716(8)	−5988(10)	1782(10)	81(910)
C(233)	10417(7)	−5593(12)	1169(8)	65(7)
C(234)	10602(8)	−4850(12)	1122(8)	108(13)
C(235)	11085(8)	−4502(10)	1689(11)	67(8)
C(236)	11383(7)	−4897(13)	2302(9)	94(11)
C(241)	9801(11)	−6372(21)	2348(14)	51(7)
C(242)	9220(12)	−8171(21)	1944(15)	72(9)
C(243)	8797(13)	−6440(24)	1397(17)	79(9)
C(244)	8978(11)	−7248(19)	1273(14)	60(7)
C(245)	9521(12)	−7604(21)	1656(15)	64(9)
C(246)	9967(13)	−7138(22)	2201(16)	69(9)
C(251)	10421(11)	−4875(15)	2797(14)	63(8)
C(252)	10047(13)	−4644(20)	2127(16)	77(9)
C(253)	10160(13)	−3845(18)	1956(16)	78(9)
C(254)	10583(12)	−3376(19)	2434(14)	76(8)
C(255)	10924(12)	−3572(17)	3113(14)	68(8)
C(296)	10854(13)	−4354(19)	3321(16)	80(10)
C(261)	9934(9)	−5591(15)	3481(11)	42(6)
C(262)	9945(10)	−4915(17)	3762(11)	56(7)
C(263)	9661(13)	−4835(28)	4104(17)	89(11)
C(264)	9396(14)	−5314(21)	4126(17)	64(10)
C(265)	9340(13)	−6100(22)	3863(16)	79(10)
C(266)	9596(5)	−6253(7)	3450(5)	66(8)
O(1)	9229(5)	−3109(7)	5003(5)	84(5)
C(1)	13548(5)	−7993(7)	4601(5)	176(21)
C(2)	13146(5)	−8456(7)	4200(5)	157(17)
O(2)	7960(5)	−2201(7)	−353(5)	94(13)
O(2)	8327(5)	−1988(7)	−352(5)	65(9)
O(3)	12073(5)	−4283(7)	5255(5)	61(9)
O(3)	11659(5)	−4577(7)	5154(5)	72(10)
O(4)	9960(5)	−7760(7)	709(5)	110(14)
O(4)	10540(5)	1950(7)	883(5)	35(6)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

diphosphino and dithiolato ring sizes are summarised in Table 2. For dppb complexes (entries 1–5) an increase in the dithiolate ring constraint increases phosphorus shielding regardless of the even–odd dithiolato ring size. The same tendency was observed when the compounds were compared with the seven-membered ring complexes **4–6**. The bicyclic, and consequently more rigid, DIOS complex **5** shows a slightly lower chemical shift than the complexes with BDT, **4**, and the binaphthyl ligand, **6**.

Table 4
Selected distances (Å) and angles (deg) for *cis*-[Pt((−)-DIOS)$(PPh_3)_2$] (**2**)

Pt2–P21	2.332(8)	S22–C204	1.86(3)
Pt2–P22	2.338(8)	S21–C201	1.80(3)
Pt2–S22	2.361(7)	C201–C202	1.58(4)
Pt2–S21	2.386(7)	C202–O21	1.40(3)
P22–C241	1.82(3)	C202–C203	1.52(3)
P22–C251	1.86(3)	C203–022	1.35(3)
P22–C261	1.90(2)	C203–C204	1.69(4)
P21–C211	1.80(3)	O21–C205	1.40(3)
P21–C221	1.83(3)	O22–C205	1.56(3)
P21–C231	1.88(2)	C205–C206	1.49(4)
		C205–C207	1.58(5)
P21–Pt2–P22	98.2(3)	P21–Pt2–S21	80.6(3)
P21 –P12–522	174.2(2)	P22–Pt2–S22	86.0(3)
P22–Pt2–S21	177.5(3)	S22–P12–S21	95.4(3)
C204–522–P12	107.5(8)	C201–S21–Pt2	109.6(14)
C202–C201–52	108.8(23)	C203–C204–S22	107.2(22)
C202–C203–C204	109.1(21)	C203–C202–C201	114.3(22)

Complexes with the more rigid diphosphine ligand dppp seem to be more sensitive to dithiolato ring size. As had been observed for diphosphine ligands [29], dithiolate rings with an odd number of members produce a higher shielding of the phosphorus atoms.

2.2. Crystal structure of complex cis-[Pt((−)DIOS)-$(PPh_3)_2$] (2)

The molecular structure of complex **2** (Fig. 3) consists of discrete mononuclear units. Atomic coordinates and selected bond distances and angles are given in Tables 3 and 4 respectively.

The platinum atom has a slightly distorted square planar geometry. The dithiolate ligand is chelated to the metal through the sulphur atoms and two triphenylphosphines are coordinated in cis position. The Pt–P distances in **2** (2.332(8) and 2.338(8) Å) are in the upper range observed for other reported complexes with PPh_3 in trans position to thiolates (Table 5, entries 1–4) [30–39]. Also, the Pt–S distances (2.361(7) and 2.386(7) Å) are slightly longer in complex **2** than in similar platinum thiolate complexes (Table 5, entries 1–9). In comparison with the Pt–P distance in the starting material *cis*-[$PtCl_2(PPh_3)_2$] (Table 5, entry 10), complex **2** has a longer value. This is in agreement with the fact that the coupling constant $^1J_{Pt-P}$ found in dithiolate complex **2** (2851.9 Hz) is smaller than the constant detected in the dichloro complex (3513.1 Hz) and confirms the higher trans influence attributed to the dithiolate.

The distortion in the square planar geometry can be seen in the values of the bond angles around the metal. Thus, the P–Pt–P and S–Pt–S angles (98.2(3)° and 95.4 (3)° respectively) are considerably higher than the cis P–Pt–S (80.6(3)° and 86.0(3)°). The reason could be the steric hindrance of the two phenyl rings bonded to the phosphorus atom in the case of P–Pt–P and the ring requirements in the dithiolate ligand. Values that are not the ideal 180° are also observed in the trans P–Pt–S, the angles being 174.2(2)° and 177.5(3)°.

Table 5
Selected distances for reported platinum and palladium phosphine thiolate complexes

Entry	Complex	Pt–P (Å)	Pt–S (Å)	Ref.
1	$[Pt(S(CH_2)_2S)(PPh_3)_2]$	2.280	2.312	[30]
		2.295	2.327	
2	*cis*-$[PtCl(SC_6H_2$-2,4,6-$^iPr_3)(PPh_3)_2]$	2.250(6) [a]	2.320(7)	[31]
		2.286(7)		
3	*cis*-$[Pt(SC_6H_2$-2,4,6-$^iPr_3)_2(PPh_3)_2]$	2.310(4)	2.359(4)	[31]
		2.335(4)	2.359(4)	
4	*cis*-$[Pt(SH)_2(PPh_3)_2]$	2.286(2)	2.360(2)	[32]
		2.279(2)	2.340(2)	
5	$[Pt(SPh)_2(dppe)]$	2.249	2.350	[33]
6	$[Pt(SC_5H_9NMe)_2(dppe)]$	2.284(1)	2.348(1)	[34]
		2.254(1)	2.367(1)	
7	$[Pt(S(CH_2)_3S)(dppm)]$	2.236(3)	2.332(4)	[28]
		2.276(4)	2.276(4)	
8	[Pt(SC(CN)C(CN)S)(dppe)]	2.257(2) [b]	2.299(7) [b]	[35]
9	[Pt(SC(C)C(CN)S)(dppb)]	2.256(7) [b]	2.301(2) [b]	[35]
10	*cis*-$[PtCl_2(PPh_3)_2]$	2.251(2)	—	[36]
		2.265(2)		
11	$[Pd(SPh)_2(dppe)]$	2.262	2.347	[37]
12	$[Pd(SPh)_2(dppm)]$	2.252	2.320	[38]
		2.267	2.348	
13	$[Pd(SC_5H_9NMe)_2(dppe)]$	2.260(1)	2.358(1)	[34]
		2.242(1)	2.371(1)	
14	$[PdCl_2(dppp)]$	2.244(1)	—	[39]
		2.249(2)		

[a] *trans* to Cl; [b] average value.

As is shown in Fig. 3, the seven-membered metallocycle formed with the dithiolate coordinated to the metal, adopts a twisted conformation which is determined by the configuration of the dioxolane ring.

2.3. Preparation of [Pd(dithiolate)(diphosphine)] complexes

Palladium diphosphine complexes [Pd(dithiolato)(diphosphine)] (dithiolato = BDT, and (−)-DIOS; diphosphine = $Ph_2P(CH_2)_4PPh_2$ (dppb) and $Phd_2P(CH_2)_3PPh_2$ (dppp)) were prepared from the corresponding diphosphinedichloro palladium(II) complexes [$PdCl_2$(diphosphine)] according to the reaction in Eq. (2). Complexes **10** to **13** were isolated as orange solids, in good yields and characterised by the usual methods.

$$[PdCl_2(P\text{–}P)] + \text{dithiolate} \xrightarrow{NEt_3} [Pd(\text{dithiolate})(P\text{–}P)] + 2Et_3NHCl \quad (2)$$

Complex	P–P	dithiolate
10	dppb	BDT
11	dppb	(−)DIOS
12	dppp	BDT
13	dppp	(−)DIOS

Preliminary experiments confirmed what has already been reported [25], namely that palladium tri-phenylphosphine complexes have a greater tendency to form polymeric materials when reacted with dithiolate ligands than platinum complexes. Reacting [$PdCl_2$-(PPh_3)$_2$] with 1,4-butanodithiol produced a highly insoluble compound not characterised. This prompted us to prepare only the diphosphine derivatives for palladium compounds.

Elemental analyses for complexes **10** to **13** agree with the proposed stoichiometries. The peaks corresponding to the molecular protonated species in the FAB mass spectra of complexes **10, 11** and **13** confirm their mononuclearity. The highest intensity peak corresponds in both cases to the [Pd(diphosphine)]$^{2+}$ ion formed by loss of the dithiolate. The molecular structure of complex **12** was determined by X-ray diffraction methods and will be discussed in Section 2.4.

^{1}H NMR data for complexes **10–13** are shown in Table 1. Complexes containing 1,4-butanodithiolato **10** and **12** show that the methylenic resonances are slightly displaced from the free ligand. Methylenic protons α to the thiolate group shift up field from the free ligand due to metal coordination. Signals corresponding to the methylenic protons of the coordinated diphosphines are downfield with respect to the free ligand as in the platinum complexes.

For all of the complexes **10** to **13**, the ^{31}P{^{1}H} NMR spectra (Section 3) show the characteristic single chemical shift which is consistent with the resonance of two equivalent phosphorus in the proposed *cis*-[Pd(diphosphine)(dithiolate)] complexes. As expected, there was an increase in the chemical displacement in relation to the free ligand. Unlike platinum complexes, in the palladium compounds phosphorus signals are shielded with respect to the starting dichloro compounds.

2.4. Crystal structure of complex [Pd((BDT)(dppp)] (12)

The structure of complex **12** is shown in Fig. 4. Atomic coordinates are given in Table 6 and selected bond distances and angles in Table 7.

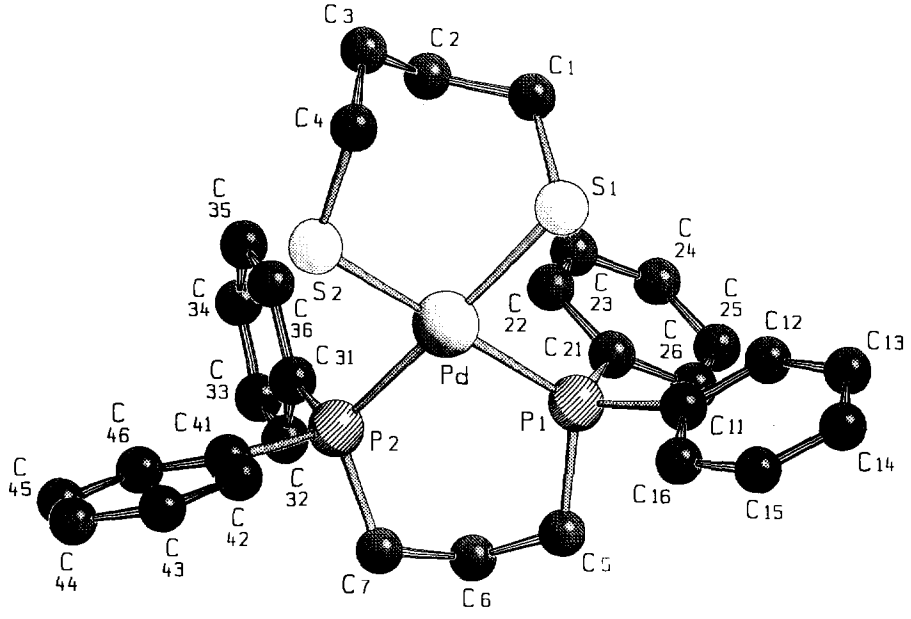


Fig. 4. Molecular structure of compound **12**, [Pd(BDT)(dppp)].

Complex **12** has a mononuclear structure in which dithiolate and diphosphine ligands act as a chelates in a slightly distorted square planar geometry. In this case P–Pd–P and S–Pd–S bond angles are quite similar (94.56(3)° and 95.62(4)°) and the differences with respect to the *cis* P–Pd–S angles (86.78(4)° and 83.47(4)°) are less important than in the case of complex **2**. The angles *trans* P–Pd–S are in this case 172.29(4)° and 176.44(4)°.

The Pd–P bond distances (2.2685(9) and 2.2757(9) Å) are similar to those reported in the literature for related palladium and platinum diphosphine complexes (palladium and platinum radii are comparable) (Table 5, entries 1, 5–9 and 11–13). The values of Pd–S bond distances (2.3535(10) and 2.3219(9) Å) are similar to those observed in related square planar dithiolate complexes. Analogously to complex **2**, an increase in the bond length Pd–P was detected in complex **12** with respect to the cis dichloro compound $[PdCl_2(dppp)]$ (Table 5, entry 14).

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for complex *cis*-$[Pt(S(CH_2)_4S)(Ph_2P(CH_2)_3PPh_2)]$

	x	*y*	*z*	U_{eq} [a]
Pd	1498(1)	1886(1)	1833(1)	28(1)
P(1)	1765(1)	2945(1)	2051(1)	31(1)
P(2)	2699(1)	1533(1)	2407(1)	33(1)
S(1)	375(1)	2293(1)	1106(1)	43(1)
S(2)	1156(1)	806(1)	1663(1)	45(1)
C(1)	618(3)	2069(2)	134(2)	51(1)
C(2)	1077(3)	1444(2)	−5(2)	48(1)
C(3)	598(3)	831(2)	165(2)	51(1)
C(4)	324(3)	743(2)	970(2)	48(1)
C(5)	2432(3)	3141(2)	2864(2)	39(1)
C(6)	3252(2)	2764(2)	2901(2)	42(1)
C(7)	3134(3)	2062(2)	3126(2)	39(1)
C(11)	852(2)	3443(2)	2249(2)	37(1)
C(12)	572(3)	3929(2)	1787(3)	54(1)
C(13)	−103(3)	4308(2)	200.1(4)	73(2)
C(14)	−508(3)	4199(2)	2668(3)	67(2)
C(15)	−262(3)	3704.(2)	3124(3)	56(1)
C(16)	420(3)	3329(2)	2916(2)	43(1)
C(21)	2333(2)	3324(2)	1290(2)	37(1)
C(22)	2653(3)	2937(2)	719(2)	46(1)
C(23)	3120(3)	3207(3)	144(2)	57(1)
C(24)	3252(3)	3858(3)	121(3)	64(1)
C(25)	2951(3)	4243(2)	677(3)	59(1)
C(26)	2505(3)	3980(2)	1270(3)	49(1)
C(31)	3534(2)	1433(2)	1719(2)	41(1)
C(32)	4349(3)	1660(2)	1835(3)	55(1)
C(33)	4942(3)	1612(3)	1278(3)	72(2)
C(34)	4760(4)	1350(3)	613(4)	91(2)
C(35)	3979(4)	1114(4)	484(3)	99(2)
C(36)	3355(3)	1155(3)	1037(3)	69(1)
C(41)	2657(2)	781(2)	2937(2)	37(1)
C(42)	1974(3)	676(2)	3396(3)	52(1)
C(43)	1953(3)	147(2)	3864(3)	57(1)
C(44)	2617(3)	−276(2)	3870(3)	54(1)
C(45)	3283(3)	−181(2)	3417(3)	54(1)
C(46)	3313(3)	350(2)	2947(3)	48(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 7
Selected distances (Å) and angles (deg) for [Pd(BDT)(dppp)] (**12**)

Pd–P1	2.2685(9)	P2–C7	1.816(4)
Pd–P2	2.2757(9)	P2–C41	1.820(4)
Pd–S2	2.3219(9)	P2–C31	1.810(4)
Pd–S1	2.3535(10)	S1–C1	1.824(4)
P1–C21	1.801(4)	S2–C4	1.805(4)
P1–C11	1.811(4)	C1–C2	1.506(6)
P1–C5	1.831(4)	C2–C3	1.508(6)
C3–C4	1.501(6)	C5–C6	1.517(5)
C6–C7	1.520(5)		
P1–Pd–P2	94.56(3)	P1–Pd–S1	83.47(4)
P1–Pd–S2	176.44(4)	P2–Pd–S1	172.29(4)
P2–Pd–S2	86.78(4)	S2–Pd–S1	95.62(4)
C1–S1–Pd	105.43(15)	C4–S2–Pd	109.22(14)
C2–C1–S1	118.4(3)	C1–C2–C3	116.7(4)
C4–C3–C2	116.0(3)	C3–C4–S2	115.1(3)

2.5. Catalytic activity

The catalytic activity of the new platinum-dithiolate complexes in styrene hydroformylation was explored. Initially, some runs were performed with the achiral [Pt(BDT)(P–P)] (P–P = $(PPh_3)_2$ (**1**) and dppb (**4**)) systems in order to find the optimal conditions for the highest aldehyde conversion. The asymmetric induction of the chiral complexes [Pt(DIOS)(P–P)] (P–P = $(PPh_3)_2$ (**2**), dppb (**5**) and dppp (**8**)) and [Pt((−)-BINAS)(P–P)] (P–P = $(PPh_3)_2$ (**3**), dppb (**6**) and dppp (**9**)) was studied. The results obtained with these systems and the reaction conditions are summarised in Table 8.

The catalyst precursor system formed with complex **1** by adding of PPh_3 (P:Rh = 4) is not active in styrene hydroformylation at 80 atm and 80 °C (entry 1). As was observed for $[PtCl_2(diphosphine)]$ systems [14], the presence of $SnCl_2$ is required for hydroformylation to take place. No conversion was detected at 80 atm and 80 °C when $SnCl_2$ was added in a ratio Pt:Sn = 1:2 (entry 2). It was necessary to increase the presence of $SnCl_2$ up to Pt:Sn = 1:20 to observe an 8% aldehyde conversion at 80 °C and 100 atm (entry 3). The regioselectivity in 3-phenylpropanal in this case was 82%. A 50% conversion into aldehydes was obtained after a 60 h reaction with complex **1**, when the pressure was 100 atm and the temperature increased to 125 °C (entry 4). In this case the regioselectivity in 2-phenylpropanal was low (19%) and hydrogenated products (6%) and the corresponding alcohols (11%) were also detected. A higher Pt:Sn ratio (1:40) did not produce better conversions in the same conditions (entry 5). Chiral complex **2** at 125 °C and 100 atm gave a lower aldehyde conversion

Table 8
Hydroformylation of styrene using [Pt(dithiolate)(P–P)$_2$] as catalyst precursors [a]

Entry	Precursor	Pt:Sn	t (h)	T (°C)	P (atm)	C_{ald} (%) [b]	2-PP [c]	3-PP [d]	ee (%) [e]	C_{hyd} (%) [f]	C_{al} (%) [g]
1	**1**	—	24	80	80	—	—	—	—	—	—
2	**1**	1:2	24	80	80	—	—	—	—	—	—
3	**1**	1:20	24	80	100	18	8	82	—	—	—
4	**1**	1:20	60	125	100	50	19	81	—	6	11
5	**1**	1:40	24	125	100	3	21	79	—	—	—
6	**2**	1:20	24	125	100	19	54	46	2(S)	4	—
7 [h,i]	**3**	1:20	60	125	100	20	49	51	3(S)	6	3
8	**3**	1:20	24	125	100	58	14	86	2(S)	4	1
9	**4**	1:20	24	125	100	11	37	63	—	4	1
10	**5**	1:20	24	125	100	59	39	61	7(S)	22	—
11	**8**	1:20	24	125	100	80	32	68	7(S)	17	—
12	**6**	1:20	24	125	100	79	44	56	4(S)	18	—
13	**9**	1:20	24	125	100	76	42	58	14(S)	24	—

[a] *Reaction conditions*: styrene (2 mmol), complex (0.01 mmol), solvent tetrahydrofurane (8 ml), pressure CO:H_2 = 2. Catalyst:substrate = 1:200, P:Pt = 4. [b] Aldehyde conversion measured by chromatography integral ratio without addition of internal standard. [c] 2-PP: 2-phenylpropanal = 100(2-PP/(2-PP + 3-PP)). [d] 3-PP: 3-phenylpropanal = 100(3-PP/(2-PP + 3-PP)). [e] *ee* was measured by chiral gas chromatography on the 2-phenylpropanol obtained by reduction of the aldehydes with $LiAlH_4$. [f] Hydrogenation conversion. [g] Alcohol conversion. [h] Catalyst:substrate = 1:1000. [i] P:Pt = 0.

(19%) than complex **1** but the selectivity in 2-phenylpropanal increased to 52% (entry 6). Unfortunately the enantioselectivty obtained with this system was low (2% in *S*-2-phenylpropanal). No alcohols were detected in this experiment but a 4% hydrogenated product was formed.

When complex **3** with no excess of PPh_3 was used as catalyst precursor in a molar ratio catalyst:substrate 1:1000, aldehyde conversion was only 20% after 60 h, the regioselectivity being 49% in 2-phenylpropanal (entry 7). In the same pressure and temperature conditions, increasing the concentration of catalyst (1:200) and in the presence of excess of PPh_3 (P:Pt = 4), the conversion into aldehydes increased to 58% in 24 h (entry 8). Regioselectivity was affected by the presence of PPh_3, decreasing to 14% in 2-phenylpropanal. The enantioselectivity given by this chiral binaphthyl system was low in both cases and the by-products detected were less than 10%.

The beneficial effect of using diphosphines in catalytic systems has been proved in the literature [40]. The dithiolato–diphosphino precursor system [Pt(BDT)(dppb)], **4**, gives higher regioselectivity in 2-phenylpropanal (37%, entry 9) than the corresponding PPh_3 system **1**, but the conversion decreased to 11% in the same reaction conditions. Chiral diphosphine-DIOS and -BINAS (entries 10 to 13) gave higher aldehyde conversions, (59–80%) with poor regioselectivity in 2-phenylpropanal (32–39%). In these cases a ca. 20% of hydrogenated product was also detected. The *ee* obtained with these diphosphino–chiral-dithiolato precursors were slightly higher than those obtained with triphenylphosphino systems (14% for precursor **9**).

Although the *ee* observed with the new Pt–dithiolato–diphosphine chiral systems are lower than those obtained with Pt–diphosphine systems, the aldehyde conversions are considerable. The regioselectivities are similar to those obtained for Pt/diphosphine systems [17–19]. Nevertheless, these results open up the possibility of modifying both ligands, dithiolates and diphosphines, in order to increase enantioselectivity.

3. Experimental

All of the complexes were synthesised using standard Schlenk techniques under a nitrogen atmosphere. Solvents were distilled and deoxygenated before use. Commercial dithiolates were used as-supplied without further purification. Dithiol $DIOSH_2$ was prepared using a method described in literature [20]. Complexes $[PtCl_2(PPh_3)_2]$ [41], $[PtCl_2(dppb)]$ [42], $[PtCl_2(dppp)]$ [42], $[PdCl_2(dppb)]$ [42] and $[PdCl_2(dppp)]$ [42] were prepared as previously reported. The C, H and S analyses were carried out using a Carlo–Erba microanalyser. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer and referenced in the standard way (TMS for ^1H and H_3PO_4 (85%) as external standard for ^{31}P). Fast atom bombardment (FAB) mass spectrometry was performed on a VG autospect in a nitrobenzylalcohol matrix. The isotopes considered for mass calculations were: H(1), C(12), O(16), Pt(195), P(31) and S(32). Gas chromatography analyses were performed on a Hewlett-Packard 5890A in an Ultra-2 (5% diphenylsilicone–95% dimethylsilicone) column (25 m × 0.2 mm Ø) for separating aldehydes and in FS-cyclodex β-I/P (50 m × 0.25 mm Ø) for separating the chiral alcohols.

3.1. Preparation of cis-[Pt(dithiolate)(PPh_3)$_2$], dithiolate = $^-S(CH_2)_4S^-$ (1), DIOS (2), BINAS (3)

General procedure. The corresponding dithiol (0.128 mmol) and NEt_3 (3–4 drops) were added to a suspension of complex [$PtCl_2(PPh_3)_2$] (0.1 g, 0.126 mmol) in approximately 5 ml of dichloromethane under a nitrogen atmosphere. The resulting suspension was refluxed until the initial product was complete dissolved. The solution was washed with H_2O (3 × 10 ml) and dried with $MgSO_4$. The product was precipitated by adding diethyl ether. Complex **1** (light yellow) (0.074 g, 70%). Anal. Found: C, 56.8; H, 4.64; S, 7.6. $C_{40}H_{38}P_2PtS_2$. Calc.: C, 57.2; H, 4.52; S, 7.6%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 24.76 ppm ($^1J_{Pt-P}$ = 2864.3 Hz). Mass spectrum (FAB): m/z 839 (M^+), 751 (M − $S(CH_2)_4$), 719 (M − BDT). Complex **2** (light yellow) (0.083 g, 72%). Anal. Found: C, 56.3; H, 4.64; S, 7.0. $C_{43}H_{42}O_2P_2PtS_2$. Calc.: C, 56.6; H, 4.61; S, 7.0%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 23.46 ppm ($^1J_{Pt-P}$ = 2851.9 Hz). Complex **3** (light yellow) (0.098 g, 76%). Anal. Found: C, 60.6; H, 4.07; S, 5.6. $C_{56}H_{42}P_2PtS_2 \cdot CH_2Cl_2$. Calc.: C, 61.0; H, 3.96; S, 5.7%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 24.31 ppm ($^1J_{Pt-P}$ = 2982.1 Hz). Mass spectrum (FAB): m/z 1037 (MH^+), 1036 (M^+), 774 (M − PPh_3) 719 (M − BINAS), 456 [$Pt(PPh_3)$].

3.2. Preparation of [Pt(dithiolato)(dppb)], dithiolate = $^-S(CH_2)_4S^-$ (4), DIOS (5), BINAS (6)

General procedure. The corresponding dithiol (0.148 mmol) and NEt_3 (3–4 drops) were added to a suspension of complex [$PtCl_2$(dppb)] (0.1 g, 0.144 mmol) in approximately 5 ml of dichloromethane under a nitrogen atmosphere. After adding the amine, immediate solution of the initial suspension took place. The solution was washed with H_2O (3 × 10 ml) and dried with $MgSO_4$. The product was precipitated by adding diethyl ether. Complex **4** (light yellow) (0.088 g, 81%). Anal. Found: C, 47.8; H, 4.69; S, 7.6. $C_{32}H_{36}P_2PtS_2 \cdot CH_2Cl_2$. Calc.: C, 47.9; H, 4.60; S, 7.7%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 16.17 ppm ($^1J_{Pt-P}$ = 2782.1 Hz). Mass spectrum (FAB): m/z 814 (MH^+), 653 (M − $S(CH_2)_4$), 620 (M − BDT), 1363 (Pt(BDTH)(dppb)). Complex **5** (light yellow) (0.076 g, 65%). Anal. Found: C, 51.5; H, 5.03; S, 7.7. $C_{35}H_{40}O_2P_2PtS_2$. Calc.: C, 51.5; H, 4.90; S, 7.8%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 15.84 ppm ($^1J_{Pt-P}$ = 2773.8 Hz). Mass spectrum (FAB): m/z 741 (M^+), 620 [Pt(dppb)]. Complex **6** (light yellow) (0.108 g, 68%). Anal. Found: C, 61.1; H, 4.14; S, 6.5. $C_{48}H_{40}P_2PtS_2$. Calc.: C, 61.5; H, 4.30; S, 6.8%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 18.12 ppm ($^1J_{Pt-P}$ = 2903.3 Hz). Mass spectrum (FAB): m/z 938 (M^+), 653 [PtS(dppb)], 620 [Pt(dppb)]).

3.3. Preparation of [Pt(dithiolato)(dppp)], dithiolate = $^-S(CH_2)_4S^-$ (7), DIOS (8), BINAS (9)

General procedure. The corresponding dithiol (0.150 mmol) and NEt_3 (3–4 drops) were added to a suspension of complex [$PtCl_2$(dppp)] (0.1 g, 0.148 mmol) in approximately 5 ml of dichloromethane under a nitrogen atmosphere. After adding the amine, immediate solution of the initial suspension took place. The resulting solution was washed with H_2O (3 × 15 ml) and dried with $MgSO_4$. The product was precipitated by addition of diethyl ether. Complex **7** (yellow) (0.068 g, 64%). Anal. Found: C, 51.3; H, 4.84; S, 9.0. $C_{31}H_{34}P_2PtS_2$. Calc.: C, 51.1; H, 4.66; S, 8.8%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 24.06 ppm ($^1J_{Pt-P}$ = 2677.3 Hz). Mass spectrum (FAB): m/z 727 (M^+), 639 (M − $S(CH_2)_4$), 606 (M − BDT). Complex **8** (light yellow) (0.074 g, 63%). Anal. Found: C, 49.2; H, 4.77; S, 8.0. $C_{34}H_{38}O_2P_2PtS_2$. Calc.: C, 50.9; H, 4.74; S, 8.0%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 1.40 ppm ($^1J_{Pt-P}$ = 2668.2 Hz). Mass spectrum (FAB): m/z 800 (MH^+), 639 ([PtS(dppp)]), 606 (M − DIOSH). Complex **9** (light yellow) (0.109 g, 66%). Anal. Found: C, 60.8; H, 4.11; S, 6.8. $C_{47}H_{38}P_2PtS_2$. Calc.: C, 61.1; H, 4.15; S, 6.9%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 2.64 ppm ($^1J_{Pt-P}$ = 2778.2 Hz). Mass spectrum (FAB): m/z 924 (MH^+), 639 ([PtS(dppp)]), 606 (M − BINAS).

3.4. Preparation of [Pd(dithiolato)(dppb)], dithiolate = $^-S(CH_2)_4S^-$ (10), DIOS (11)

General procedure. The corresponding dithiol (0.170 mmol) and NEt_3 (3–4 drops) were added to a suspension of complex [$PdCl_2$(dppb)] (0.1 g, 0.166 mmol) in approximately 5 ml of dichloromethane under a nitrogen atmosphere. After adding the amine, immediate solution of the initial suspension took place. The resulting solution was washed with H_2O (3 × 15 ml) and dried with $MgSO_4$. The product was precipitated by addition of diethyl ether. Complex **10** (orange) (0.080 g, 74%). Anal. Found: C, 53.5; H, 5.19; S, 8.8. $C_{32}H_{36}P_2PdS_2 \cdot CH_2Cl_2$. Calc.: C, 53.7; H, 5.15; S, 8.7%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 22.05 ppm. Mass spectrum (FAB): m/z 653 (MH^+), 532 (M − BDT). Complex **11** (light yellow) (0.084 g, 69%). Anal. Found: C, 55.3; H, 5.16; S, 8.2. $C_{35}H_{40}P_2PdS_2O_2 \cdot CH_2Cl_2$. Calc.: C, 55.5; H, 5.39; S, 8.2%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 22.54 ppm. Mass spectrum (FAB): m/z 725 (MH^+), 532 (M − DIOS).

3.5. Preparation of [Pd(dithiolate)(dppp)], dithiolate = $^-S(CH_2)_4S^-$ (12), DIOS (13)

General procedure. The corresponding dithiol (0.175 mmol) and NEt_3 (3–4 drops) were added to a

suspension of complex $[PdCl_2(dppp)]$ (0.1 g, 0.170 mmol) in approximately 5 ml of dichloromethane under a nitrogen atmosphere. After adding the amine, immediate solution of the initial suspension took place. The resulting solution was washed with H_2O (3 × 15 ml) and dried with $MgSO_4$. The product was precipitated by addition of diethyl ether. Complex **12** (orange) (0.080 g, 47%). Anal. Found: C, 57.8; H, 5.14; S, 10.1. $C_{31}H_{34}P_2PdS_2$. Calc.: C, 58.0; H, 5.30; S, 10.0%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 7.35 ppm. Complex **13** (orange) (0.064 g, 52%). Anal. Found: C, 57.0; H 5.45; S, 9.3. $C_{34}H_{38}O_2P_2PdS_2$. Calc.: C, 57.2; H, 5.33; S, 9.0%. $^{31}P\{^1H\}$ NMR ($CDCl_3$ sol.): δ 7.31 ppm. Mass spectrum (FAB): m/z 710 (M^+), 518 (M − DIOS).

3.6. Catalysis.

Hydroformylation experiments were carried out in an autoclave with magnetic stirring. The catalytic solution was contained in a Teflon vessel and the inside of the autoclave's cap was also Teflon covered to prevent the solution coming into direct contact with the stainless steel. Constant temperature was maintained by an electric heating mantle.

3.6.1. Standard hydroformylation experiment

A solution of the substrate (20 mmol), the catalyst precursor (0.1 mmol) and the phosphorus compound in the corresponding ratio, in 15 ml of solvent was introduced into the evacuated autoclave. The gas mixture was introduced and the system was heated. When thermal equilibrium was reached, the gas mixture was introduced until the desired pressure. After the reaction time, the autoclave was cooled to room temperature and depressurised. Samples were analysed by gas chromatography. The *ee* were measured by GC with a chiral column on the alcohols obtained by reducing the resulting aldehydes using the following procedure: after the catalytic run, 2 ml of the catalytic solution was added drop by drop to a stirred suspension of lithium aluminium tetrahydride (110 mg) in 5 ml of anhydrous tetrahydrofurane. After 5 min, methanol was added until bubbling stopped. Aluminium salts were removed by filtration through Celite. The filtrate was evaporated until dry, dissolved in diethyl ether (30 ml), washed with sulphuric acid (10%) (3 × 15 ml), dried over magnesium sulphate, distilled and analysed by GC.

3.7. Crystal structure determination for complexes cis-[Pt((−)-DIOS)(PPh$_3$)$_3$] (2) and [Pd((BDT)(dppp)] (12)

Suitable crystals of complexes **2** and **12** were grown from a 1,2-dichloroethane–ethanol and dichloromethane–hexane solutions respectively and mounted on a Mar Research image plate scanner.

Crystal data. Compound **2**: $C_{43}H_{44}O_2P_2PtS_2$, M = 913.37, monoclinic, a = 27.993(6), b = 16.949(4), c = 24.234(6) Å, β = 125.00(1)°, U = 9418.3 Å3, space group $C2$ (no. 5), Z = 2, D_c = 1.348 g cm^{-3}, $F(000)$ = 3824. Yellow, crystal dimensions 0.2 × 0.2 × 0.1 mm^3, μ(Mo Kα) = 31.72 cm^{-1}, Absolute structure parameter 0.02(2). Compound **12**: $C_{31}H_{34}P_2S_2Pd$, M = 639.04, orthorhombic, a = 15.836(6), b = 20.728(6), c = 17.712(6) Å, $\alpha = \beta = \gamma$ = 90.00(6)°, U = 5813.9 Å^3, space group *Pbca* (no. 61), Z = 8, D_c = 1.460 g cm^{-3}, $F(000)$ = 2624. Orange, crystal dimensions 0.1 × 0.2 × 0.2 mm^3, μ(Mo Kα) = 9.11 cm^{-1}.

The data collection and processing was performed on a Mar Research image plate scanner, graphite-monochromated Mo Kα radiation used to measure 95 2° frames, 120 s frame, XDS package used to give: 6793 unique (merging R = 0.0670) **2**, and 4997 unique (merging R = 0.0336) **12**.

The structures were solved by the direct method SHELX86 and refined using SHELXL, by full-matrix least squares of 503 (**2**) and 348 (**12**) variables, to a final R-factor of 0.064 (**2**) and 0.037 (**12**) for 4303 (**2**) and 4125 (**12**) reflections with $[F_o] > 4\sigma(F_o)$. All atoms (including hydrogen atoms) were revealed by the Fourier map difference. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed geometrically and refined with a fixed temperature factor of 0.05. The weighting scheme $w = 1/[\sigma 2(F_o^2) + (0.1204 \times P)^2 + 106.20 \times P]$ where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$ (**2**) and $w = 1/[\sigma^2(F_o^2) + (0.0489 \times P)^2 + 7.55 \times P]$ where $P = (\text{Max}(F_o^2,0) + 2F_c^2)/3$ (**12**) with σ(Fo) from counting statistics gave satisfactory agreement analyses. Final R and R' values are 0.064, 0.097 (**2**) and 0.037, 0.054 (**12**).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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