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Enantioselective catalysis Part 147. A Rh(cod) complex with the chiral $[Pt_2S_2\{(-)diop\}_2]$ ligand☆

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Abstract

The trinuclear complex $[Pt_2Rh(\mu_3\text{-}S)_2\{(-)\text{-diop}\}_2(cod)]Cl$ (**3**) was synthesized starting from the chiral "ligand" $[Pt_2(\mu\text{-}S)_2\{(-)\text{-diop}\}]$ (**2**) and $[Rh(cod)Cl]_2$, and characterized by X-ray crystallography. Compound **3** was used as a catalyst in the hydrosilylation of acetophenone with diphenylsilane and in the hydrogenation of ketopantolactone.

Keywords: Enantioselective catalysis; Heterometallic complexes; Platinum; Rhodium

1. Introduction

Heterometallic complexes of the transition metals have been synthesized in recent years due to their potential application in catalytic processes. The $\{Pt_2S_2\}$ unit is a versatile metal ligand for binding to other metal fragments [2]. It consists of two square-planar platinum(II) moieties linked by sulfido bridges in a roof-shaped arrangement. The high nucleophilicity [2,3] allows the synthesis of a variety of heterometallic compounds [4,5]. Usually, the square-planar geometry of the platinum atoms is completed with mono- or bidentate phosphine ligands [6–10]. Briant et al. [11] used $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ and $[RhCl(LL)]_2$ (LL = cod (η^4-C_8H_{12}) or $2C_2H_4$) for the synthesis of the complexes $[Pt_2Rh(\mu_3\text{-}S)_2(PPh_3)_4(LL)]PF_6 \cdot CH_2Cl_2$ [12].

In analogy to the ligand $[Pt_2S_2(PPh_3)_4]$ and the complex $[Pt_2Rh(\mu_3\text{-}S)_2(PPh_3)_4(LL)]PF_6$, we synthesized their chiral counterparts using (−)-diop as a bidentate phosphine instead of two PPh_3 ligands. Reaction of the chiral ligand $[Pt_2(\mu\text{-}S)_2\{(-)\text{-diop}\}]$ (**2**) with $[Rh(cod)Cl]_2$ resulted in the formation of the chiral heterometallic trinuclear complex $[Pt_2Rh(\mu_3\text{-}S)_2\{(-)\text{-diop}\}_2(cod)]Cl$ (**3**), which was used as a catalyst in several enantioselective transformations [13].

2. Synthesis

Commercially available $[PtCl_2(PhCN)_2]$ and an equimolar amount of (−)-diop gave $[PtCl_2(-)\text{-diop}]$ (**1**) as a pale white solid [14]. $[Pt_2(\mu\text{-}S)_2\{(-)\text{-diop}\}]$ (**2**) was synthesized by reaction of **1** with a fivefold excess of $Na_2S \cdot 9H_2O$ in benzene for 24 h at room temperature [7,9,10]. Weigand et al. [15] had published the synthesis of compound **2** from elemental sulfur and $[Pt\{(-)\text{-diop}\}(\eta^2\text{-}C_2H_4)]$ in CH_2Cl_2. Reaction of equimolar amounts of $[RhCl(cod)]_2$ and **2** in THF afforded complex **3** (Scheme 1). By slow diffusion of hexane into a dilute solution of **3** in CH_2Cl_2 yellow crystals could be obtained suitable for X-ray analysis.

3. NMR spectra

The $^{31}P\{^1H\}$-NMR spectrum of compound **2** exhibits only one set of signals (Fig. 1A), although the molecule

☆ For Part 146 see Ref. [1].

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[1] X-ray structure analysis.

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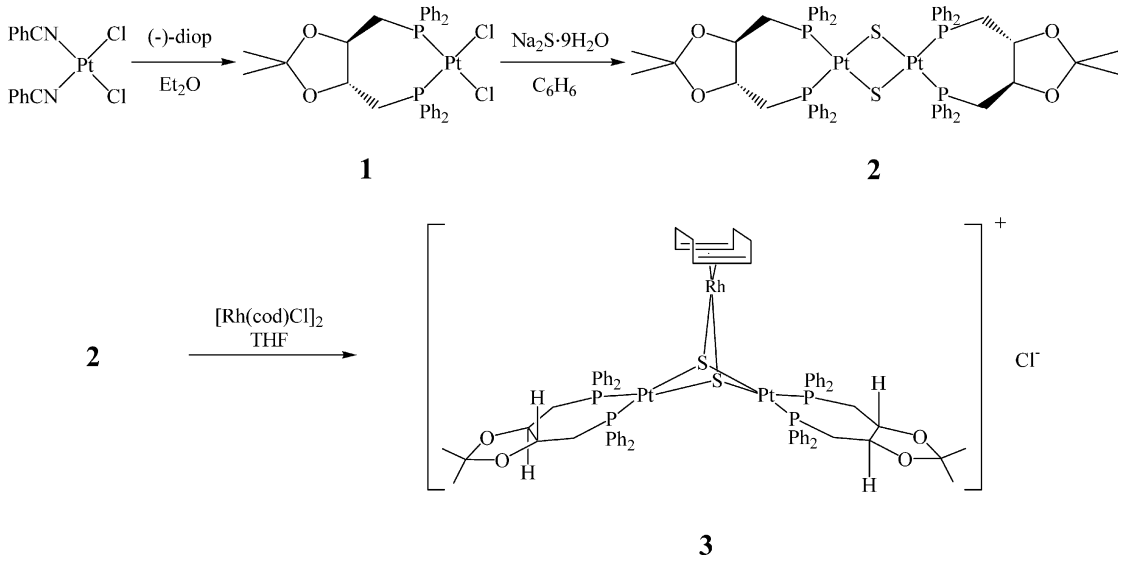


Scheme 1. Synthesis of the chiral trinulcear complex **3**.

contains two different kinds of phosphorus atoms — a point which has not been addressed before [15]. It must be assumed that the two pairs of phosphorus atoms have the same chemical shift. The spectrum consists of several parts as a consequence of the natural occurrence of platinum-195 (33.8%), the statistical distribution of

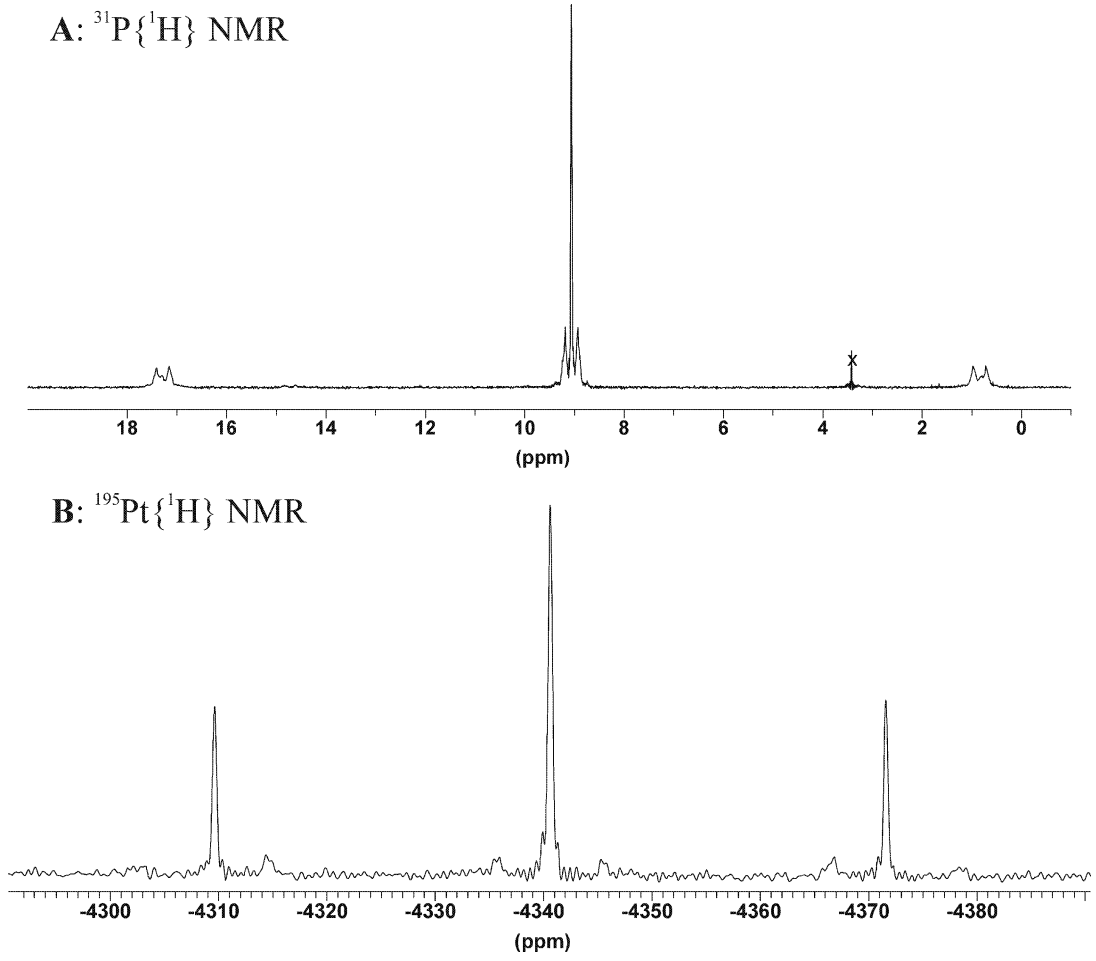


Fig. 1. NMR spectra of **2**. (A) $^{31}P\{^{1}H\}$-NMR: 162 MHz, C_6D_6, 21 °C and (B) $^{195}Pt\{^{1}H\}$-NMR: 86 MHz, C_6D_6, 21 °C.

which leads to a characteristic signal and intensity pattern. Molecules with no platinum-195 give rise to a singlet at 9.06 ppm, whereas molecules with one and two platinum-195 show $^{31}P-^{195}Pt$ couplings through one and three bonds ($^1J(^{31}P, ^{195}Pt) = 2667$ Hz) and ($^3J(^{31}P, ^{195}Pt) = -42$ Hz), respectively. A coupling between the isochronous phosphorus atoms is not observed.

The $^{195}Pt\{^1H\}$-NMR spectrum (Fig. 1B) shows one set of signals at a chemical shift of -4340.6 ppm (line width: 41 Hz). Like before, the distribution of the platinum-195 atoms determines the coupling of the various species. Compounds with one platinum-195 lead to a triplet of a triplet because of the coupling to two phosphorus atoms through one ($^1J(^{195}Pt, ^{31}P) = 2667$ Hz) or three bonds ($^3J(^{195}Pt, ^{31}P) = -42$ Hz). Compounds with two platinum-195 atoms exhibit a weak platinum-195–platinum-195 coupling ($^1J(^{195}Pt, ^{195}Pt) = 855$ Hz) because the platinum atoms are chemically identical but magnetically different.

In the $^{31}P\{^1H\}$-NMR spectrum of the C_2 symmetric compound **3**, the two kinds of phosphorus atoms have slightly different chemical shifts (3.91 and -1.03 ppm, Fig. 2C) lifting the degeneracy observed for **2**. Both types of phosphorus atoms couple to neighboring platinum-195 atoms through one bond ($^1J(^{195}Pt, ^{31}P) = 3034$ Hz and $^1J(^{195}Pt, ^{31}P) = 3094$ Hz) or three bonds. Also a coupling to rhodium-103 is observed. According to these long-range couplings, a splitting of the signals is observed.

The $^{195}Pt\{^1H\}$-NMR spectrum of complex **3** shows a triplet of broad peaks resulting from the coupling to the closest phosphorus atoms. Due to the large number of other possible couplings no resolution of the individual signals is possible (line width: 130 Hz).

4. X-ray structure analysis

Complex **3** is C_2 symmetric the C_2 axis passing through the rhodium atom and bisecting the Pt_2S_2 system. The rhodium atom and the two platinum atoms show square-planar coordination. Distances of 3.0 Å (Pt–Rh) and 3.3 Å (Pt–Pt) exclude bonding interactions between the metal atoms. The two Pt_2S planes adopt an angle of 133.4(12)°. Also, the distance between the sulfur

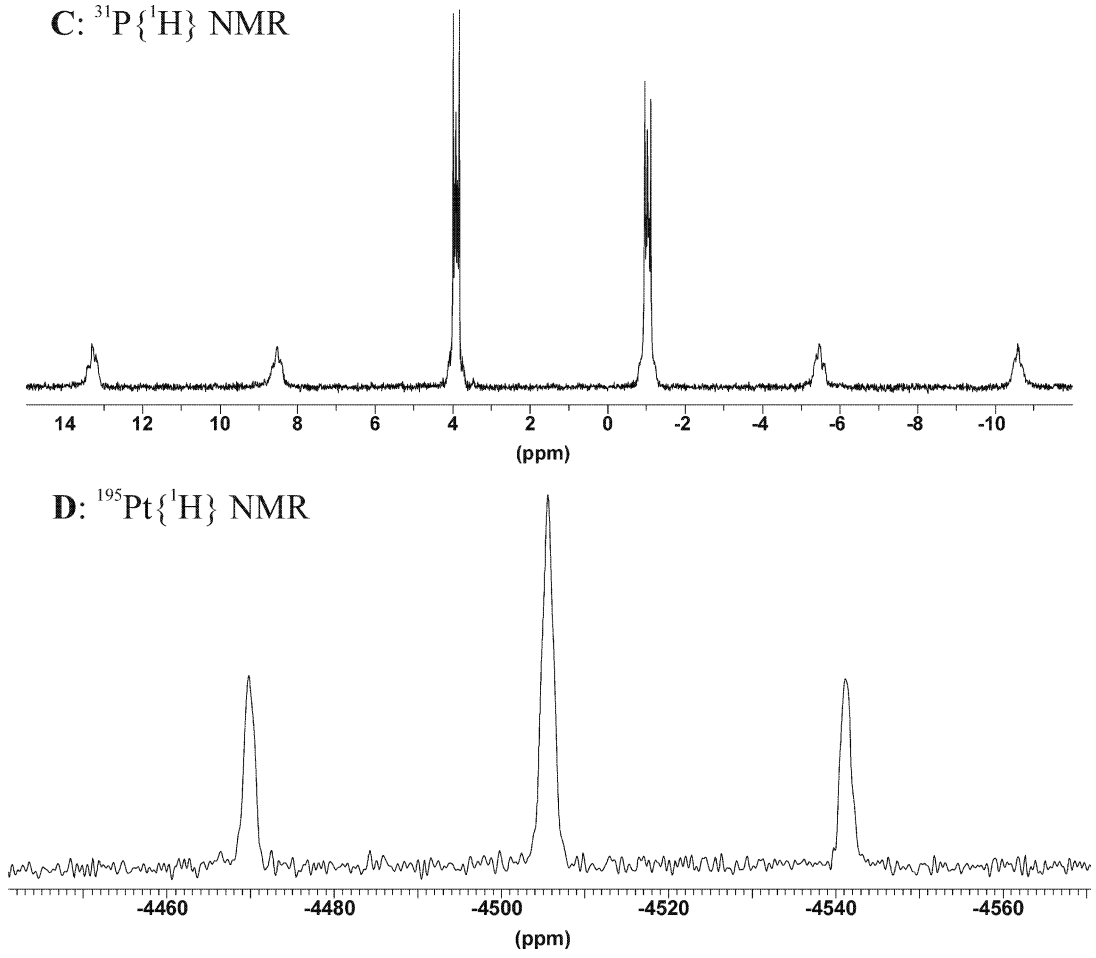


Fig. 2. NMR spectra of **3**. (C) $^{31}P\{^1H\}$-NMR: 162 MHz, C_6D_6, 21 °C and (D) $^{195}Pt\{^1H\}$-NMR: 86 MHz, C_6D_6, 21 °C.

Table 1
Selected bond lengths, bond angles and torsion angles of **3**

Bond length (Å)	
Pt1–S1	2.362(3)
Pt1–S1*	2.362(4)
Pt1–P1	2.289(3)
Pt1–P2	2.287(4)
S1–Rh1	2.362(4)
Bond angles (°)	
S1–Pt1–S1*	80.67(12)
S1–Pt1–P2	92.14(13)
P1–Pt1–P2	97.31(12)
P1–Pt1–S1*	89.52(12)
S1–Pt1–P1	169.78(14)
S1*–Pt1–P2	170.75(14)
Pt1–S1–Pt1*	88.85(13)
S1–Rh1–S1*	80.67(12)
Torsion angles (°)	
Rh1–S1–Pt1–P1	−29.0(8)
Rh1–S1–Pt1–P2	128.68(13)
Pt1–S1–S1*–Pt1*	133.4(12)

atoms (3.1 Å) is outside bonding interaction (Table 1 and Fig. 3).

The phosphine ligands form puckered seven-membered rings typical for platinum(diop) complexes [16] strictly adhering to C_2 symmetry.

5. Catalysis

Complex **3** was tested as a catalyst in two different models of enantioselective catalysis. To obtain information whether the complex decomposes during catalysis, data of the system (−)-diop/$[Rh(cod)Cl]_2$ are reported for comparison (Table 2, entry 2 and Table 3, entry 1).

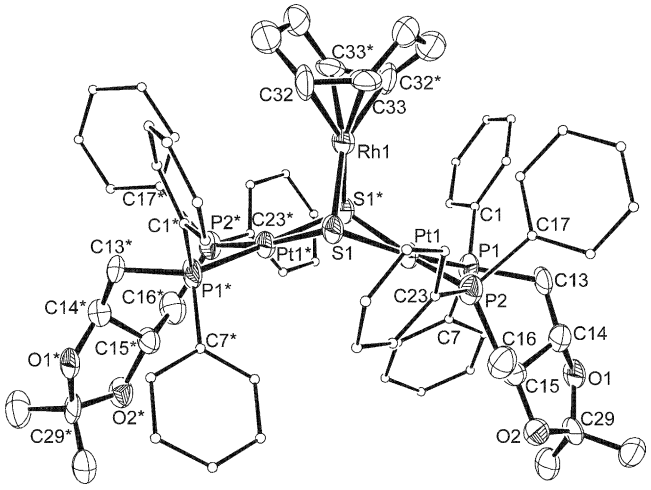


Fig. 3. Structure of the C_2 symmetric complex **3** in the crystal. Ellipsoids are drawn at the 50% probability level. The hydrogen atoms and the counterion have been omitted for clarity. The phenyl rings are drawn schematically.

5.1. Hydrosilylation of acetophenone

Reaction with diphenylsilane in the presence of a rhodium(I) catalyst is a well-known method for the reduction of prochiral ketones to the corresponding alcohols. Addition of a Si–H bond to the carbonyl function of acetophenone affords the silylalkyl ether, the acidic hydrolysis of which leads to the chiral alcohol 1-phenylethanol. Silylation of the enol of acetophenone gives the silylenol ether as a side product which on hydrolysis reverts to the starting material acetophenone. Work up and analysis were carried out as published [17].

The heterometallic complex **3** showed moderate catalytic activity and after 144 h all the diphenylsilane had disappeared. The silylalkyl ether was formed in a yield of 42–47%. 1-Phenylethanol obtained was racemic (Table 2, entry 3). The fact that only 1–2% of silylenol ether was observed demonstrates the stability of complex **3**, because free Rh(I) gives considerable amounts of silylenol ether (Table 2, entry 1). In a catalyst/substrate ratio of 1:1000, compound **3** showed very low reactivity and after 336 h the product 1-phenylethanol was obtained in a yield of 74–76% as a racemic mixture (Table 2, entry 4). In this experiment, more silylenol ether was found (10–12%) indicating a decomposition of the trinuclear complex **3** to Rh(I) and other compounds. On the other hand, if there were Rh(I) and (−)-diop in solution they should combine to the rhodium/(−)-diop complex and give 24% ee (Table 2, entry 2). These results show that removal of the cod ligand in **3**, a prerequisite for catalytic activity, is not easy. This is in accord with observations of Briant et al. [11]. They found a surprisingly low tendency of the cod ligand in $[Pt_2Rh(\mu_3\text{-}S)_2(PPh_3)_4(cod)]PF_6$ to be substituted by H_2, CO, SO_2 and dppe, respectively, under mild conditions.

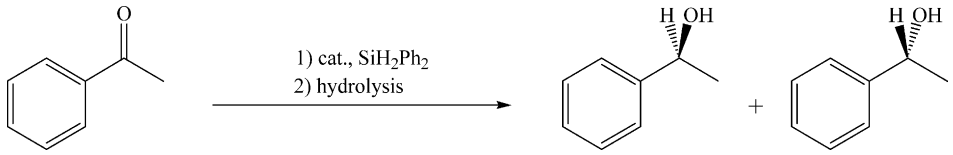
5.2. Hydrogenation of ketopantolactone

The catalytic hydrogenation of ketopantolactone to pantolactone was carried out as described [19]. Complex **3** used as a catalyst in toluene afforded pantolactone in a yield of 31% with very low enantioselectivity (Table 3, entry 2). In THF the hydrogenation gave a lower yield (14–16%) but a considerably higher enantioselectivity of 58–59% (Table 3, entry 3). Comparing this result with the system $[Rh(cod)Cl]_2$/(−)-diop allows the interpretation that partial decomposition of **3** to Rh(I) and (−)-diop occurred to give the enantioselectivity expected for the known rhodium/(−)-diop catalyst (Table 3, entry 3).

6. Experimental

All compounds were prepared in an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents were dried and nitrogen saturated before use.

Table 2
Enantioselective hydrosilylation of acetophenone with diphenylsilane without solvent in an argon atmosphere [a]



Number	Catalyst	Ratio [b]	Reaction time (h)	Yield (%) [c,d]	ee (%) [d] (configuration)
1	$[Rh(cod)Cl]_2$	1:200	24	5.1/46.3/48.6	–
2	$[Rh(cod)Cl]_2$, (−)-diop [18]	1:2.2:200	24	10.7/ < 1/89.3	23.8 (*R*)
				8.8/ < 1/91.2	24.3 (*R*)
3	**3**	1:200	144	46.7/1.4/51.9	Racemic
				41.8/1.7/56.5	Racemic
4	**3**	1:1000	336	76.1/10.2/13.7	Racemic
				74.3/12.8/12.9	Racemic

[a] Temperature from 0 °C to room temperature.
[b] Catalyst/ligand/substrate or catalyst/substrate.
[c] Acetophenone/silylenol ether/silylalkyl ether.
[d] For work up and enantiomer analysis, see Ref. [17].

Melting points: Büchi SMP 20 (not corrected). Elemental analyses: Elementar Vario EL III. IR spectra: Bio-Rad IR-Spectrometer FTS 155. Optical rotations: Perkin–Elmer 241 Polarimeter (room temperature (r.t.)). $^1H\{^{31}P\}$-, $^{31}P\{^1H\}$-, $^{13}C\{^1H\}$- and $^{195}Pt\{^1H\}$-NMR spectra: Bruker ARX 400 Spectrometer. Mass spectra: Finnigan MAT 95 (FAB) and Thermo Quest Finnigan TSQ 7000 [ESI]. X-ray structural analyses: STOE-IPDS Diffractometer (Mo–K_α radiation, 173 K (Oxford Cryosystems Cooler), graphite monochromator), SIR-97 [20] and SHELXL-97 [21]. Literature methods were used to prepare (−)-diop [22–24] and $[Rh(cod)Cl]_2$ [25].

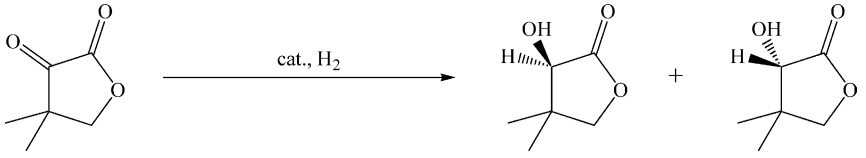
6.1. $PtCl_2$[(−)-diop] (1)

1 was prepared as published [14]. IR (KBr, cm^{-1}): *v* 3020w, 2965w, 2890w, 2825w, 2809w, 1458m, 1410s, 1352m, 1218s, 1206s, 1132m, 1070s, 1041s, 968m, 803s, 712s, 661s. $^1H\{^{31}P\}$-NMR (400.1 MHz, TMS, CD_2Cl_2): δ 7.85−7.76 (m, 4H, Ph-*H*), 7.69−7.61 (m, 4H, Ph-*H*), 7.60−7.44 (m, 12H, Ph-*H*), 3.91 (m, 2H, C*H*), 3.09 (m, 2H, diop-H^AH^B), 2.63 (m, 2H, diop-H^AH^B), 1.13 (s, 6H, $2CH_3$). $^{31}P\{^1H\}$-NMR (162.0 MHz, 85% H_3PO_4, CD_2Cl_2): δ −0.68 (s, $^1J(^{31}P, ^{195}Pt) = 3520$ Hz).

6.2. $Pt_2(\mu\text{-}S)_2$[(−)-diop]$_2$ (2)

1 (400 mg, 0.52 mmol) was suspended in 15 ml of benzene. A fivefold excess of $Na_2S\cdot 9H_2O$ (650 mg, 2.62 mmol) was added and the suspension was stirred at r.t. for 24 h. The reaction mixture turned orange and cleared up. After filtration the solvent was removed and the resulting orange solid was dried. Yield: 380 mg (0.26 mmol, 97%), m.p.: 165–167 °C. $C_{62}H_{64}O_4P_4Pt_2S_2$ (1451.4). IR (KBr, cm^{-1}): *v* 3402w br, 3051w, 2985w,

Table 3
Enantioselective hydrogenation of ketopantolactone to pantolactone at 50 °C and 50 bar of hydrogen pressure for 40 h



Number	Catalyst	Solvent	Yield (%) [a]	ee (%) (configuration) [a]
1	(−)-diop, $[Rh(cod)Cl]_2$ [19]	Toluene	100	54.4 (*R*)
2	**3**	Toluene	31.1	1.6 (*R*)
			31.2	1.7 (*R*)
3	**3**	THF	15.9	58.2 (*R*)
			13.5	58.7 (*R*)

[a] For work up and enantiomer analysis, see Ref. [19].

1624w, 1481m, 1433s, 1375m, 1241s, 1161s, 1099s, 1049s, 885s, 741s, 692s, 508s. $^1H\{^{31}P\}$-NMR (400.1 MHz, TMS, C_6D_6): δ 7.90–7.81 (m, 8H, Ph-*H*), 7.54–7.44 (m, 8H, Ph-*H*), 7.07–6.91 (m, 24H, Ph-*H*), 4.08 (m, 4H, diop-*H*), 3.18 (m, 4H, diop-H^AH^B), 2.44 (m, 4H, diop-H^AH^B), 1.16 (s, 12H, CH_3). $^{31}P\{^1H\}$-NMR (162.0 MHz, 85% H_3PO_4, C_6D_6): δ 6.94 (d, $^1J(^{195}Pt, ^{31}P) = 2690$ Hz). $^{195}Pt\{^1H\}$-NMR (85.6 MHz, 1.2 M Na_2PtCl_6 in D_2O, C_6D_6): δ −4340.6 (tdd, $^1J(^{195}Pt, ^{31}P) = 2667$ Hz, $^2J(^{195}Pt, ^{195}Pt) = 855$ Hz, $^3J(^{195}Pt, ^{31}P) = -42$ Hz). $^{13}C\{^1H\}$-NMR (100.6 MHz, TMS, C_6D_6): δ 135.1 (4*C*H), 134.1 (4C^q), 133.7 (4*C*H), 132.8 (4C^q), 129.9 (8*C*H), 129.0 (8*C*H), 127.8 (m, 8*C*H), 127.2 (m, 8*C*H), 108.2 (2C^qMe$_2$), 78.0 (m, 4C^{diop}H), 32.4 (4C^{diop}H$_2$), 27.0 (4*C*H$_3$). FAB-MS: *m*/*z*, 1451.4 [M^+, 100%].

6.3. [$Pt_2Rh(\mu$-S)$_2${(−)-diop}$_2(\eta$-C_8H_{12})]Cl (**3**)

To a solution of **2** (420 mg, 0.29 mmol) in 20 ml of THF was added a solution of [RhCl(cod)]$_2$ (72 mg, 0.29 mmol) in 20 ml of THF with stirring at 0 °C. After stirring for 2 h at r.t. the solvent was removed to give a yellow solid. Crystals of **3** were obtained by recrystallization from CH_2Cl_2 and hexane. Yield: 270 mg (55%), m.p.: > 250 °C. Anal. Found: C, 49.04; H, 4.62; S, 3.48. Calc. for $C_{70}H_{76}ClO_4P_4Pt_2RhS_2$ (1697.9): C, 49.52; H, 4.51; S, 3.78%. IR (KBr, cm^{-1}): *v* 3427w br, 3054w, 2986w, 2935w, 2877w, 2370w, 2341w, 1436m, 1240m, 1160m, 1100s, 1054s, 886m, 799m, 745m, 696s, 508s. $^1H\{^{31}P\}$-NMR (400.1 MHz, TMS, $CDCl_3$): δ 7.88–7.78 (m, 8H, Ph-*H*), 7.73–7.66 (m, 2H, Ph-*H*), 7.62–7.53 (m, 6H, Ph-*H*), 7.47–7.35 (m, 6H, Ph-*H*), 7.29–7.20 (m, 6H, Ph-*H*), 7.08–6.92 (m, 12H, Ph-*H*), 3.70–3.58 (m, 4H, diop-*H*), 3.33 (m, 2H, cod-*H*), 3.19 (m, 2H, diop-H^AH^B), 3.03 (m, 2H, diop-H^AH^B), 3.01 (m, 2H, cod-*H*), 2.74 (m, 2H, diop-H^AH^B), 2.38 (m, 2H, diop-H^AH^B), 2.01–1.79 (m, 6H, cod-H_2), 1.59 (m, 2H, cod-H_2), 1.18 (s, 6H, CH_3), 1.03 (s, 6H, CH_3). $^{31}P\{^1H\}$-NMR (162.0 MHz, 85% H_3PO_4, $CDCl_3$): δ 3.91 (d, $^1J(^{31}P, ^{195}Pt) = 3034$ Hz), −1.03 (d, $^1J(^{31}P, ^{195}Pt) = 3094$ Hz). $^{195}Pt\{^1H\}$-NMR (85.6 MHz, 1.2 M Na_2PtCl_6 in D_2O, $CDCl_3$): δ −4505.6 (t, $^1J(^{195}Pt, ^{31}P) = 3076$ Hz). $^{13}C\{^1H\}$-NMR (100.6 MHz, TMS, C_6D_6): δ 135.1 (m, 2*C*H), 134.2 (m, 2*C*H), 132.9 (C^q), 132.4 (C^q), 132.3 (C^q), 132.2 (4*C*H), 132.0 (m, 2*C*H), 131.9 (4*C*H), 131.8 (C^q), 131.3 (m, 2*C*H), 130.8 (4*C*H), 130.7 (C^q), 130.3 (C^q), 130.1 (C^q), 129.9 (4*C*H), 129.7 (C^q), 128.6 (m, 8*C*H), 127.8 (m, 4*C*H), 127.7 (m, 4*C*H), 109.0 (2C^qMe$_2$), 77.0 (d, $^1J(^{13}C, ^{103}Rh) = 11$ Hz, 2C^{cod}H), 76.9 (m, 2C^{diop}H), 76.4 (d, $^1J(^{13}C, ^{103}Rh) = 11$ Hz, 2C^{cod}H), 75.6 (m, 2C^{diop}H), 32.5 (2C^{cod}H$_2$), 31.6–30.8 (m, 4C^{diop}H$_2$), 29.4 (2C^{cod}H$_2$), 26.7 (2*C*H$_3$), 26.5 (2*C*H$_3$). ESI-MS: *m*/*z*, 1662.6 [cation$^+$, 100%].

6.4. Crystallographic data and structure determination

$C_{70}H_{76}ClO_4P_4Pt_2RhS_2$ (**3**): yellow plates, $F_w = 1697.85$, orthorhombic, space group *C* 2 2 21, $a = 10.5720(8)$ Å, $b = 22.707(3)$ Å, $c = 27.563(2)$ Å, $V = 6616.7(11)$ Å^3, $Z = 4$, $D_x = 1.704$ mg m^{-3}, μ(Mo–K$_\alpha$) = 4.71 mm^{-1}, absorption correction: numerical, crystal dimensions $0.24 \times 0.20 \times 0.20$ mm^3, $\lambda = 0.71073$ Å (Mo–K$_\alpha$ radiation, graphite monochromator, STOE imaging plate diffraction system). Data collection at $T = 173$ K, $1.94 < \theta < 25.09°$, *h*: 12 → 12, *k*: 27 → 26, *l*: 32 → 32, 21 106 reflections measured, 5723 unique, merging $R_{int} = 0.1146$. The structure was solved by direct methods (SIR-97) and refined by full-matrix least-squares based on F^2 (SHELXL-97) with weights $w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2)/3$. Most of the H atoms were calculated geometrically and a riding model was used during the refinement process. The final consistence indexes for all data were $R_1 = 0.0517$, $wR_2 = 0.1030$ and goodness-of-fit = 0.910. The last difference Fourier map showed peaks between −0.887 and 3.250 e Å^{-3}. The correct absolute configuration was confirmed by the Flack parameter −0.01(1).

7. Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 200813. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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