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Synthesis, structure determination and catalytic activity of (+)-*cis*-[dicarbonyl-μ-chloro-μ-[5β-methyl-2α-(1-methylethyl)cyclohexanethiolato]]-bis[tris(1,1-dimethylethyl)arsine]dirhodium

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Abstract

The title compound, 5, which is the first dirhodium complex to contain both arsenic and a chiral substituent, has been synthesized from $[Rh(CO)_2]_2(\mu\text{-}Cl)_2$, $As(^tBu)_3$ and (+)-(neomenthanethio)trimethylsilane. The complex was found to catalyze the hydrogenation of methyl *N*-acetamidocinnamate, albeit with low enantioselectivity. X-Ray diffraction studies revealed that 5 exists in the crystal as a pair of epimers.

Introduction

The superior ability of dinuclear complexes to catalyze multi-substrate reactions [1] has been demonstrated in our laboratories by application of dirhodium compounds of general formula *cis*-$[(^tBu_3P)(CO)Rh]_2(\mu\text{-}Cl)(\mu\text{-}SR)$ to various organic hydrogen transfer processes [2–5]. Modification of these complexes, either by substitution of the bulky phosphine ligands, or by changing the nature of the sulfur-bound R group, proved to affect their catalytic properties greatly. For example, a substantial rate increase was observed in hydrogenation of cyclohexene either upon replacement of the tertiary phosphine by arsine [6], or upon attachment of the dirhodium complexes to insoluble supports [3–5]. Introduction of a chiral tertiary phosphine ligand into the various dirhodium compounds gave enantioselective hydrogenation catalysts [7].

We now report the preparation of (+)-*cis*-[dicarbonyl-μ-chloro-μ-[5β-methyl-2α-(1-methylethyl)cyclohexanethiolato]]bis[tris(1,1-dimethylethyl)arsine]dirhodium (5), which is the first dirhodium complex to contain both arsenic and a chiral substituent.

Results and discussion

The synthesis of **5** was accomplished by reaction of $[Rh(CO)_2]_2(\mu\text{-}Cl)_2$ (**1**) with two equivalents of $^tBu_3As$ (**2**) (eq. 1), followed by one equivalent (+)-(neomenthanethio)trimethylsilane ([1*S*-(1α,2α,5β)][5-methyl-2-(1-methylethyl)cyclohexanethio]trimethylsilane) (**4**) (eq. 2).

$$\underset{(\mathbf{1})}{[Rh(CO)_2]_2(\mu\text{-}Cl)_2} + \underset{(\mathbf{2})}{2\,^tBu_3As} \rightarrow \underset{(\mathbf{3})}{[(^tBu_3As)(CO)Rh]_2(\mu\text{-}Cl)_2} + 2CO \qquad (1)$$

$$\mathbf{3} + \underset{(\mathbf{4})}{(+)\text{-}Me_3SiSR} \rightarrow \underset{(\mathbf{5})}{(+)\text{-}cis\text{-}\left[(^tBu_3As)(CO)Rh\right]_2(\mu\text{-}Cl)(\mu\text{-}SR)} + Me_3SiCl \qquad (2)$$

(R = 5β-methyl-2α-(1-methylethyl)cyclohexyl)

The intermediate **3** exists in solution as a mixture of isomers. When the reaction is conducted in the cold or left to stand for a prolonged period prior to the addition of **4**, the *trans*-isomer of **3**, which reacts only very slowly with the thio-ether, separates.

X-Ray diffraction analysis of a crystal of **5** (see Tables 1 and 2) revealed that each unit cell consists of two *cis*-oriented epimers: one pair in which the chiral moiety has the (1*R*,2*R*,5*S*)-configuration, and one in which it has the (1*S*,2*R*,5*S*)-configuration. (See Fig. 1 for a stereoscopic view of one half of the unit cell). The ORTEP drawings of the two isomers of **5** are presented in Fig. 2a and 2b. By placing these two figures in such a way that the atoms of both molecules—with the exception of those of the chiral portion—are superimposed, one can see that C(1)–C(3) of the cyclohexane moieties are also superimposable. In such an arrangement C(5) of one epimer occupies position C(7) in the other and *vice versa*. The cyclohexane ring which is attached to the sulfur bridge by the secondary C(1) atom occupies a pseudo-axial position in the dimetallacyclobutane structure in a similar fashion as in *cis*-[dicarbonylbis(tri-tert-butylphosphine)dirhodium [8]. This configuration of **5** is opposite to that found in compounds in which the R group is attached to the sulfur through a primary carbon atom (e.g., in (−)-*cis*-{dicarbonyl-μ-chloro-(6,6-dimethylbicyclo[3.1.1]heptane-2-methanethiolato)bis[tris(1,1-dimethylethyl)phosphine]dirhodium [9]).

Table 1

Crystal data and refinement details for 5

Formula	$C_{36}H_{73}As_2ClO_2SRh_2$	V (Å^3)	2159(1)
Molecular weight	961.1	Z	2
Crystal system	triclinic	ρ_{calcd}, g cm^{-3}	1.48
Space group	$P\bar{1}$	μ(Mo-K_α), μ^{-1}	22.97
a (Å)	16.290(6)	No. of unique reflections	5593
b (Å)	14.224(4)	No. of reflections with $I \geq 3\sigma(I)$	4292
c (Å)	10.066(6)	R	0.065
α (°)	109.77(3)	R_w	0.085
β (°)	93.18(2)	w^{-1}	$\sigma_F^2 + 0.000691 \cdot F^2$
γ (°)	79.62(3)		

Table 2

Fractional atomic coordinates for **5** (esd's in parentheses)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh(1)	0.26904(6)	0.26431(7)	0.3270(1)	C(12)	0.1759(8)	0.571(1)	0.613(1)
Rh(2)	0.22399(5)	0.50910(7)	0.44518(9)	C(13)	0.293(1)	0.150(1)	−0.074(1)
As(1)	0.24645(7)	0.13129(9)	0.1001(1)	C(14)	0.294(1)	0.062(1)	−0.213(2)
As(2)	0.14868(8)	0.63894(9)	0.3470(1)	C(15)	0.380(1)	0.177(1)	−0.037(2)
S	0.2930(2)	0.3870(2)	0.5433(3)	C(16)	0.238(1)	0.244(1)	−0.098(2)
Cl	0.2997(2)	0.3924(2)	0.2356(3)	C(17)	0.1206(8)	0.136(1)	0.079(2)
O(1)	0.2143(8)	0.1629(8)	0.505(1)	C(18)	0.093(1)	0.085(1)	−0.080(2)
O(2)	0.1468(6)	0.6035(8)	0.726(1)	C(19)	0.091(1)	0.088(1)	0.178(2)
C(1,1′)	0.4062(7)	0.3954(9)	0.537(1)	C(20)	0.0824(9)	0.251(1)	0.124(2)
C(2)	0.438(2)	0.455(2)	0.691(3)	C(21)	0.2973(8)	−0.014(1)	0.092(1)
C(3,3′)	0.440(1)	0.383(2)	0.778(2)	C(22)	0.257(1)	−0.096(1)	−0.027(2)
C(4)	0.489(2)	0.290(4)	0.735(4)	C(23)	0.395(1)	−0.032(1)	0.061(2)
C(5,7′)	0.4635(9)	0.221(1)	0.559(2)	C(24)	0.2881(9)	−0.025(1)	0.233(2)
C(6)	0.455(2)	0.291(2)	0.479(3)	C(25)	0.154(1)	0.787(1)	0.474(2)
C(7,5′)	0.3955(8)	0.558(1)	0.756(1)	C(26)	0.141(1)	0.795(1)	0.623(2)
C(8)	0.384(2)	0.623(3)	0.656(4)	C(27)	0.239(1)	0.806(1)	0.453(2)
C(9)	0.434(2)	0.629(4)	0.884(3)	C(28)	0.082(1)	0.867(1)	0.440(2)
C(10)	0.520(2)	0.124(3)	0.525(6)	C(29)	0.0269(7)	0.621(1)	0.328(2)
C(2′)	0.464(2)	0.330(2)	0.612(3)	C(30)	−0.014(1)	0.658(1)	0.476(2)
C(4′)	0.450(2)	0.482(3)	0.834(3)	C(31)	−0.028(1)	0.675(1)	0.237(2)
C(6′)	0.416(2)	0.511(2)	0.602(3)	C(32)	0.030(1)	0.501(1)	0.261(2)
C(8′)	0.484(2)	0.175(2)	0.392(3)	C(33)	0.1891(9)	0.626(1)	0.149(1)
C(9′)	0.529(2)	0.163(2)	0.633(4)	C(34)	0.156(1)	0.716(1)	0.102(2)
C(10′)	0.435(4)	0.650(4)	0.812(5)	C(35)	0.169(1)	0.528(1)	0.043(2)
C(11)	0.2364(8)	0.195(1)	0.428(1)	C(36)	0.288(1)	0.615(1)	0.159(2)

The formation of **5** as a 1 : 1 mixture of epimers by use of **4** of > 99.5% optical purity (as indicated (i) by Horeau's method [10], (ii) by the chiral lanthanide shift reagent technique, and (iii) by hydrolysis to give > 99.5% optically pure (+)-

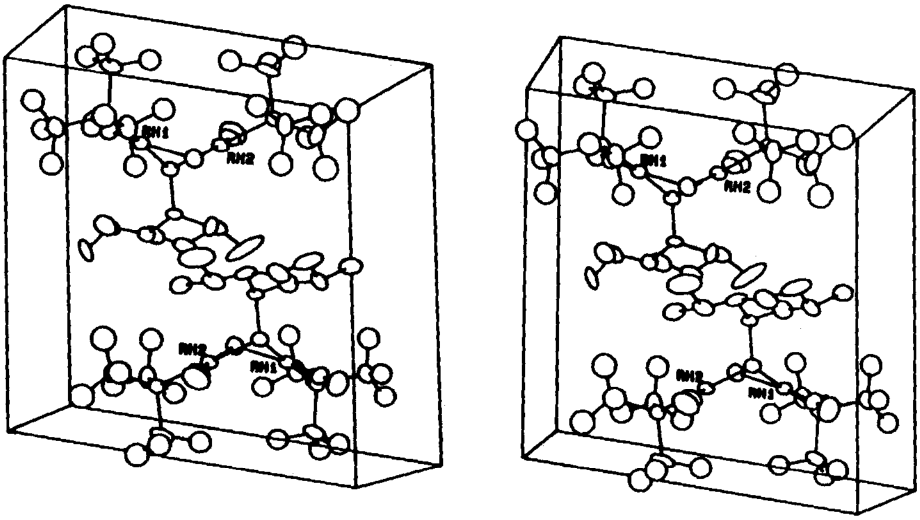


Fig. 1. Stereoscopic view of one half unit cell of **5**.

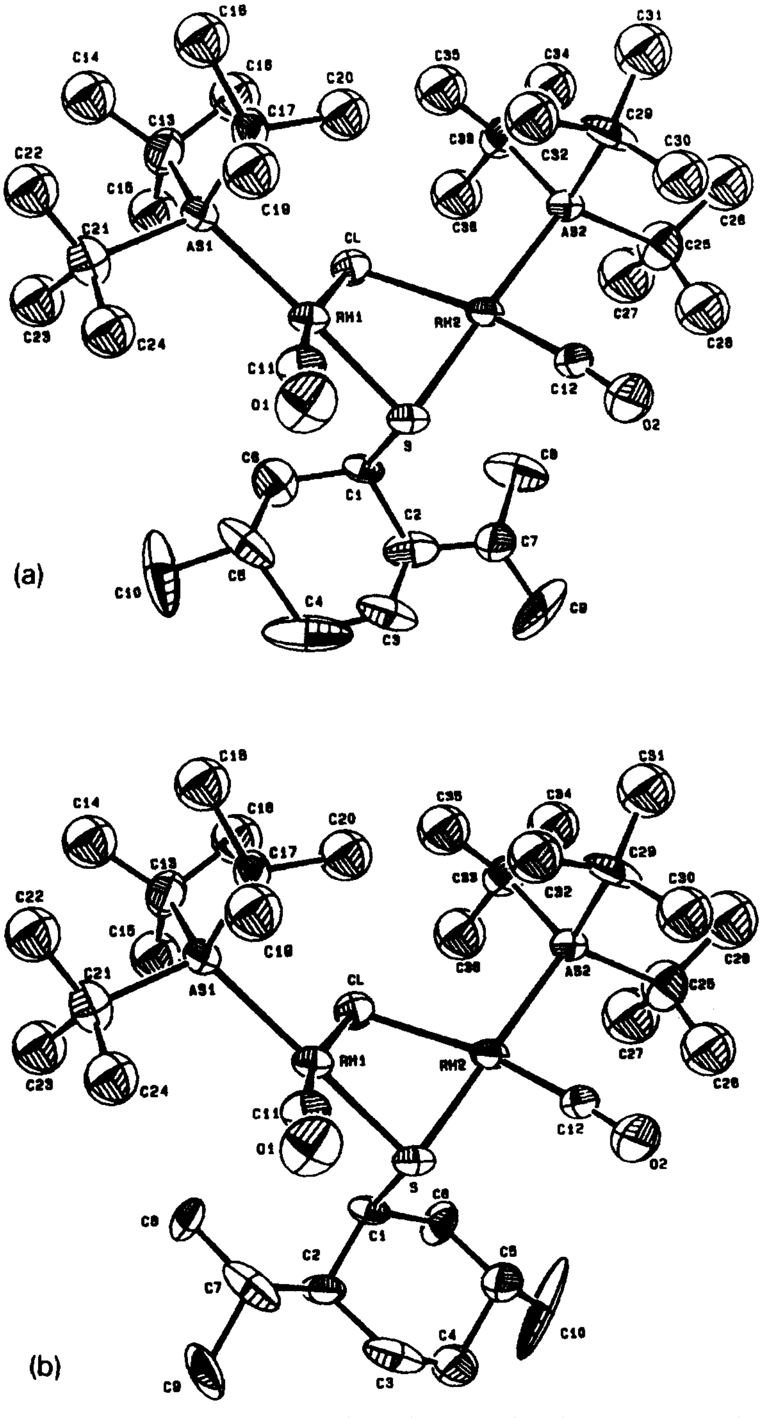
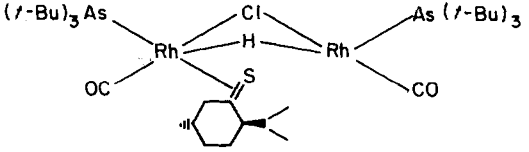


Fig. 2. ORTEP drawings of (a) the 1*R*,2*R*,5*S*-isomer of **5b** and (b) the 1*S*,2*R*,5*S*-isomer of **5b**.

neomenthanethiol [11]), suggests that the replacement of one chlorine atom in intermediate **3** involves the reversible formation of a complex of type **6**. The suggestion that **6** is generated is supported by the observation that some chlorine-bridged dirhodium complexes are capable of inducing reversible β-hydrogen elimination [2,5].



(6)

Complex **5** was shown to be a highly active hydrogenation catalyst for unhindered alkenes. Cyclohexene e.g., is transformed by **5** to cyclohexane at a comparable rate to that of hydrogenation in the presence of the Wilkinson catalyst [12]. Sterically hindered C=C bonds were found to be reduced much more slowly. The complex was shown to promote asymmetric hydrogenation of some prochiral substrates such as methyl *N*-acetamidocinnamate (**7**) (eq. 3). Its enantioselectivity,

$$Z\text{-PhCH=C(NHCOMe)(COOMe)} + H_2 \xrightarrow{5} S\text{-(+)-PhCH}_2\text{CH(NHCOMe)(COOMe)} \qquad (3)$$

however, proved inferior to that of our neomenthyldiphenylphosphine dirhodium catalyst [7]. After 20 h, e.g., the hydrogenation of **7** in a 1 : 2 mixture of MeOH–PhH at 120 °C and 100 psi H_2 furnished 16% of the (+)-*N*-acetylphenylalanine methyl ester (**8**), in only 22% ee. When the reaction was conducted in pure PhH, the reduction rate increased (63, 77 and 98% yield were obtained after 30, 60 and 120 min, respectively), but the corresponding ee values were only 10, 8, and 0%. We attribute the low optical purity in part to the existence of **5** as pairs of epimers, and in part to the catalytic hydrogen scrambling in the initially formed optically active product [13].

Experimental

(+)-(Neomenthanethio)trimethylsilane (4)

To a stirred solution of 10.52 g (61 mmol) of > 99.5% optically pure (+)-neomenthanethiol [11] in 40 cm³ of EtOH under Ar was added a solution of 11.64 g (30 mmol) of $Pb(OAc)_2 \cdot 3H_2O$ in 350 cm³ of H_2O. The mixture was stirred for 24 h at room temperature. The yellow precipitate was washed successively with EtOH and dried at 0.05 mm to give 14.52 g (87%) of the lead salt of neomenthanethiol. M.p. 182 °C (dec.); $[\alpha]_D^{20} = +22.5°$ ($c = 0.2$, $CHCl_3$). Found: C, 43.75; H, 6.92. $C_{20}H_{38}PbS_2$ (549.84) calcd.: C, 43.68; H, 6.98%.

A stirred mixture of 14.11 g (26 mmol) of the lead salt and 20 cm³ of freshly distilled Me_3SiCl was refluxed under Ar for 10 days. The $PbCl_2$ was filtered off and washed twice with 10 cm³ of Me_3SiCl. The excess of Me_3SiCl was removed under reduced pressure and the residue was distilled at 0.1 mm to give 10.75 g (85%) of **4**. B.p. 91 °C (0.1 mmHg); $[\alpha]_D^{20} = +80.4°$; ^{1}H-NMR (300 MHz, C_6D_6): δ 0.238 (s, 9H, $Si(CH_3)_3$); 0.768–0.831 (m, 3H); 0.859–1.018 (m, 9H, $CH(CH_3)_2$, CH_3); 1.157–1.251 (m, 1H); 1.478–1.865 (m, 4H); 2.206–2.228 (m, 1H); 3.334 (dt, 1H,

$J_d = 2.4$ Hz, $J_t = 2.5$ Hz, C*H*S). ^{13}C{^{1}H} NMR (75 MHz, C_6H_6): δ 1.77 (Si(C*H*$_3$)$_3$); 20.96, 21.08, 22.40, 25.28, 26.08, 30.17, 35.90, 43.16, 45.24, 50.06 (*C*HS). Found: C, 63.94; H, 11.48. $C_{13}H_{28}SSi$ (244.52) calcd.: C, 63.86; H, 11.54%.

Preparation of 5

To a stirred solution of 300 mg (0.77 mmol) of **1** in 30 cm^3 of n-pentane at 20 °C under Ar was added a solution of 365 mg (1.48 mmol) of ^{t}Bu$_3$As in 20 cm^3 of the same solvent. The mixture was warmed during 30 min to 35 °C and kept for 2 h at this temperature, and a solution of 188 mg (0.77 mmol) of **4** in 20 cm^3 of n-pentane was added. Stirring was continued for 4 h and the pale orange micro-crystals of **5** then filtered off under Ar and washed three times with 3 cm^3 of n-pentane. Crystallization from a 1 : 1 mixture of degassed CH_2Cl_2 and pentane afforded 460 mg (62%) of **5**. M.p. 190–205 °C (dec.). $[\alpha]_D^{20} = +7.9°$ ($c = 0.052$, PhH); IR (KBr): ν(CO) 1950, 1960 cm^{-1}; ^{1}H-NMR (200 MHz, C_6D_6): δ 0.831–0.899 (m, 1H); 1.087 (d, 3H, $J = 6.6$ Hz, C*H*$_3$CHCH$_3$); 1.153 (d, 3H, $J = 6.6$ Hz, CH$_3$CHC*H*$_3$); 1.231–1.274 (m, 1H); 1.431 (s, 54H, As[C(C*H*$_3$)$_3$]$_3$); 1.599–1.617 (m, 2H); 1.705 (d, 3H, $J = 6.6$ Hz, CHC*H*$_3$); 1.741–1.903 (m, 1H); 2.010–2.258 (m, 1H); 2.655–2.964 (m, 2H); 3.667–3.875 (m, 1H); 4.310 (m, 1H, C*H*S); ^{13}C-NMR (75 MHz, C_6D_6): δ 21.56, 22.88, 23.66, 25.20, 26.64, 30.46, 32.52, (As[C(*C*H$_3$)$_3$]$_3$); 36.49, 43.16 (As[*C*(CH$_3$)$_3$]$_3$); 50.17, 51.50, 51.63, 188.35 (d, ^1J(Rh, *C*) = 40.1 Hz, Rh–CO). Found: C, 44.89; H, 7.80. $C_{36}H_{73}As_2ClO_2Rh_2S$ (961.15) calcd.: C, 44.99; H, 7.66%.

X-Ray crystal structure analysis of 5

A suitable crystal was obtained by slow recrystallization from benzene. Data were measured on a PW1100/20 Philips Four-Circle Computer-Controlled Diffractometer. Mo-K_α ($\lambda = 0.71069$ Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 20 centered reflections in the range of $10 \leqslant \theta \leqslant 13°$. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 45°. The scan width, $\Delta\omega$, for each reflection was $1.00 + 0.35 \cdot \tan\theta$ with a scan speed of 3.0 deg/min. Background measurements were made for a total of 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by a SHELXS-87 direct-method analysis [14]. Refinement proceeded to convergence by minimization of the function $\Sigma w(|F_o| - |F_c|)^2$. A final difference Fourier synthesis map showed several peaks less than 1.1 e/Å^3 scattered about the unit cell.

The discrepancy indices, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2$ are shown, with other pertinent crystallographic data, in Table 1. Selected positional parameters, bond lengths and angles are given in Tables 2 and 3. Lists of positional parameters for the various hydrogen atoms, anisotropic thermal parameters, and observed and calculated structure factors for **5** are available from the authors.

Hydrogenation of Z-methyl α-acetamidocinnamate (7)

Typically a mixture of 184.5 mg (0.84 mmol) of **7**, 49 mg (0.042 mmol) of **5**, 10 cm^3 of PhH and 5 cm^3 of MeOH was placed in a mini-autoclave, purged with Ar and

Table 3

Selected bond lengths (Å) and bond angles (°) for **5** (esd's in parentheses)

Bond lengths					
Rh(1)–As(1)	2.483(1)	C(1,1′)–C(2′)	1.55(3)	C(13)–C(14)	1.53(2)
Rh(1)–S	2.350(3)	C(1,1′)–C(6′)	1.58(3)	C(13)–C(15)	1.54(2)
Rh(1)–Cl	2.435(4)	C(2)–C(3,3′)	1.55(4)	C(13)–C(16)	1.55(2)
Rh(1)–C(11)	1.80(2)	C(2)–C(7,5′)	1.44(3)	C(17)–C(18)	1.59(2)
Rh(2)–As(2)	2.485(2)	C(3,3′)–C(4)	1.35(5)	C(17)–C(19)	1.52(3)
Rh(2)–S	2.364(4)	C(3,3′)–C(2′)	1.62(3)	C(17)–C(20)	1.56(2)
Rh(2)–Cl	2.430(3)	C(3,3′)–C(4′)	1.36(4)	C(21)–C(22)	1.57(2)
Rh(2)–C(12)	1.77(1)	C(4)–C(5,7′)	1.78(4)	C(21)–C(23)	1.60(2)
As(1)–C(13)	2.07(2)	C(5,7′)–C(6)	1.47(4)	C(21)–C(24)	1.49(2)
As(1)–C(17)	2.04(1)	C(5,7′)–C(10)	1.46(3)	C(25)–C(26)	1.49(3)
As(1)–C(21)	2.06(1)	C(5,7′)–C(2′)	1.47(3)	C(25)–C(27)	1.49(3)
As(2)–C(25)	2.07(1)	C(5,7′)–C(8′)	1.61(3)	C(25)–C(28)	1.59(2)
As(2)–C(29)	2.04(1)	C(5,7′)–C(9′)	1.55(4)	C(29)–C(30)	1.54(2)
As(2)–C(33)	2.07(1)	C(7,5′)–C(8)	1.63(4)	C(29)–C(31)	1.60(2)
S–C(1,1′)	1.87(1)	C(7,5′)–C(9)	1.53(4)	C(29)–C(32)	1.60(2)
O(1)–C(11)	1.12(2)	C(7,5′)–C(4′)	1.65(4)	C(33)–C(34)	1.51(2)
O(2)–C(12)	1.17(2)	C(7,5′)–C(6′)	1.49(3)	C(33)–C(35)	1.51(2)
C(1,1′)–C(2)	1.60(3)	C(7,5′)–C(10′)	1.49(6)	C(33)–C(36)	1.60(2)
C(1,1′)–C(6)	1.49(3)				
Bond angles					
As(1)–Rh(1)–S	178.5(1)	C(2)–C(1,1′)–C(6)	112(2)	C(14)–C(13)–C(16)	107(1)
As(1)–Rh(1)–Cl	99.1(1)	C(2′)–C(1,1′)–C(6′)	111(2)	C(15)–C(13)–C(16)	107(1)
As(1)–Rh(1)–C(11)	92.25(5)	C(1,1′)–C(2)–C(3,3′)	106(2)	As(1)–C(17)–C(18)	113(1)
S–Rh(1)–Cl	81.8(1)	C(1,1′)–C(2)–C(7,5′)	116(2)	As(1)–C(17)–C(19)	109(1)
S–Rh(1)–C(11)	87.0(5)	C(3,3′)–C(2)–C(7,5′)	117(2)	As(1)–C(17)–C(20)	105.1(9)
Cl–Rh(1)–C(11)	116.7(6)	C(2)–C(3,3′)–C(4)	120(2)	C(18)–C(17)–C(19)	112(1)
As(2)–Rh(2)–S	178.5(1)	C(2′)–C(3,3′)–C(4′)	114(2)	C(18)–C(17)–C(20)	107(1)
As(2)–Rh(2)–Cl	99.80(8)	C(3,3′)–C(4)–C(5,7′)	110(3)	C(19)–C(17)–C(20)	111(1)
As(2)–Rh(2)–C(12)	92.7(4)	C(4)–C(5,7′)–C(6)	107(2)	As(1)–C(21)–C(22)	112(1)
S–Rh(2)–Cl	81.6(1)	C(4)–C(5,7′)–C(10)	105(3)	As(1)–C(21)–C(23)	108.2(9)
S–Rh(2)–C(12)	85.9(5)	C(6)–C(5,7′)–C(10)	126(3)	As(1)–C(21)–C(24)	110(1)
Cl–Rh(2)–C(12)	167.2(5)	C(2′)–C(5,7′)–C(8′)	111(2)	C(22)–C(21)–C(23)	109(1)
Rh(1)–As(1)–C(13)	114.0(4)	C(2′)–C(5,7′)–C(9′)	112(2)	C(220–C(21)–C(24)	111(1)
Rh(1)–As(1)–C(17)	106.6(5)	C(8′)–C(5,7′)–C(9′)	107(2)	C(23)–C(21)–C(24)	107(1)
Rh(1)–As(1)–C(21)	114.2(5)	C(1,1′)–C(6)–C(5,7′)	120(2)	As(2)–C(250–C(26)	108(1)
C(13)–As(1)–C(17)	109.1(6)	C(2)–C(7,5′)–C(8)	115(2)	As(2)–C(25)–C(27)	107(1)
C(13)–As(1)–C(21)	106.1(6)	C(2)–C(7,5′)–C(9)	120(3)	As(2)–C(25)–C(28)	113(1)
C(17)–As(1)–C(21)	106.5(6)	C(8)–C(7,5′)–C(9)	98(2)	C(26)–C(25)–C(27)	111(1)
Rh(2)–As(2)–C(25)	113.7(4)	C(4′)–C(7,5′)–C(6′)	107(2)	C(26)–C(25)–C(28)	106(2)
Rh(2)–As(2)–C(29)	106.6(4)	C(4′)–C(7,5′)–C(10′)	103(3)	C(27)–C(25)–C(28)	112(1)
Rh(2)–As(2)–C(33)	114.8(4)	C(6′)–C(7,5′)–C(10′)	108(3)	As(2)–C(29)–C(30)	110(1)
C(25)–As(2)–C(29)	108.5(7)	C(1,1′)–C(2′)–C(3,3′)	105(2)	As(2)–C(29)–C(31)	116(1)
C(25)–As(2)–C(33)	105.8(6)	C(1,1′)–C(2′)–C(5,7′)	117(2)	As(2)–C(29)–C(32)	105(1)
C(29)–As(2)–C(33)	107.1(6)	C(3,3′)–C(2′)–C(5,7′)	113(2)	C(30–C(29)–C(31)	108(1)
Rh(1)–S–Rh(2)	86.6(1)	C(3,3′)–C(4′)–C(7,5′)	115(2)	C(30)–C(29)–C(32)	109(1)
Rh(1)–S–C(1,1′)	104.6(5)	C(1,1′)–C(6′)–C(7,5′)	114(2)	C(32)–C(29)–C(32)	110(1)
Rh(2)–S–C(1,1′)	104.0(4)	Rh(1)–C(11)–O(1)	171(2)	As(2)–C(33)–C(34)	115(1)
Rh(1)–Cl–Rh(2)	83.3(1)	Rh(2)–C(12)–O(2)	173(1)	As(2)–C(33)–C(35)	109.1(9)
S–C(1,1′)–C(2)	110(1)	As(1)–C(13)–C(14)	116.2(9)	As(2)–C(33)–C(36)	106(1)
S–C(1,1′)–C(6)	109(1)	As(1)–C(13)–C(15)	108(1)	C(34)–C(33)–C(35)	111(1)
S–C(1,1′)–C(2′)	114(1)	As(1)–C(13)–C(16)	108(1)	C(34)–C(33)–C(36)	108(1)
S–C(1,1′)–C(6′)	108(1)	C(14)–C(13)–C(15)	111(1)	C(35)–C(33)–C(36)	108(1)

charged with 100 psi H_2. The stirred mixture was kept at $120 \pm 0.5\,°C$ for 20 h. The solvent was evaporated off and the residue chromatographed on alumina, with mixtures of $MeOH-CH_2Cl_2$ as eluent. It was subjected to GC and and optical-activity analysis and its NMR spectrum was recorded.

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