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Diastereoselective oxidative addition of cyclic thiosulfinates to platinum(0) compounds: chiral platinum(II) complexes with sulfenato ligands Crystal structures of $S(O)-CH_2-CH(OAc)-CH(OAc)-CH_2-S$ and dppePt[$S(O)-(CH_2)_4-S$]☆ Part 16. Metal complexes of functionalized sulfur-containing ligands

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Dedicated to Professor Henri Brunner on the occasion of his 65th birthday

Abstract

The oxidative addition reactions of the racemic thiosulfinates $S-(CH_2)_4-S(O)$ (**1**) and $S-CH_2-(C_6H_4)-CH_2-S(O)$ (**4**) with dppePt(η^2-C_2H_4) (**6**) led to the 1-sulfenato-4-thiolato platinum(II) complexes dppePt[$S(O)-(CH_2)_4-S$] (**8**) and dppePt[$S(O)-CH_2-(C_6H_4)-CH_2-S$] (**9**); the crystal structure of complex **8** was determined. The oxidative addition of the racemic thiosulfinate $S-CH_2-CH(OAc)-CH(OAc)-CH_2-SO$) [($R^*_{SO}$, R^*, R^*)-**2**] to ($Ph_3P)_2$Pt(η^2-C_2H_4) (**5**) gave two diastereoisomers of compound ($Ph_3P)_2$Pt[$S(O)-CH_2-CH(OAc)-CH(OAc)-CH_2-S$] (**10**) in a ratio 1:1. The thiosulfinates [(R^*_{SO}, R^*,R^*)-**2**] and [(R^*_{SO},R^*,S^*)-**3**] reacted with [(R, R-diop)]Pt(η^2-C_2H_4) (**7**) to yield four diastereoisomers each of the complexes [(R,R-diop)]Pt[$S(O)-CH_2-CH(OAc)-CH(OAc)-CH_2-S$] (**11**) and **12** in a ratio 100:100:1:1 and 10:10:1:1, respectively. [(R^*_{SO}, R^*, S^*)-**3**] was characterized structurally. Treatment of the mixture of diastereoisomers of complex **11** with two equivalents of dppe gave only one diastereoisomer of complex dppePt[$S(O)-CH_2-CH(OAc)-CH(OAc)-CH_2-S$] (**13**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Platinum; Oxidative addition; Thiosulfinates; Sulfenato complexes; Thiolato complexes; Diastereoselectivity

1. Introduction

The synthesis of transition metal complexes containing anions of sulfenic acids ($R-SO^-$) as ligands are limited to just a few examples. It has been demonstrated that metal-coordinated thiolato ligands (L_nM-SR; M = Co, Ru, Ni, Pd) can act as oxygen atom acceptors to form η^1-*S*-coordinated sulfenato ligands [$L_nM-S(O)R$] [2]. Such type of ligands has also been synthesized via oxidative addition reactions of methyl sulfinyl chloride to iridium(I) [3] and of thiosulfinates [R–S(O)–S–R] as well as *N*-sulfinyl phthalimides [R–S(O)–phth] to platinum(0) compounds [4], respectively. The sulfur–sulfur bond energies in thiosulfinates are about 20–30 kcal mol^{-1} less than those of the corresponding disulfides [5]. Thus, thiosulfinates are suitable for the insertion reaction of platinum(0) into the sulfur–sulfur bond.

We have studied previously the oxidative addition of ($Ph_3P)_2$Pt(η^2-C_2H_4) with acyclic thiosulfinates give firstly the products of *trans* oxidative addition, which

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loose one equivalent of triphenyl phosphine in solution to form the diplatinum thiolato-bridged sulfenato complexes [4b]. The *cis* isomers containing the 1-sulfenato-3-thiolato and the 1-sulfenato-4-thiolato ligands are formed by an oxidative addition of cyclic five- and six-membered thiosulfinates, respectively [4b,6]. In this paper we report the results obtained for the oxidative addition of racemic mixtures of cyclic thiosulfinates to platinum(0) compounds containing achiral and chiral phosphines, respectively.

2. Results and discussion

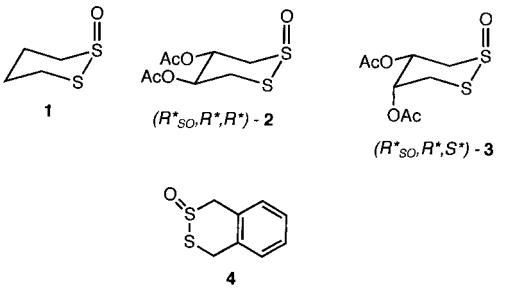
2.1. Syntheses of thiosulfinates 1–4; crystal structure of 2

The racemic mixtures of thiosulfinates **1**–**3** (Scheme 1) were prepared at 0°C from the corresponding disulfides in acetic acid using 30% hydrogen peroxide as oxidant; these reactions led in the case of compounds **2** and **3** to single diastereoisomers (R^*_{SO}, R^*, R^*) and (R^*_{SO}, R^*, S^*), respectively. The preparation of thiosulfinate **4** was achieved by reaction of the disulfide with *m*-chloroperoxybenzoic acid (*m*CPBA). The oxygen on one of the sulfur atoms of the chair 1,2-dithiane rings in these products was expected to be in an axial position, due to stereoelectronic effects [7]. This has been proven by X-ray crystal structure analysis (Fig. 1). We were able to isolate single crystals suitable for X-ray structure analysis of thiosulfinate **3**, which is present as a 1,2-dithiane six-membered ring chair conformation with the S–O group in an axial position; the relative configuration is *l*, *u*. Selective bond distances and bond angles are listed in Table 2. Key bond lengths in **3** are 148.6(2) pm for the S–O bond and 209.95(9) pm for the S–S bond, which are similar to those found for (3a*R*, 5*R*, 7a*R*)-2,2-dimethyl-4,4,7,7-tetraphenyl-tetrahydro-1,2-dithiino[4,5-*d*][1,3]dioxole 5-oxide [4d].

2.2. Oxidative addition reactions Schemes 2 and 3

The reactions of thiosulfinates **1** and **4** with (dppe)Pt(η^2-C_2H_4) (**6**) in tetrahydrofurane at room temperature give the 1-sulfenato-4-thiolato platinum(II) complexes **8** and **9**. When $(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$ (**5**) is treated with two equivalents of thiosulfinate **2**, two products in the ratio 1:1 are observed by ^{31}P-NMR spectroscopy whose structures have been assigned on the basis of the similarity of the spectroscopic data of the diastereoisomers (R^*_{SO}, R^*, R^*)/(R^*_{SO}, S^*, S^*)-**10**; no diastereoselectivity has been observed.

The reactions of the optically pure platinum(0) complex [(*R*,*R*)-diop]Pt(η^2-C_2H_4) (**7**) with a fourfold excess of (R^*_{SO}, R^*, R^*)-**2** and (R^*_{SO}, R^*, S^*)-**3**, respectively, in toluene were monitored by ^{31}P-NMR spectroscopy. In the early stages of the reaction of **7** with **2** at 0°C integration of the ^{31}P resonance signals assigned to the



Scheme 1.

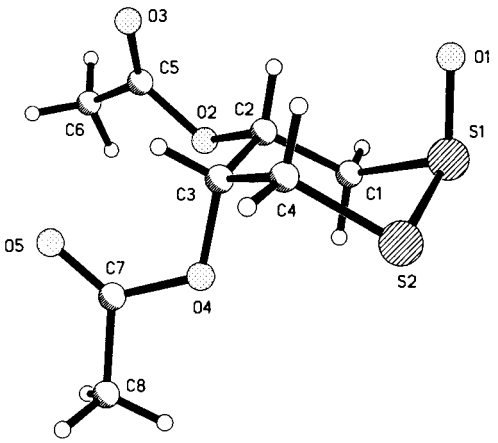
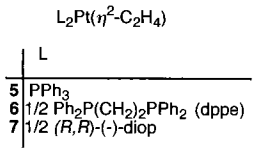
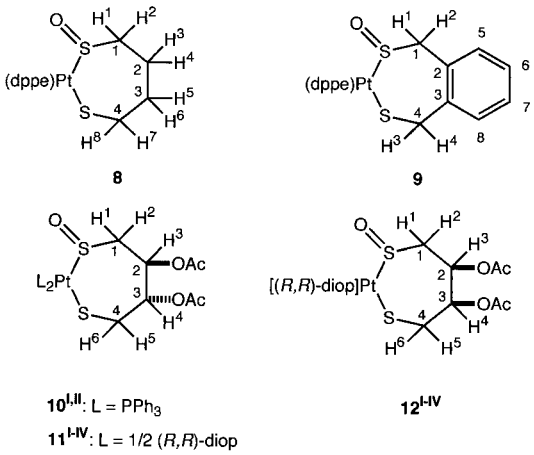


Fig. 1. Molecular structure of **3** in the crystal.



Scheme 2.



Scheme 3.

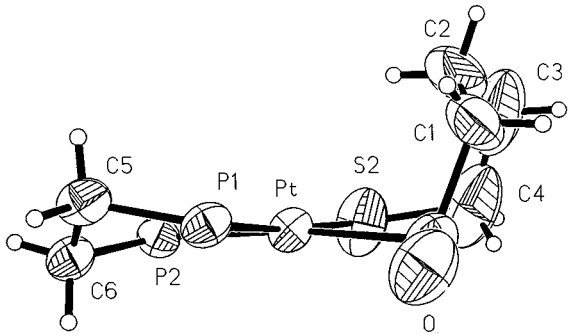


Fig. 2. Molecular structure of **8** in the crystal.

Table 1
Crystallographic data collection parameters of **3** and **8**

	3	**8**
Formula	$C_8H_{12}O_5S_2$	$C_{30}H_{32}OP_2PtS_2 \cdot 1/2C_6H_{14}$
Formula weight	252.3	772.8
Crystal size (mm)	$0.6 \times 0.4 \times 0.2$	$0.22 \times 0.24 \times 0.05$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a (pm)	1224.5(2)	951.8(2)
b (pm)	961.0(1)	2409.0(6)
c (pm)	969.6(2)	1379.5(4)
β (°)	101.76(1)	104.48(2)
V (nm^3)	1.1170(3)	3.0627(1)
Z	4	4
D_{calc} (g cm^{-3})	1.500	1.676
λ (pm)	71.073	71.073
Absorption coefficient μ (mm^{-1})	0.475	4.887
Θ range (°)	2.72–25.00	2.50–25.00
Index ranges	$-14 \le h \le 14$, $-11 \le k \le 11$, $0 \le l \le 11$	$0 \le h \le 11$, $0 \le k \le 28$, $-16 \le l \le 15$
Residuals	$R_1 = 0.0347$ $[I > 2\sigma(I)]$, $wR_2 = 0.0721$ $[I > 2\sigma(I)]$	$R = 0.0667$ $[\|F\| > 3\sigma\|F\|]$, $R_g = 0.0338$ $[\|F\| > 3\sigma\|F\|]$

formation of all four possible diastereoisomers **11$^{I–IV}$** with ca. 3:3:1:1; with **3** a mixture of the four diastereoisomers **12$^{I–IV}$** was obtained in a ratio of 2:2:3:3. The ^{31}P-NMR spectra exhibit sharp signals of four well-defined AB spin patterns with the expected ^{31}P–^{195}Pt couplings. The diastereoisomers **11$^{I–IV}$**/**12$^{I–IV}$**, which differ in each case in the configuration of the sulfoxidic sulfur atom, may be formed under kinetic control. In a thermodynamically controlled reaction at room temperature the ^{31}P-NMR spectra show that the minor (**11$^{I–IV}$**) and the main (**12$^{I–IV}$**) peaks diminished in intensity. After stirring the mixtures of diastereoisomers for two hours (**11$^{I–IV}$**) and 48 h (**12$^{I–IV}$**), respectively, we observed a ratio of $>$100:100:1:1 (**11$^{I–IV}$**) and 10:10:1:1 (**12$^{I–IV}$**), respectively. The reaction of a twofold excess of dppe with **11** in toluene leads stereospecifically to one of two possible diastereoisomers of complex **13** with the relative configuration R^*_{SO}, R^*, R^*.

We have reported previously the oxidative addition of the enantiomerically pure thiosulfinate–TADDOL [4d] with **7** yielding in a highly stereoselective reaction one of the two possible diastereoisomers. Its all-(*R*) configuration was established by X-ray crystal structure determination [4d].

We assume that the platinum(0) complex fragment attacks at the soft thiolate sulfur atom rather than at the sulfoxidic sulfur atom. The cyclic thiosulfinates are opened to give a quasi-racemization at the sulfoxidic sulfur atom. In contrast, a double chiral induction [8] as the chirality in both (*R*, *R*)-**7** and the thiosulfinates (R^*_{SO}, *R**; *R**)-**2** and (R^*_{SO}; *R**; *S**)-**3** affects the diastereoselective course of the oxidative addition.

The IR spectra of complexes **8**–**13** exhibit strong ν(SO) bands in the typic range of 965–985 cm^{-1} which are in agreement with these absorptions observed for other thiosulfinato complexes [2q,4c]. The ν(SO) bands in the complexes are shifted 80–100 cm^{-1} to lower wavenumbers compared to those of the corresponding thiosulfinates.

The protons and the carbon atoms in complexes **8**–**13** have been assigned on the basis of ^{1}H-COSY and ^{1}H–^{13}C correlation experiments. The diastereotopic protons H-1 and H-2 (protons bound to C-1 atom) of complexes **8**–**13** are considerably shielded and strongly separated [1.6 ppm (**9**)]; the resonances of these protons are shifted upfield by 1.5–2.9 ppm compared with those of the respective protons of the thiosulfinates **1**–**3** (Section 3). The protons bound to C-1 and C-4 atoms of complexes **9** and **10** exhibit strong ^{1}H–^{31}P [^4J(HP) ca. 14 Hz] and ^{1}H–^{195}Pt coupling constants [^3J(HPt) ca. 23–103 Hz].

Slow crystallisation of complex **8** from dichloromethane/hexane at room temperature gave yellow crystals suitable for X-ray structure analysis, and the molecular structure is shown in Fig. 2. Selected bond length and angles are given in Table 2, crystallographic data in Table 1. The molecular structure of **8** shows a boat conformation of the seven-membered ring and the coordination at the platinum(II) is slightly distorted from planar with a twist (6.3°) in the coordination plane between the PtP_2 and the PtS_2 units. This value is considerably smaller than that one observed in $(Ph_3P)Pt[S(O)(CH_2)_4S]$ [4b] which is due to the contractive property of the ethylene bridge of the dppe-ligand. Key bond lengths in **8** are 230.1(3) pm for the Pt–P bond, which is trans to the sulfoxidic sulfur atom, and 225.9(3) pm for the other Pt–P bond. The first value shows the stronger trans influence of the sulfenato group compared with that of the thiolato group.

Table 2
Selected bond distances (pm) and bond angles (°) of **3** and **8**

Bond distances		Bond angles	
Compound ***3***			
S(1)–O(1)	148.6(2)	C(1)–S(1)–O(1)	105.74(11)
S(1)–S(2)	209.95(9)	C(1)–S(1)–S(2)	97.40(8)
S(1)–C(1)	181.6(2)	O(1)–S(1)–S(2)	108.90(7)
S(2)–C(4)	181.7(2)	C(4)–S(2)–S(1)	98.48(8)
Compound ***8***			
Pt–P(1)	225.9(3)	P(1)–Pt–P(2)	85.5(1)
Pt–P(2)	230.1(3)	P(1)–Pt–S(1)	90.3(1)
Pt–S(1)	234.1(3)	P(2)–Pt–S(1)	172.1(1)
Pt–S(2)	234.8(3)	P(1)–Pt–S(2)	174.9(1)
S(1)–O	150.1(9)	P(2)–Pt–S(2)	93.0(1)
C(1)–S(1)	180.5(15)	S(1)–Pt–S(2)	91.7(1)
C(4)–S(2)	181.1(15)	Pt–S(1)–O	112.3(4)
		Pt–S(1)–C(1)	104.3(4)
		Pt–S(2)–C(4)	108.5(4)

3. Experimental

All manipulations were carried out under an inert atmosphere (N_2), using standard Schlenk technique. Solvents were dried and freshly distilled under N_2 prior to use. Thiosulfinates **1** [9], **2**, **3** [10], **4** [11] and the platinum(0) complexes **5** [12], **6** [13] and **7** [14] were prepared according to reported procedures. ^{1}H- and ^{13}C-NMR spectra were recorded by using a Jeol EX 400 MHz spectrometer and referenced to TMS. ^{31}P-NMR measurements were performed on a JEOL GSX 270 MHz spectrometer (external standard 85% aqueous H_3PO_4). *J* values are given in Hz. Mass spectra were obtained using pos-FAB-MS on a VG-ZAB-VSEQ spectrometer. IR spectra were recorded on a Nicolet ZDX 5 spectrometer. K_2PtCl_4 was a gift from DEGUSSA AG, Werk Wolfgang.

3.1. $Ph_2\overline{P(CH_2)_2PPh_2}–\overline{Pt}–\overline{S(O)–(CH_2)_4–S}$ (8)

A solution of **1** [9] (15 mg, 0.11 mmol) in 4 ml of tetrahydrofurane (THF) was added dropwise to an ice-cold suspension of **6** [13] (68 mg, 0.11 mmol). The orange–yellow mixture was stirred for 24 h at room temperature (r.t.) and the suspension was filtered through Celite. The deep yellow solution was concentrated under vacuum to 2 ml. Addition of 25 ml of hexane caused precipitation of the bright yellow crude material which was collected by centrifugation and washed twice with 10 ml of hexane. The product crystallized as yellow plates from a mixture of dichloromethane–hexane (1:1) at r.t. After drying in vacuo the yellow product was identified as **8**. Yield: 44 mg (55%). M.p. 210–212°C. Anal. Calc. for $C_{30}H_{32}OP_2PtS_2$ (729.7 g mol^{-1}): C, 49.37; H, 4.42. Found: C, 48.89; H, 4.28%. IR: ν(SO) 965 s cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ, 1.39 (m_c, 1H, 3-H^5), 1.56 (m_c, 1H, 3-H^6), 1.65 (m_c, 1H, 2-H^3), 2.08 [m_c, ^2J(HH) = 11.5, 1H, 1-H^1], 2.72 (m_c, 1H, 2-H^4), 2.80 (m_c, 1H, 4-H^7), 2.99 (m_c, 1H, 1-H^2), 3.15 [dt, ^2J(HH) = 14.0, ^3J(HH) = 4.8, 1H, 4-H^8], 1.98–2.69 (m, 4H, PCH_2CH_2P), 7.40–7.68/8.04–8.08 (m, 20H, Ph). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ 19.48 (s, C-4), 25.24 (s, C-2), 29.54 (s, C-3), 55.89 (s, C-1), 29.06/30.36 [dd, ^1J(CP) = 37.4, ^2J(CP) = 12.1, CH_2-P]. ^{31}P{^{1}H}-NMR (CH_2Cl_2): δ 31.39/47.12, ^1J(PPt) = 2131/3115, ^2J(PP) = 10.8.

3.2. $Ph_2\overline{P(CH_2)_2PPh_2}–\overline{Pt}\overline{[S(O)–(CH_2)–(C_6H_4)–(CH_2)–S]}$ (9)

A suspension of **4** [11] (37 mg, 0.2 mmol) and **6** [13] (124 mg, 0.2 mmol) in 20 ml of THF was stirred at r.t.. The color changed quickly from pearl-grey to yellow. Stirring was continued for 5 h, the resulting yellow precipitate was collected by centrifugation and crystallized as yellow powder from a mixture of dichloromethane–hexane (1:1). After drying in vacuo the bright yellow product was identified as **9**. Yield: 65 mg (42%). M.p. 185–187°C. Anal. Calc. for $C_{34}H_{32}OP_2PtS_2$ (777.7 g mol^{-1}): C, 52.50; H, 4.15; S, 8.24. Found: C, 51.78; H, 4.27; S, 8.04%. IR: ν(SO) 964 s cm^{-1}. ^{1}H-NMR (CD_2Cl_2): d 1.81–2.19 (m, 4H, PCH_2CH_2P), 3.17–3.28 [dd, ^2J(HH) = 13.4, ^4J(HP) = 3.4, ^3J(HPt) = 32, 1H, H^2_{eq}], 3.60–3.79 [dd, ^2J(HH) = 12.3, ^4J(HP) = 10.0, ^3J(HPt) = 54, 1H, H^4_{eq}], 4.03–4.12 [dd, ^2J(HH) = 12.4, ^4J(HP) = 3.7, ^3J(HPt) = 22, 1H, H^3_{ax}], 4.73–4.90 [dd, ^2J(HH) = 13.4, ^4J(HP) = 11.2, ^3J(HPt) = 54, 1H, H^1_{ax}], 6.85–7.93 (m, 24H, aromatic-H). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ 28.91/29.63 [dd, ^1J(CP) = 37.8, ^2J(CP) = 11.8, CH_2–P], 26.85 (s, C-4), 59.71 (s, C-1), 144.71 (s, C-2), 134.65 [d, ^4J(CP) = 2.7 Hz, C-3], 129.82 (s, C-5), 125.43 (s, C-6), 126.59 (s, C-7), 129.25 (s, C-8). ^{31}P{^{1}H}-NMR (CH_2Cl_2): δ 33.06/47.49, ^1J(PPt) = 2139/3127, ^2J(PP) = 9.7.

3.3. $(Ph_3P)_2\overline{Pt[S(O)\text{-}CH_2–CH(OAc)–CH(OAc)–CH_2–S]}$ ($10^{I,II}$)

A solution of (R^*_{SO},R*,R*)-**2** [10] (75 mg, 0.3 mmol) in 3 ml of THF was added dropwise at r.t. to a solution of **5** [12] (224 mg, 0.3 mmol) in 7 ml of THF. After stirring the bright yellow solution for 18 h a yellow solid began to separate. The precipitate was collected by centrifugation and washed twice with 10 ml of hexane. After drying in vacuo the bright yellow product **10** was identified as a mixture of two diastereoisomeres (1:1). Yield: 93 mg (32%). M.p. 181–182°C. Anal. Calc. for $C_{44}H_{42}O_5P_2PtS_2$ (972.0 g mol^{-1}): C, 57.37; H, 4.36; S, 6.60. Found: C, 57.33; H, 4.43; S, 6.40%. IR: ν(SO) 985 s cm^{-1}. ^{1}H-NMR (CD_2Cl_2): 10^I: δ 1.44–1.49 [dt,

^2J(HH) = 14.7, ^3J(HH) = 3.0, ^4J(HP) = 3.0, 1H, H^1], 1.96 (s, 3H, OCH_3), 2.06 (s, 3H, OCH_3), 2.15–2.23 [dt, ^2J(HH) = 14.7, ^3J(HH) = 12.8, ^4J(HP) = 4.4, 1H, H^2], 2.46 [t, ^2J(HH) = 14.7, ^4J(HP) = 14.7, ^3J(HP) = 69, 1H, H^5], 3.35 [d, ^2J(HH) = 14.4, ^3J(HPt) = 23, 1H, H^6], 4.85 [dt, ^3J(HH) = 9.5, ^3J(HH) = 2.2, 1H, H^4], 6.22–6.25 (m, 1H, 2-H^3), 7.08–7.66 (m, 30H, Ph). **10^{II}**: δ 1.72–1.77 [dt, ^2J(HH) = 12.5, ^3J(HH) = 3.7, ^4J(HP) = 3.7, 1H, H^1], 1.99 (s, 3H, OCH_3), 2.10 (s, 3H, OCH_3), 2.77 [dd, ^2J(HH) = 11.7, ^4J(HP) = 5.0, ^3J(HPt) = 51, 1H, H^2], 2,93 [ddd, ^2J(HH) = 15.2, ^3J(HH) = 2.9, ^4J(HP) = 11.7, ^3J(HPt) = 103, 1H, H^5], 5.20 [dt, ^2J(HH) = 15.4, ^3J(HH) = 3.7, ^4J(HP) = 3.7, ^3J(HPt) = 54, 1H, H^6], 5.05 [dt, ^3J(HH) = 9.5, ^3J(HH) = 2.9, 1H, H^4], 6.26–6.31 (m, 1H, H^3). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ **10^{I}**: 20.81 (s, OCH_3), 21.12 (s, OCH_3), 18.12 [dd, ^3J(CP) = 5.8, ^4J(CP) = 2.6, C–4], 51.01 (s, C-1), 70.21 (s, C-2), 73.54 (s, C-3), 169.82 (s, CO), 170.19 (s, CO). **10^{II}**: 21.08 (s, OCH_3), 21.23 (s, OCH_3), 25.85 [d, ^3J(CP) = 6.4, C-4], 52.00 (s, C-1), 74.94 (s, C-3), 76,07 [dd, ^4J(CP) = 4.2, ^5J(CP) = 2.3, ^3J(CPt) = 49.7 Hz, C-2], 169.97 (s, CO), 170.24 (s, CO). ^{31}P{^{1}H}-NMR (CH_2Cl_2): δ 19.10/19.52, ^1J(PPt) = 2402/2866, ^2J(PP) = 31.6; 21.92/22.90, ^1J(PPt) = 2283/3309, ^2J(PP) = 24.5. MS (pos-FAB), *m*/*z* (relative intensity%): 972 (13) $[M+H]^+$; 954 (20) $[M-H-^{16}O]^+$; 719 (100) $[(Ph_3P)_2Pt]^+$.

*3.4. [(R,R)-diop]-Pt[S(O)–CH$_2$–CH(OAc)–CH(OAc)–CH$_2$–S] (**11$^{I–IV}$**)*

To a solution of **7** [14](144 mg, 0.2 mmol) in 10 ml of toluene, a solution of thiosulfinate (R^*_{SO},*R**,*R**)-**2** [10] (200 mg, 0.8 mmol) in 4 ml of toluene was injected at 0°C. The starting beige solution became deep yellow and the reaction was monitored by ^{31}P{^{1}H}-NMR spectroscopy for 30 min at 0°C; the ^{31}P{^{1}H}-NMR spectroscopy revealed formation of four diastereoisomers **I**–**IV**. After stirring for additional 16 h at r.t. the solvent was evaporated under vacuo and the resulting solid was washed thoroughly with a 1:1 ether–hexane solvent mixture to remove the excess of thiosulfinate **2**. After drying in vacuo the yellow product was identified as a mixture of two diastereoisomers (1:1). Yield: 95 mg (51%). M.p. 154–157°C. Anal. Calc. for $C_{39}H_{44}O_7P_2PtS_2$ (946.0 g mol^{-1}): C, 49.52; H, 4.69; S, 6.78. Found: C, 50.03; H, 4.75; S, 7.08%. IR: ν(SO) 983 s cm^{-1}. ^{1}H-NMR (CD_2Cl_2): **11^{I}**: δ 0.94 [d, ^2J(HH) = 13.3, 1H, H^1], 0.77 [s, 3H, C(CH$_3$)$_2$], 1.18 [s, 3H, C(CH$_3$)$_2$], 1.98 (s, 3H, OCCH$_3$), 2.00 (s, 3H, OCCH$_3$), 2.13 (m, 1H, H^2), 1.05 (m, 1H, H^5], 5,20 (m, 1H, H^6), 5.00 [dt, ^3J(HH) = 10.1, ^3J(HH) = 5.0, 1H, H^4], 5.97 (m, 1H, H^3), 7.18–7.73 (m, 20H, Ph). **11^{II}**: δ 1.15 (m, 1H, H^1), 1.13 [s, 3H, C(CH$_3$)$_2$], 1.23 [s, 3H, C(CH$_3$)$_2$], 1.95 (s, 3H, OCCH$_3$), 2.06 (s, 3H, OCCH$_3$), 2.20 (m, 1H, H^2), 1.15 (m, 1H, H^5), 5,30 (m, 1H, H^6), 4.93 (m, 1H, H^4), 6.05 (m, 1H, H^3), 7.18–7.73 (m, 20H, Ph). **11^{III}**: δ 1.06 (m, 1H, H^1), 1.05 [s, 3H, C(CH$_3$)$_2$], 1.23 [s, 3H, C(CH$_3$)$_2$], 1.91 (s, 3H, OCCH$_3$), 2.00 (s, 3H, OCCH$_3$), 2.78 (m, 1H, H^2), 2.46 (m, 1H, H^5), 3.29 (m, 1H, H^6), 4.68 [ddd, ^3J(HH) = 11.1/9.4/8.8, 1H, H^4], 6.05 [m, ^3J(HH) = 9.4/11.1, 1H, H^3], 7.18–7.73 (m, 20H, Ph). **11^{IV}**: δ 1.26 (m, 1H, H^1), 0.68 [s, 3H, C(CH$_3$)$_2$], 1.15 [s, 3H, C(CH$_3$)$_2$], 1.93 (s, 3H, OCCH$_3$), 2.03 (s, 3H, OCCH$_3$), 2.71 (m, 1H, H^2), 2.40 (m, 1H, H^5), 3.32 (m, 1H, H^6), 4.75 (m, 1H, H^4), 6.03 (m, 1H, H^3), 7.18–7.73 (m, 20H, Ph). ^{31}P{^{1}H}-NMR (CH_2Cl_2): **11^{I}**: δ 0.29/5.30, ^1J(PPt) = 2268/2785, ^2J(PP) = 32.4. **11^{II}**: δ −1.89/1.81, ^1J(PPt) = 2229/2780, ^2J(PP) = 35.2. **11^{III}**: δ 1.60/2.54, ^1J(PPt) = 2034/3236, ^2J(PP) = 25.8. **11^{IV}**: δ 0.43/10.58, ^1J(PPt) = 2079/3275, ^2J(PP) = 22.4.

*3.5. [(R,R)-diop]-Pt[S(O)–CH$_2$–CH(OAc)–CH(OAc)–CH$_2$–S] (**12$^{I–IV}$**)*

The reaction was carried out in an analogous way using the corresponding thiosulfinte (R^*_{SO},*R**,*S**)-**3** [10]. The reaction was monitored by ^{31}P{^{1}H}-NMR spectroscopy for 30 min at 0°C; the ^{31}P{^{1}H}-NMR spectroscopy revealed formation of four diastereoisomers **I**–**IV**. After stirring for additional 16 h at r.t. the solvent was evaporated under vacuo and the resulting solid was washed thoroughly with a 1:1 ether–hexane solvent mixture to remove the excess of thiosulfinate **3**. After drying in vacuo the yellow product was identified as a mixture of four diastereoisomers (10:10:1:1). Yield: 81 mg (43%). M.p. 166–169°C. Anal. Calc. for $C_{39}H_{44}O_7P_2PtS_2$ (946.0 g mol^{-1}): C, 49.52; H, 4.69; S, 6.78. Found: C, 49.13; H, 4.78; S, 7.21%. IR: ν(SO) 983 s cm^{-1}. ^{1}H-NMR (CD_2Cl_2): **12$^{I/II}$**: δ 0.54/1.00 (m, 1H, H^1), 0.41/1.02/1.09/1.18 [s, 6H, C(CH$_3$)$_2$], 1.95/1.98/1.99/2.06 (s, 6H, OCCH$_3$), 2.20–2.30 (m, 1H, H^2), 1.02 (m, 1H, H^5), 5,22/5.40 (m, 1H, H^6), 4.86–4.89 (m, 2H, H^4), 6.04–6.08/6.09–6.13 [m, ^3J(HH) = 11.5/8.7/2.9, 1H, H^3), 7.18–7.73 (m, 20H, Ph). **12$^{III/IV}$**: δ 0.77 (m, 1H, H^1), 0.45/0.94/1.05/1.11 [s, 6H, C(CH$_3$)$_2$], 1.91/1.93/2.00/2.03 (s, 6H, OCCH$_3$), 2.25/2.75 (m, 1H, H^2), 2.45–3.31 (m, 2H, H$^{5/6}$), 4.60–4.62 (m, 2H, H^4), 6.16–6.21/6.26–6.31 [m, ^3J(HH) = 11.9/8.8/3.2 1H, H^3], 7.18–7.73 (m, 20H, Ph). ^{31}P{^{1}H}-NMR (CH_2Cl_2): **12^{I}**: δ 0.10/5.65, ^1J(PPt) = 2261/2808, ^2J(PP) = 32.6. **12^{II}**: δ −2.98/1.31, ^1J(PPt) = 2207/2764, ^2J(PP) = 35.2. **12^{III}**: δ 1.10/1.98, ^1J(PPt) = 2071/3230, ^2J(PP) = 25.8. **12^{IV}**: δ −0.08/11.02, ^1J(PPt) = 2119/3268, ^2J(PP) = 22.7.

*3.6. Reaction of complex **11** with dppe: Ph$_2$P(CH$_2$)$_2$PPh$_2$–Pt[S(O)–CH$_2$–CH(OAc)–CH(OAc)–CH$_2$–S] (**13**)*

Complex **11** (95 mg, 0.1 mmol) (1:1 mixture of two diastereoisomers) in 10 ml of dichloromethane was

treated with two equivalents of dppe (80 mg, 0.2 mmol) and the reaction was monitored by $^{31}P\{^{1}H\}$-NMR spectroscopy at r.t.. After stirring the yellow solution for 20 h at room temperature the solvent was removed under vacuo. The resulting solid was washed thoroughly with a 1:1 ether–hexane solvent mixture to remove the excess of dppe. After drying in vacuo the yellow product was identified as complex **13** (one diastereoisomer). Yield: 83 mg (49%). M.p. 189–191°C. Anal. Calc. for $C_{34}H_{36}O_5P_2PtS_2$ (845.8 g mol^{-1}): C, 48.28; H, 4.29. Found: C, 47.52; H, 4.44%. IR: ν(SO) 972 s cm^{-1}. $^{31}P\{^{1}H\}$-NMR (CH_2Cl_2): δ 32.38/48.19, $^{1}J(PPt) = 2186/3134$, $^{2}J(PP) = 11.1$.

3.7. Crystal-structure determination of thiosulfinate **3**

X-ray intensities were collected at 170 K on a Siemens P4 diffractometer employing graphite monochromated Mo–K_α radiation. A total of 4070 reflections were obtained using ω-scan mode, yielding 1977 unique reflections. An empirical extinction parameter has been refined [0.0068(9)]. Hydrogen atoms were placed in calculated positions. All non-hydrogen atoms were refined anisotropically (142 parameters). The final difference Fourier synthesis showed features in the range between $+0.57$ and -0.24 e $Å^{-3}$. Further crystallographic details are given in Table 1.

3.8. Crystal-structure determination of complex **8**

X-ray intensities were collected at r.t. on a Siemens R3m/V four circle diffractometer employing graphite monochromated Mo–K_α radiation. A total of 5963 reflections were obtained using ω-scan mode, yielding 5354 unique reflections. A numerical absorption correction was applied. The calculations made use of the SHELXTL programme system. The refinement revealed disorderd hexane molecules. Hydrogen atoms were placed in calculated positions (except hexane-H-atoms). All non-hydrogen atoms were refined with anisotropic displacement parameters (367 parameters). The largest features in the final difference Fourier synthesis were $+1.25$ and -1.35 e $Å^{-3}$. Further crystallographic details are given in Table 1.

4. Supplementary material

Crystallographic data for the structure analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 154665 for compound **3** and No. 154666 for complex **8**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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