Journal of Organometallic Chemistry, 412 (1991) 273–289
Elsevier Sequoia S.A., Lausanne
JOM 21764

Chiral cyclopentadienyl hydrogenation catalysts: crystal structures of $[Rh(C_5R_4R^\star)Cl_2]_2$ ($R = H$, $R^\star$ = neomenthyl; $R = Me$, $R^\star$ = menthyl)

Peter A. Schofield, Harry Adams, Neil A. Bailey, Edoardo Cesarotti [1] and Colin White *

Department of Chemistry, The University, Sheffield S3 7HF (UK)

(Received January 7th, 1991)

Abstract

The syntheses and crystal structures of the title compounds are reported. The corresponding tetramethylmenthyl derivative was co-crystallized with triphenylphosphineoxide, i.e. as $[Rh\{C_5Me_4(menthyl)\}Cl_2]_2 \cdot 2[(C_6H_5)_3PO]$. Both compounds are active hydrogenation catalysts in the presence of Et_3N but with prochiral alkenes the enantioselectivity is low (i.e. $\leqslant$13% ee).

Introduction

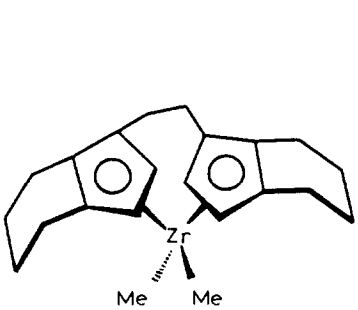
Initially enantioselective catalysis of organic reactions using chiral transition-metal complexes focussed on the use of chiral phosphine ligands. Such studies have been spectacularly successful [1]; however, further studies have shown that chiral phosphines are not successful in all types of reactions or with certain substrates and this has stimulated the development of alternative effective chiral ligands such as tartrates [2] and amines [3]. Given that many types of organic reactions including alkene hydrogenation [4], hydroformylation [5], polymerization [6], and oxidation [7] are known to be catalysed by one or more cyclopentadienyl complexes, an effective chiral cyclopentadienyl ligand would have extensive applications.

The first reports on the use of chiral cyclopentadienyl catalysts were by one of us over ten years ago [8] and concerned the use of the hydrogenation catalysts $[Ti(C_5H_4R^\star)_2Cl_2]$ ($R^\star$ = menthyl or neomenthyl). These were moderately successful in that they hydrogenate 2-phenyl-1-butene in up to 25% ee. Since these initial reports there have been only a limited number of investigations on the use of chiral cyclopentadienyl catalysts [9] but two catalysts have proved to be particularly

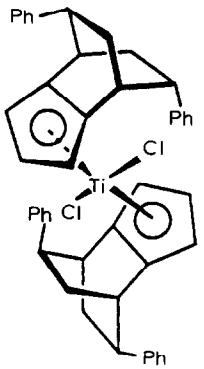
[1] Permanent address: Dipartimento di Chimica Inorganica e Metallorganica, Centro CNR, Via Venezian 21, 20133 Milano, Italy.

0022-328X/91/$03.50

effective. The first is the ethylenebis(4,5,6,7-tetrahydro-1-indenyl) complex (**1**) which, in the presence of $Al(Me)O]_n$, catalyzes the asymmetric hydro-oligomerization of propene [10]. Similarly, the complex **2** has been reported to hydrogenate 2-phenyl-1-butene in up to 96% ee [11]. However, both **1** and **2** suffer from the disadvantages of a multistage synthesis involving a resolution.



(1)



(2)

We report herein the syntheses, crystal structures and catalytic properties of the hydrogenation catalysts $[Rh(C_5R_4R^*)Cl_2]_2$ {where R = H, R^* = neomenthyl (**3**); R = Me, R^* = menthyl (**4**)}. An attractive feature of these chiral cyclopentadienyl ligands is that they may be prepared optically pure in one step from the corresponding cyclopentadiene [12].

Results and discussion

Synthetic studies

Reaction of tetramethylcyclopentadienide with neomenthyl tosylate proceeded in a straight forward manner to give a 20% yield of 1-menthyl-2,3,4,5-tetramethylcyclopentadiene. In contrast, a similar reaction with the more sterically hindered menthyl tosylate failed to yield any of the corresponding 1-neomenthyl-2,3,4,5-tetramethylcyclopentadiene although as reported previously menthyl tosylate does react with the unsubstituted cyclopentadiene to give neomenthylcyclopentadiene [12].

The corresponding rhodium complexes **3** and **4** were prepared by reacting $RhCl_3$ with the appropriate chiral cyclopentadiene. For the complex **3** it was found necessary to add the neomenthylcyclopentadiene very slowly to a refluxing methanol solution of $RhCl_3$ to avoid obtaining the product as an oily, impure polymer. Interestingly, in the case of 1-menthyl-2,3,4,5-tetramethylcyclopentadiene, $[Rh(C_5Me_4H)Cl_2]_2$ (**5**) was isolated as a minor (5%) product of the reaction. No tetramethylcyclopentadiene was detected in the GCMS spectrum of the 1-menthyl-2,3,4,5-tetramethylcyclopentadiene starting material and it is proposed that **5** arises from tetramethylcyclopentadiene generated during the prolonged (120 h) reaction reflux.

The chloride ligands of $[Rh(C_5R_4R^*)Cl_2]_2$ are readily substituted and reaction with NaI in acetone rapidly and quantitatively gave $[Rh(C_5R_4R^*)I_2]_2$ [R = Me, R^* = menthyl (**6**); R = H, R^* = neomenthyl (**7**)].

Description of structure

The molecular structures of **3** and **4** are illustrated in Figures 1 and 2 respectively. Tables 1a and 1b give selected bond lengths and angles with estimated standard deviations and Tables 2a and 2b lists atomic positional parameters with estimated standard deviations.

The structures of the two metal complexes are, in most ways, very similar. In each case the central core is a Rh_2Cl_4 unit in which the two rhodium atoms are bridged by two chlorine atoms (slightly asymmetrically in the ordered structure of **4**) and each carries a terminal chlorine. The three chlorines on each rhodium comprise a facial array and the opposite coordination sites of the formal octahedron are occupied by the substituted cyclopentadienyl ligand. In all cases, whether attached equatorially (menthyl) or axially (neomenthyl) the chiral cyclic substituent is positioned to lie predominantly towards the side of the cyclopentadienyl ring which is remote from the rhodium. The perpendicular distance from the mean cyclopenta-

Table 1a

Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for $[Rh\{C_5H_4(neomenthyl)\}Cl_2]_2$ (**3**)

Rh(1)–Cl(1)	2.422(4)	Rh(1)–Cl(2)	2.440(4)
Rh(1)–Cl(3)	2.360(5)	Rh(1)–C(5)	2.237(22)
Rh(1)–C(1)	2.153(22)	Rh(1)–C(2)	2.060(19)
Rh(1)–C(3)	2.090(19)	Rh(1)–C(4)	2.200(20)
Rh(1)–C(5′)	2.100(22)	Rh(1)–C(1′)	2.148(22)
Rh(1)–C(2′)	2.165(19)	Rh(1)–C(3′)	2.127(19)
Rh(1)–C(4′)	2.087(20)	Rh(2)–Cl(1)	2.428(4)
Rh(2)–Cl(2)	2.436(5)	Rh(2)–Cl(4)	2.354(6)
Rh(2)–C(20)	2.209(21)	Rh(2)–C(16)	2.193(19)
Rh(2)–C(17)	2.120(19)	Rh(2)–C(18)	2.090(19)
Rh(2)–C(19)	2.146(21)	Rh(2)–C(20′)	2.115(22)
Rh(2)–C(16′)	2.113(19)	Rh(2)–C(17′)	2.126(18)
Rh(2)–C(18′)	2.135(19)	Rh(2)–C(19′)	2.128(21)
Rh(3)–Cl(5)	2.439(4)	Rh(3)–Cl(6)	2.447(5)
Rh(3)–Cl(7)	2.365(5)	Rh(3)–C(35)	2.116(22)
Rh(3)–C(31)	2.130(20)	Rh(3)–C(32)	2.131(18)
Rh(3)–C(33)	2.117(19)	Rh(3)–C(34)	2.107(21)
Rh(3)–C(35′)	2.250(22)	Rh(3)–C(31′)	2.170(20)
Rh(3)–C(32′)	2.046(19)	Rh(3)–C(33′)	2.053(19)
Rh(3)–C(34′)	2.181(21)	Rh(4)–Cl(5)	2.425(4)
Rh(4)–Cl(6)	2.431(4)	Rh(4)–Cl(8)	2.366(5)
Rh(4)–C(50)	2.122(22)	Rh(4)–C(46)	2.119(21)
Rh(4)–C(47)	2.136(18)	Rh(4)–C(48)	2.150(19)
Rh(4)–C(49)	2.142(20)	Rh(4)–C(50′)	2.221(20)
Rh(4)–C(46′)	2.147(19)	Rh(4)–C(47′)	2.058(19)
Rh(4)–C(48′)	2.080(19)	Rh(4)–C(49′)	2.181(19)
Cl(1)–Rh(1)–Cl(2)	81.0(1)	Cl(1)–Rh(1)–Cl(3)	91.4(2)
Cl(2)–Rh(1)–Cl(3)	90.2(2)	Cl(1)–Rh(2)–Cl(2)	81.0(1)
Cl(1)–Rh(2)–Cl(4)	91.5(2)	Cl(2)–Rh(2)–Cl(d4)	89.4(3)
Cl(5)–Rh(3)–Cl(6)	80.9(1)	Cl(5)–Rh(3)–Cl(7)	91.1(2)
Cl(6)–Rh(3)–Cl(7)	90.2(2)	Cl(5)–Rh(4)–Cl(6)	81.5(1)
Cl(5)–Rh(4)–Cl(8)	91.0(2)	Cl(6)–Rh(4)–Cl(8)	90.4(2)
Rh(1)–Cl(1)–Rh(2)	99.3(2)	Rh(1)–Cl(2)–Rh(2)	98.6(2)
Rh(3)–Cl(5)–Rh(4)	99.0(2)	Rh(3)–Cl(6)–Rh(4)	98.6(2)

Table 1b

Selected bond lengths (Å) and bond angles (°) with estimated standard deviations for $[Rh\{C_5Me_4(menthyl)\}Cl_2]_2$

Rh(1)–Cl(1)	2.480(4)	Rh(2)–Cl(2)	2.479(4)
Rh(1)–Cl(2)	2.419(4)	Rh(2)–Cl(1)	2.441(4)
Rh(1)–Cl(3)	2.361(4)	Rh(2)–Cl(4)	2.371(4)
Rh(1)–C(1)	2.128(10)	Rh(2)–C(20)	2.138(10)
Rh(1)–C(2)	2.1380)	Rh(2)–C(21)	2.119(10)
Rh(1)–C(3)	2.081(10)	Rh(2)–C(22)	2.115(10)
Rh(1)–C(4)	2.130(9)	Rh(2)–C(23)	2.125(9)
Rh(1)–C(5)	2.148(8)	Rh(2)–C(24)	2.130(9)
C(5)–C(10)	1.469(13)	C(24)–C(29)	1.524(13)
Cl(1)–Rh(1)–Cl(2)	84.05(12)	Cl(2)–Rh(2)–Cl(1)	83.64(12)
Cl(1)–Rh(1)–Cl(3)	89.51(14)	Cl(2)–Rh(2)–Cl(4)	88.43(12)
Cl(2)–Rh(1)–Cl(3)	90.59(14)	Cl(1)–Rh(2)–Cl(4)	90.97(14)
Rh(1)–Cl(1)–Rh(2)	95.81(12)	Rh(1)–Cl(2)–Rh(2)	96.40(12)
C(4)–C(5)–C(10)	132.3(8)	C(23)–C(24)–C(29)	129.2(8)
C(1)–C(5)–C(10)	123.2(8)	C(20)–C(24)–C(29)	123.0(8)
C(5)–C(10)–C(15)	113.9(8)	C(24)–C(29)–C(34)	112.1(8)
C(5)–C(10)–C(11)	113.9(8)	C(24)–C(29)–C(30)	111.6(8)

dienyl plane to the rhodium atom is very consistent in all determinations (1.74 and 1.75 Å for **4**: in the range 1.74–1.78 Å for the eight independent determinations in the disordered structure of **3**). In **4**, the methyl substituents are displaced by small amounts (less than 0.04 Å) from the mean ring plane; in each fragment, three are displaced away from, and one slightly towards the metal. The menthyl group is displaced by rather more (0.12 and 0.14 Å) in a direction away from the rhodium. The conformations of the menthyl fragments in **4** are chair-shaped and their geometries are normal. The geometries of the neomenthyl fragments in **3** were constrained and cannot therefore be further discussed: however, it is interesting to note that for each pair of disordered neomenthylcyclopentadienyl ligands, one neomenthyl is displaced from the cyclopentadienyl ring plane in a direction away from, and one towards the rhodium. This is probably no more than a reflection of the limitations of the refinement. In the structure of **4**, the geometries of the triphenylphosphine oxide molecules are unexceptional.

The crystal packing of di-μ-chlorodichlorobis(η⁵-neomenthyl-cyclopentadienyl)di-rhodium

Although the disorder model described below is undoubtedly the best description of the 'volume-average' structure, a careful analysis of intermolecular contacts reveals that a much more restricted packing arrangement actually occurs, whilst still permitting bulk disorder.

Table 3 lists all intermolecular contacts less than 3.42 Å between carbon atoms of neomenthyl groups. Although this value is somewhat less than the normally accepted carbon van-der-Waals diameter, it is not unusual to find a small number of contacts around this value in crystal structures. In fact, in the present structure, there are a number of unavoidable contacts of about this magnitude (but all greater than 3.37 Å) to cyclopentadienyl carbon atoms, and the contacts listed in Table 3 are

Table 2a

Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for [Rh{C_5H_4(neomenthyl)}Cl_2]$_2$ (3) [a]

Atom	x	y	z	U_{eq}
Rh(1)	0	0	0	30(1) [b]
Rh(2)	404(1)	3468(2)	3724(2)	30(1) [b]
Rh(3)	5005(1)	−1699(2)	557(2)	33(1) [b]
Rh(4)	5426(1)	−5145(2)	4170(2)	33(1) [b]
Cl(1)	204(2)	3261(5)	316(5)	61(1) [b]
Cl(2)	200(2)	187(6)	3426(6)	83(2) [b]
Cl(3)	715(1)	−985(9)	−415(10)	109(3) [b]
Cl(4)	−312(2)	4330(13)	4221(9)	111(3) [b]
Cl(5)	5215(1)	−1839(5)	3970(5)	50(1) [b]
Cl(6)	5215(2)	−5037(7)	767(6)	79(2) [b]
Cl(7)	5719(1)	−976(9)	64(7)	84(2) [b]
Cl(8)	4713(1)	−5929(7)	4626(8)	82(2) [b]
C(1)	−543(7)	−1811(27)	−45(28)	50(1)
C(2)	−271(7)	−2298(27)	−1465(28)	50(1)
C(3)	−286(7)	−772(27)	−2715(28)	50(1)
C(4)	−566(7)	657(27)	−2069(28)	50(1)
C(5)	−725(7)	15(27)	−419(28)	50(1)
C(6)	−1011(3)	1156(17)	880(18)	50(1)
C(7)	−1448(3)	272(17)	1086(18)	50(1)
C(8)	−1727(3)	244(17)	−858(18)	50(1)
C(9)	−1816(3)	2282(17)	−1502(18)	50(1)
C(10)	−1385(3)	3230(17)	−1673(18)	50(1)
C(11)	−1094(3)	3200(17)	242(18)	50(1)
C(12)	−1371(3)	−1747(17)	1801(18)	50(1)
C(13)	−1086(3)	−1703(17)	3731(18)	50(1)
C(14)	−1810(3)	−2605(17)	2029(18)	50(1)
C(15)	−1478(3)	5285(17)	−2254(18)	50(1)
C(16)	952(7)	3188(26)	5962(27)	50(1)
C(17)	687(7)	4806(26)	6261(27)	50(1)
C(18)	691(7)	5991(26)	4692(27)	50(1)
C(19)	958(7)	5105(26)	3423(27)	50(1)
C(20)	1120(7)	3373(26)	4208(27)	50(1)
C(21)	1409(3)	1912(18)	3271(16)	50(1)
C(22)	1848(3)	1390(18)	4413(16)	50(1)
C(23)	2141(3)	3103(18)	4546(16)	50(1)
C(24)	2219(3)	3645(18)	2536(16)	50(1)
C(25)	1783(3)	4150(18)	1371(16)	50(1)
C(26)	1484(3)	2456(18)	1258(16)	50(1)
C(27)	1777(3)	812(18)	6420(16)	50(1)
C(28)	1500(3)	−952(18)	6293(16)	50(1)
C(29)	2220(3)	379(18)	7575(16)	50(1)
C(30)	1861(3)	4673(18)	−643(16)	50(1)
C(31)	4423(7)	−2410(28)	−1181(26)	50(1)
C(32)	4665(7)	−1204(28)	−2179(26)	50(1)
C(33)	4716(7)	517(28)	−1123(26)	50(1)
C(34)	4505(7)	375(28)	527(26)	50(1)
C(35)	4324(7)	−1434(28)	492(26)	50(1)
C(36)	4010(3)	−2028(17)	1873(17)	50(1)
C(37)	3549(3)	−2648(16)	1119(17)	50(1)
C(38)	3273(3)	−913(16)	417(17)	50(1)
C(39)	3243(3)	485(16)	2095(17)	50(1)
C(40)	3699(3)	1101(16)	2913(17)	50(1)

Table 2a (continued)

Atom	x	y	z	U_{eq}
C(41)	3984(3)	−629(16)	3554(17)	50(1)
C(42)	3569(3)	−4093(16)	−528(17)	50(1)
C(43)	3832(3)	−5852(16)	198(17)	50(1)
C(44)	3105(3)	−4653(16)	−1303(17)	50(1)
C(45)	3664(3)	2446(16)	4629(17)	50(1)
C(46)	5999(7)	−6702(25)	3735(29)	50(1)
C(47)	5754(7)	−7761(25)	4865(29)	50(1)
C(48)	5714(7)	−6709(25)	6567(29)	50(1)
C(49)	5934(7)	−5000(25)	6489(29)	50(1)
C(50)	6110(7)	−4995(25)	4739(29)	50(1)
C(51)	6420(3)	−3506(17)	4192(16)	50(1)
C(52)	6878(3)	−4106(17)	3753(16)	50(1)
C(53)	7154(3)	−4705(17)	5597(16)	50(1)
C(54)	7189(3)	−3019(17)	7012(16)	50(1)
C(55)	6734(3)	−2371(17)	7449(16)	50(1)
C(56)	6451(3)	−1819(17)	5606(16)	50(1)
C(57)	6852(3)	−5761(17)	2301(16)	50(1)
C(58)	7313(3)	−6377(17)	1914(16)	50(1)
C(59)	6589(3)	−5131(17)	438(16)	50(1)
C(60)	6772(3)	−658(17)	8830(16)	50(1)
C(1′)	−566(7)	−1503(25)	433(29)	50(1)
C(2′)	−326(7)	−2599(25)	−799(29)	50(1)
C(3′)	−290(7)	−1525(25)	−2422(29)	50(1)
C(4′)	−509(7)	235(25)	−2192(29)	50(1)
C(5′)	−680(7)	249(25)	−427(29)	50(1)
C(6′)	−1014(3)	1744(18)	167(17)	50(1)
C(7′)	−1473(3)	1200(18)	510(17)	50(1)
C(8′)	−1735(3)	675(18)	−1403(17)	50(1)
C(9′)	−1773(3)	2396(18)	−2681(17)	50(1)
C(10′)	−1318(3)	2998(18)	−3015(17)	50(1)
C(11′)	−1048(3)	3469(18)	−1106(17)	50(1)
C(12′)	−1446(3)	−481(18)	1837(17)	50(1)
C(13′)	−1188(3)	67(18)	3751(17)	50(1)
C(14′)	−1907(3)	−1012(18)	2163(17)	50(1)
C(15′)	−1359(3)	4748(18)	−4256(17)	50(1)
C(16′)	968(7)	2623(27)	5498(26)	50(1)
C(17′)	728(7)	3971(27)	6493(26)	50(1)
C(18′)	700(7)	5671(27)	5482(26)	50(1)
C(19′)	922(7)	5372(27)	3863(26)	50(1)
C(20′)	1087(7)	3488(27)	3872(26)	50(1)
C(21′)	1419(3)	2697(17)	2575(17)	50(1)
C(22′)	1876(3)	2001(17)	3387(17)	50(1)
C(23′)	2149(3)	3707(17)	4084(17)	50(1)
C(24′)	2190(3)	4962(17)	2389(17)	50(1)
C(25′)	1736(3)	5650(17)	1521(17)	50(1)
C(26′)	1454(3)	3955(17)	879(17)	50(1)
C(27′)	1847(3)	690(17)	5049(17)	50(1)
C(28′)	1587(3)	−1048(17)	4322(17)	50(1)
C(29′)	2306(3)	61(17)	5891(17)	50(1)
C(30′)	1780(3)	6856(17)	−205(17)	50(1)
C(31′)	4466(7)	−1926(26)	−1675(27)	50(1)
C(32′)	4729(7)	−352(26)	−1813(27)	50(1)
C(33′)	4702(7)	826(26)	−180(27)	50(1)
C(34′)	4423(7)	−19(26)	966(27)	50(1)

Table 2a (continued)

Atom	x	y	z	U_{eq}
C(35′)	4277(7)	−1720(26)	42(27)	50(1)
C(36′)	3990(3)	−3154(18)	876(16)	50(1)
C(37′)	3562(3)	−3588(18)	−370(16)	50(1)
C(38′)	3266(3)	−1808(18)	−465(16)	50(1)
C(39′)	3163(3)	−1253(18)	1547(16)	50(1)
C(40′)	3587(3)	−854(18)	2838(16)	50(1)
C(41′)	3893(3)	−2603(18)	2895(16)	50(1)
C(42′)	3656(3)	−4197(18)	−2381(16)	50(1)
C(43′)	3945(3)	−5999(18)	−2280(16)	50(1)
C(44′)	3225(3)	−4590(18)	−3623(16)	50(1)
C(45′)	3480(3)	−353(18)	4856(16)	50(1)
C(46′)	5958(7)	−7146(26)	4165(27)	50(1)
C(47′)	5699(7)	−7421(26)	5642(27)	50(1)
C(48′)	5727(7)	−5797(26)	6857(27)	50(1)
C(49′)	6002(7)	−4518(26)	6130(27)	50(1)
C(50′)	6145(7)	−5352(26)	4466(27)	50(1)
C(51′)	6443(3)	−4451(16)	3172(17)	50(1)
C(52′)	6873(3)	−5518(16)	2954(17)	50(1)
C(53′)	7161(3)	−5478(16)	4878(17)	50(1)
C(54′)	7262(3)	−3421(16)	5459(17)	50(1)
C(55′)	6837(3)	−2292(16)	5637(17)	50(1)
C(56′)	6537(3)	−2387(16)	3748(17)	50(1)
C(57′)	6785(3)	−7568(16)	2302(17)	50(1)
C(58′)	7218(3)	−8613(16)	2066(17)	50(1)
C(59′)	6493(3)	−7590(16)	390(17)	50(1)
C(60′)	6942(3)	−224(16)	6146(17)	50(1)

[a] Atoms Rh(1), Rh(2), Cl(1)–Cl(4), C(1)–C(30) comprise molecule 1; atoms Rh(3), Rh(4), Cl(5)–Cl(8), C(31)–C(60) comprise molecule 2; the carbon atoms carrying a superscript prime (′) are those of the second disorder component.

[b] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

classified as major (< 3.25 Å) and marginal (between 3.25 and 3.42 Å). Only the former are used to justify the partially ordered model now described; however, the latter group are entirely consistent with the proposal. It is noteworthy that, with only one exception, all short intermolecular contacts are between two atoms of the same neomenthyl fragments (of one or other disorder component) which are related by cell-edge or face-diagonal translation in the A-face. There are no short intramolecular contacts between neomenthyl groups of the same molecule, thus there are four possible combinations of (neomenthyl)cyclopentadienyl components permissible for each of the two crystallographically independent molecules:

- Molecules and neomenthyl fragments will be cited as defined in Table 3, as will the intermolecular contacts.
- Contact 1 requires that two molecules II separated by the *b* cell translation may not both carry C-type neomenthyls.
- Contact 4 requires that two molecules II separated by the *c* cell translation may not both carry D-type neomenthyls.
- Contacts 5 and 6 require that two molecules II separated by the (011) A-face-diagonal may not alternate C and C′ or D and D′-type neomenthyls.

Table 2b

Atomic positional parameters with estimated standard deviations for [Rh{C_5Me_4(menthyl)}Cl_2]$_2$ (4) [a]

Atom	x	y	z
Rh(1)	0.06969(4)	−0.07649(10)	0.20685(3)
Rh(2)	−0.08265(4)	0.07550(10)	0.29900(3)
Cl(1)	−0.07630(15)	−0.1405(3)	0.24540(11)
Cl(2)	0.05921(15)	0.1422(3)	0.25691(10)
Cl(3)	−0.01987(20)	0.0268(4)	0.13360(11)
Cl(4)	0.01538(18)	−0.0309(4)	0.36878(11)
P(1)	0.69756(19)	0.6006(4)	0.05630(11)
P(2)	0.70266(19)	0.8845(3)	0.55404(11)
O(1)	0.6275(5)	0.5249(10)	0.0195(3)
O(2)	0.6327(5)	0.9650(11)	0.5194(3)
C(1)	0.2031(6)	−0.1333(12)	0.2447(4)
C(2)	0.1438(6)	−0.2515(11)	0.2455(4)
C(3)	0.1086(6)	−0.2860(11)	0.1920(4)
C(4)	0.1554(6)	−0.1984(10)	0.1599(3)
C(5)	0.2118(5)	−0.0957(10)	0.1891(3)
C(6)	0.2523(6)	−0.0616(14)	0.2931(3)
C(7)	0.1160(9)	−0.3240(15)	0.2952(5)
C(8)	0.0444(7)	−0.4065(14)	0.1762(5)
C(9)	0.1418(8)	−0.2021(14)	0.0993(5)
C(10)	0.2778(6)	0.0120(12)	0.1731(4)
C(11)	0.3488(7)	−0.0469(14)	0.1375(4)
C(12)	0.4212(7)	0.0678(14)	0.1300(4)
C(13)	0.3749(8)	0.2027(15)	0.1050(5)
C(14)	0.3039(7)	0.2634(14)	0.1391(4)
C(15)	0.2306(8)	0.1489(12)	0.1489(4)
C(16)	0.3900(8)	−0.1913(14)	0.1551(5)
C(17)	0.4590(9)	−0.1830(19)	0.2053(6)
C(18)	0.4364(10)	−0.2660(18)	0.1123(6)
C(19)	0.2541(9)	0.3957(15)	0.1141(6)
C(20)	−0.1568(6)	0.2043(11)	0.3504(4)
C(21)	−0.1259(6)	0.2904(11)	0.3072(4)
C(22)	−0.1667(6)	0.2335(11)	0.2581(4)
C(23)	−0.2229(6)	0.1191(10)	0.2692(4)
C(24)	−0.2178(6)	0.0956(11)	0.3254(4)
C(25)	−0.1321(7)	0.2282(13)	0.4067(4)
C(26)	−0.0630(8)	0.4123(14)	0.3135(5)
C(27)	−0.1504(7)	0.2920(12)	0.2054(5)
C(28)	−0.2800(7)	0.0339(14)	0.2272(4)
C(29)	−0.2739(6)	−0.0070(11)	0.3565(4)
C(30)	−0.3796(6)	0.0080(12)	0.3405(4)
C(31)	−0.4302(7)	−0.0975(13)	0.3759(4)
C(32)	−0.3981(7)	−0.2466(14)	0.3706(5)
C(33)	−0.2913(7)	−0.2594(12)	0.3882(4)
C(34)	−0.2404(6)	−0.1608(12)	0.3530(4)
C(35)	−0.4140(7)	0.1594(13)	0.3388(4)
C(36)	−0.5141(9)	0.1704(19)	0.3125(7)
C(37)	−0.4126(9)	0.2248(15)	0.3945(6)
C(38)	−0.2592(9)	−0.4106(16)	0.3858(5)
C(39)	0.8170(7)	0.5511(11)	0.0483(4)
C(40)	0.8666(8)	0.6200(15)	0.0130(5)
C(41)	0.9535(9)	0.5648(17)	0.0031(5)
C(42)	0.9913(8)	0.4516(15)	0.0311(5)

Table 2b (continued)

Atom	x	y	z
C(43)	0.9400(9)	0.3838(15)	0.0651(5)
C(44)	0.8546(8)	0.4312(15)	0.0752(4)
C(45)	0.6897(7)	0.7877(13)	0.0491(4)
C(46)	0.7605(9)	0.8786(14)	0.0678(5)
C(47)	0.7509(9)	1.0272(16)	0.0632(5)
C(48)	0.6691)9)	1.0869(17)	0.0349(5)
C(49)	0.5997(8)	0.9913(15)	0.0180(5)
C(50)	0.6095(7)	0.8452(14)	0.0242(4)
C(51)	0.6791(6)	0.5607(12)	0.1244(4)
C(52)	0.7234(8)	0.6318(14)	0.1662(5)
C(53)	0.7038(9)	0.5992(16)	0.2181(5)
C(54)	0.6391(10)	0.4941(16)	0.2246(5)
C(55)	0.5952(8)	0.4185(16)	0.1836(5)
C(56)	0.6144(8)	0.4503(15)	0.1315(5)
C(57)	0.8197(7)	0.9378(14)	0.5463(4)
C(58)	0.8576(8)	1.0559(13)	0.5722(4)
C(59)	0.9458(9)	1.1082(15)	0.5651(5)
C(60)	0.9940(7)	1.0396(13)	0.5273(5)
C(61)	0.9592(7)	0.9206(15)	0.5009(4)
C(62)	0.8714(7)	0.8783(13)	0.5096(4)
C(63)	0.6908(7)	0.9190(15)	0.6233(4)
C(64)	0.7421(7)	0.8466(12)	0.6645(4)
C(65)	0.7298(7)	0.8826(12)	0.7161(4)
C(66)	0.6686(8)	0.9862(14)	0.7272(5)
C(67)	0.6186(7)	1.0558(15)	0.6869(5)
C(68)	0.6283(7)	1.0245(12)	0.6348(4)
C(69)	0.6960(7)	0.6930(12)	0.5448(4)
C(70)	0.6107(7)	0.6394(15)	0.5204(4)
C(71)	0.6005(8)	0.4924(15)	0.5135(5)
C(72)	0.6711(9)	0.4035(15)	0.5317(5)
C(73)	0.7539(8)	0.4558(13)	0.5532(4)
C(74)	0.7662(7)	0.5990(12)	0.5625(4)

[a] Atoms sets [O(1), P(1), C(39)–C(56)] and [O(2), P(2), C(57)–C(74)] comprise the two triphenylphosphine-oxide molecules which are incorporated in the lattice.

Since sterically permissible layers of all C′ or all D′ could never be matched by layers of all C or all D neomenthyls, the determined 50 : 50% disorder can only be achieved if, for each layer of molecules II, disorder components for both neomenthyls C and D alternate parallel to both *b* and *c* cell edges (i.e. C ··· C′ ··· C ··· and D ··· D′ ··· D ···), giving identical neomenthyl disorder components parallel to both A-face-diagonals. This is also consistent with 'marginal' contacts 10 and 11.

Contacts 2, 3, 7 and 8 similarly require that, for each layer of molecules I, disorder components for both neomenthyls A and B alternate parallel to both *b* and *c* cell edges (i.e. A ··· A′ ··· A ··· and B ··· B′ ··· B ···), and again the same neomenthyl disorder components occur parallel to both A-face-diagonals. This is also consistent with 'marginal' contacts 12 and 13.

If this systematic packing was repeated by *a*-cell translation in every layer, it would give rise to a super-lattice, for which there was no evidence.

Each layer of each of molecules I and II must comprise two (because of the need for alternation) of the four different composite molecules derived from the four

Table 3

Intermolecular carbon-carbon contacts less than 3.42 Å involving neomenthyl group carbon atoms in di-μ-chlorodichlorobis(neomenthylcyclopentadienyl)dirhodium (3) [a]

Contacts less than 3.25 Å		Contact number	Symmetry operation	Contacts between 3.25 and 3.42 Å	
C43 · · · C40	3.02	1	a	C43 · · · C34	3.35
C28′ · · · C25′	3.09	2	a	C28′ · · · C19′	3.32
C13′ · · · C10′	3.11	3	b	C13′ · · · C4′	3.36
C59 · · · C55	3.02	4	c	C59 · · · C49	3.26
C43′ · · · C45	2.50	5	d		
C44′ · · · C45	2.82		d		
C42′ · · · C45	3.15		d		
C59′ · · · C60	2.59	6	d	C57′ · · · C60	3.25
C58′ · · · C60	2.91		d		
C30′ · · · C28	3.00	7	e	C30′ · · · C29	3.41
C15′ · · · C13	3.13	8	e	C15′ · · · C14	3.42
C58′ · · · C14′	3.16	9	f		
		10	g	C60′ · · · C57′	3.35
			g	C60′ · · · C58′	3.37
		11	b	C45′ · · · C44′	3.38
			b	C45′ · · · C42′	3.41
		12	c	C30 · · · C27	3.40
		13	b	C13 · · · C3	3.39

[a] Symmetry operations are as follows: a: $x, y-1, z$; b: $x, y, z+1$; c: $x, y, z-1$; d: $x, y-1, z-1$; e: $x, y+1, z-1$; f: $x+1, y-1, z$; g: $x, y+1, z$. Molecule I comprises Rh1, Rh2, Cl1–Cl4, C1–C30, C1′–C30′. Molecule II comprises Rh3, Rh4, Cl5–Cl8, C31–C60, C31′–C60′. Neomenthyls A and A′ comprise sets C6–C15 and C6′–C15′ respectively. Neomenthyls B and B′ comprise sets C21–C30 and C21′–C30′ respectively. Neomenthyls C and C′ comprise sets C36–C45 and C36′–C45′ respectively. Neomenthyls D and D′ comprise sets C51–C60 and C51′–C60′ respectively.

permissible combinations of disorder components. This results in four different possible combinations of layers of molecules I and II, each of which can be stacked in two ways, with or without a relative cell translation parallel to b (and therefore to c too), giving eight possible stacking methods.

The four permissible layers parallel to the A-face may be described as follows:

L_1 I(AB)/I(A′B′) L_3 II(CD)/II(C′D′)

L_2 I(AB′)/I(A′B) L_4 II(CD′)/II(C′D)

where, for example, I(AB′) means molecule I carrying neomenthylcyclopentadienyl groups A and B′. The eight possible stacking methods are thus:

$L_1 + L_3$ $L_1 + L_3$(disp)

$L_1 + L_4$(disp) $L_1 + L_4$

$L_2 + L_3$ $L_2 + L_3$(disp)

$L_2 + L_4$(disp) $L_2 + L_4$

where (disp) denotes a relative b or c cell edge displacement.

It thus becomes necessary to investigate the packing between layers. There are no restrictions in the packing of layers of molecules, I and II as specified in Table 3, that is between molecules based on rhodium atoms at $x \approx 0$ and $x \approx 0.5$. However,

between layers of molecules II and I based on rhodium atoms at $x = 0.5$ and $x \approx 1.0$, contact 9, the only one in Table 3 between atoms of different neomenthyl groups, restricts this stacking to the four 'overlays' in the left-hand column above.

Notwithstanding these significant restrictions on intermolecular packing, there is still sufficient flexibility to permit bulk disorder of the crystal lattice as observed.

Catalytic studies

Both the complexes $[Rh(C_5R_4R^\star)Cl_2]_2$ (R = H, $R^\star$ = neomenthyl; R = Me, $R^\star$ = menthyl) are active hydrogenation catalysts in the presence of a suitable base (e.g. Et_3N) and readily reduce simple alkenes under ambient conditions. Thus, 2-phenyl-1-butene was readily reduced by either catalyst but in each case the 2-phenyl butane was found to be only marginally optically active (ee $\leqslant 1\%$). Functionalized alkenes were also hydrogenated but require slightly more forcing conditions i.e. 5 atm. hydrogen and 50 °C. Once again, however, the optical yields were disppointing, i.e. Z-PhCH=C(NHCOMe)CO_2Me was reduced in $< 1\%$ ee using $[Rh(nmcp)Cl_2]_2$ and CH_2=C(NHCOMe)CO_2Me was hydrogenated in $\leqslant 5\%$ *R* ee using $[Rh\{C_5Me_4$-(menthyl)$\}Cl_2]_2$. The greatest optical induction (13% *S* ee) was observed when CH_2=C(CO_2H)CH_2CO_2H was hydrogenated using $[Rh\{C_5Me_4(menthyl)\}Cl_2]_2$. Interestingly, this reduction occurred most rapidly and most stereoselectively in the absence of Et_3N, a cocatalyst usually essential for active catalysis by these systems.

Preliminary experiments have also shown that in the presence of two equivalents of NaO^iPr, $[Rh\{C_5Me_4(menthyl)\}Cl_2]_2$ (**4**) catalysed hydrogen transfer from propan-2-ol; thus amino-acetophenone derivatives are reduced to the corresponding β-amino-α-phenylethanol products at 55 °C but again the optical induction appears to be low (i.e. $\leqslant 7\%$ ee).

In conclusion $[Rh(nmcp)Cl_2)_2$ essentially hydrogenates prochiral alkenes non-enantioselectively whilst the optical induction observed for $[Rh\{C_5Me_4(menthyl)\}Cl_2]_2$ can at best be described as modest. The greater stereoselectivity of the latter is not unexpected given that the adjacent methyl substituents should restrict the mobility of the chiral substituent. Presumably a similar argument accounts for the fact that whereas negligible enantioselectivity was observed with these rhodium catalysts in the reduction of 2-phenyl-1-butene, the corresponding reduction with $[Ti(C_5H_4R^\star)_2Cl_2]$ ($R^\star$ = neomenthyl or neomenthyl) gives $\leqslant 25\%$ ee. Thus, the greater coordination number of the titanium systems together with the fact that each cyclopentadienyl ring bears a bulky substituent will clearly restrict the mobility of the chiral substituents. Further, having two chiral cyclopentadienyl ligands, as in the titanium complexes, obviously makes it more difficult for a substrate to avoid an interaction with the chiral substituent.

Experimental

General procedures

Proton and ^{13}C spectra were recorded on a Bruker AM-250 FT-NMR spectrometer; the numbering system used for the assignments is that shown in Figs. 1 and 2. Tetrahydrofuran was dried over sodium benzophenone; all solvents were freshly distilled before use. Reactions were carried out under an atmosphere of nitrogen although the compounds were subsequently found not to be air-sensitive.

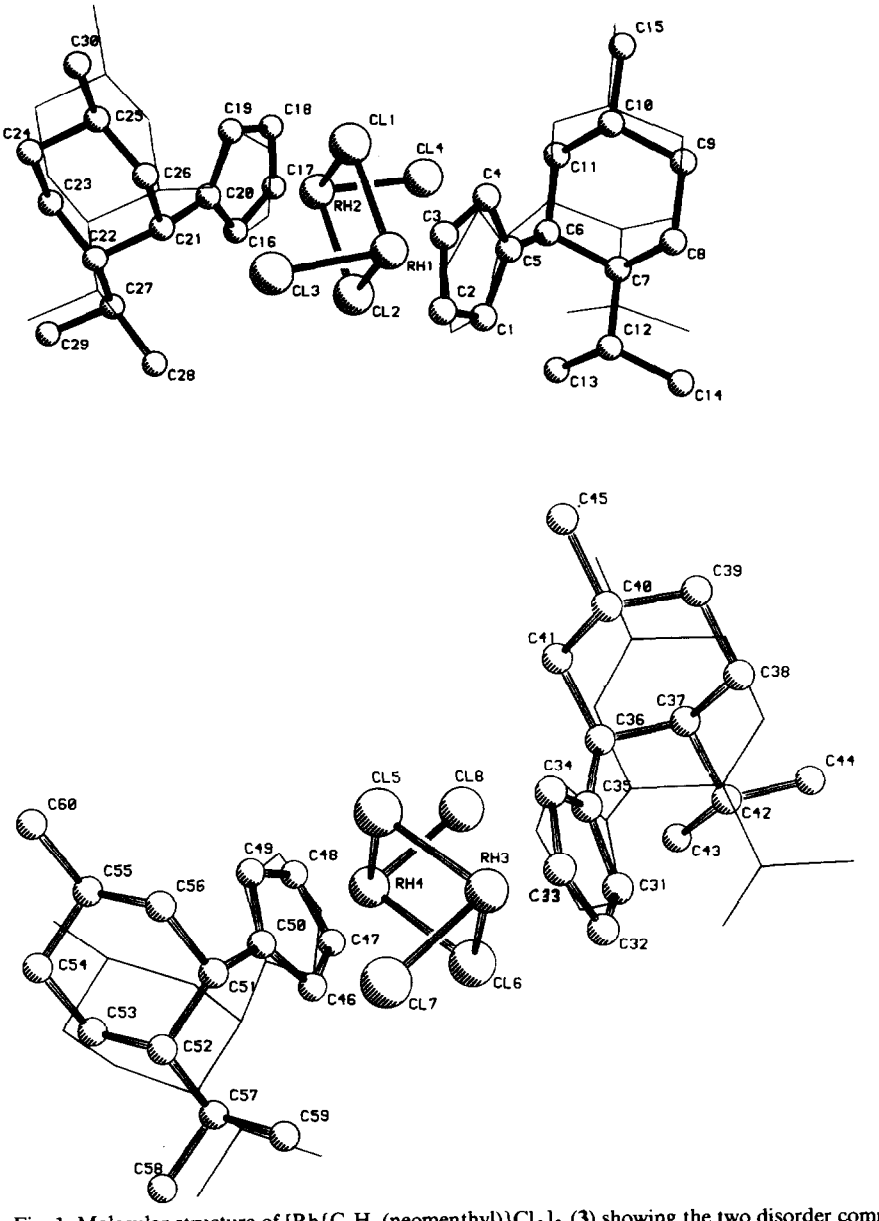


Fig. 1. Molecular structure of $[Rh\{C_5H_4(neomenthyl)\}Cl_2]_2$ (3) showing the two disorder components of each of the two crystallographically independent molecules and their relationship to each other; call components have equal occupancy, but in each molecule, one component is shown in outline only.

Di-μ-chlorodichlorobis(η⁵-neomenthylcyclopentadienyl)dirhodium, $[Rh\{\eta^5\text{-}C_5H_4(neomenthyl)\}Cl_2]_2$ (3)

A solution of $RhCl_3 \cdot 3\ H_2O$ (3.0 g, 11.4 mmol) in methanol (90 cm^3) was refluxed gently under nitrogen. Neomenthylcyclopentadiene [12] (3.63 g, 17.8 mmol) was dissolved in freshly distilled THF (20 cm^3) and the solution added to the

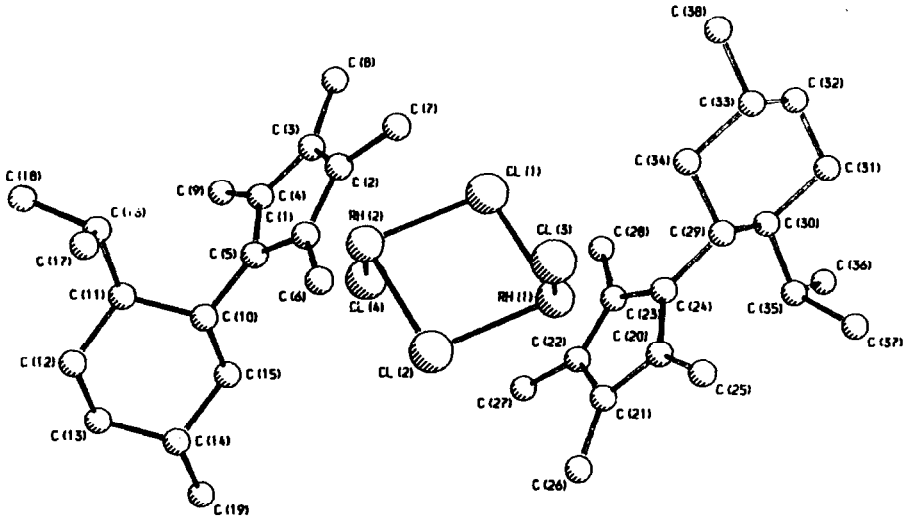


Fig. 2. Molecular structure of $[Rh\{C_5Me_4(menthyl)\}Cl_2]_2$ (4).

reaction flask over a 40 h period using a low-geared syringe pump. The mixture was refluxed for a further 24 h and then cooled to 5 °C. The red crystalline product was filtered off, washed with methanol and dried *in vacuo* to give 1.93 g; concentration and cooling of the filtrate gave a further 370 mg of similar material (total yield 54%). Found: C, 47.6; H, 6.0; Cl, 18.7; R.M.M. 752 ($CHCl_3$, osmometry). $C_{30}H_{46}Cl_4Rh_2$ calc.: C, 47.8; H, 6.1; Cl, 18.8%; R.M.M. 754.2. δ_H (250 MHz, $CDCl_3$, $SiMe_4$): 5.78 (m, 1H), 5.60 (m, 3H) (C_5H_4); 2.99 (m, H(6)); 2.52 (m, 1H); 1.85–1.05 (m, 8H); 0.95 (d, $J = 6$ Hz, Me); 0.92 (d, $J = 6$ Hz, Me); 0.77 (d, $J = 6$ Hz, Me). δ_C (63 MHz, $CDCl_3$, $SiMe_4$): 104.9 (d, J(Rh–C) = 8.5 Hz, C(5)); 86.8 (d, J(Rh–C) = 8 Hz), 85.6 (d, J(Rh–C) = 8 Hz), 83.6 (d, J(Rh–C) = 8 Hz), C(1–4); 47.8 (s, C(7)), 39.7 (s, C(11)), 35.0 (s, C(9)), 34.6 (s, C(6)), 29.6 (s, C(10)), 28.2 (s, C(12)), 24.9 (s, C(8)); 22.4 (s), 21.9 (s), 20.7 (s), 3Me.

Menthyltetramethylcyclopentadiene

A solution of butyl lithium (2.5 *M* in hexanes, 25.6 cm^3, 51.2 mmol) was added dropwise to a vigorously stirred solution of tetramethylcyclopentadiene [13] (6.3 g, 51.6 mmol) in THF (100 cm^3) under argon. The reaction mixture became warm and a thick white precipitate of lithium tetramethylcyclopentadienide formed; the mixture was stirred for 15 min and cooled to room temperature. Neomenthyl tosylate (16 g, 51.5 mmol) was added rapidly to the stirred mixture which was then refluxed for 2 h under argon. After cooling, solvent was removed *in vacuo* and the residue extracted with petroleum ether (b.p. 40–60 °C, 3 × 50 cm^3) and the extracts passed down an alumina column (10 cm) to remove most of the neomenthyl tosylate; the column was eluted with additional petroleum ether (50 cm^3). Any remaining neomenthyl tosylate was precipitated out by concentrating the solution and washings from the column to ca 25 cm^3 and storing at 5 °C for two days. After filtering off the neomenthyl tosylate, the yellow liquid was distilled under reduced pressure. Menthyltetramethylcyclopentadiene was collected at 68–70 °C and 0.5 mmHg (2.6 g, 20%). GC-MS showed three isomers of mass 120 and the ^1H NMR spectrum

consisted of two equally intense groups of signals centred at δ 1.75 and 0.85. IR (neat) 3000–2810vs, 1645w, 1620w, 1450s, 1381s, 1368s, 1344w. $[\alpha]_D^{20} = -36.5$ ($c = 1$, $CHCl_3$).

Di-μ-chlorodichlorobis(η^5-menthyltetramethylcyclopentadienyl)dirhodium and *di-μ-chlorodichlorobis(η^5-tetramethylcyclopentadienyl)dirhodium, $[Rh\{\eta^5\text{-}C_5Me_4R\}Cl_2]_2$ (R = menthyl (4) or H (5))*

Menthyltetramethylcyclopentadiene (1.00 g, 3.85 mmol) and $RhCl_3 \cdot 3\ H_2O$ were refluxed in a mixture of THF (15 cm^3) and methanol (25 cm^3) under nitrogen for 120 h. The deep red solution was then evaporated to dryness using a rotary evaporator, and the residue extracted into ether (3×20 cm^3). Slow evaporation of the ether solution gave red crystals of $[Rh\{\eta^5\text{-}C_5Me_4(menthyl)\}Cl_2]_2$ (**4**) (450 mg, 34%). Found: C, 52.8; H, 7.2; Cl, 16.0. $C_{38}H_{62}Cl_4Rh_2$ calc.: C, 52.7; H, 7.2; Cl, 16.4%. δ_H (250 MHz, $CDCl_3$, $SiMe_4$): 1.77 s, 1.69 s, 1.62 s, 1.57 s (Me_4); 2.55 (1H, m, H(10)); 2.07–1.00 (9H, m); 0.94 (3H, d, J 6 Hz, Me); 0.80 (3H, d, J 8 Hz, Me); 0.62 (3H, d, J 8 Hz, Me). δ_C (63 MHz, $CDCl_3$, $SiMe_4$): 99.4 (2C, d, J(Rh–C) 9 Hz), 93.6 (d, J(Rh–C) 9 Hz), 93.2 (d, J(Rh–C) 10 Hz), 92.0 (d, J(Rh–C) 9 Hz), C_5Me_4; 44.7 (C11), 41.3 (C15), 37.0 (C10), 34.9 (C13), 33.3 (C14), 28.4 (C16), 25.0 (C12); 22.0, 21.8, 16.1, 3Me; 12.0, 10.7, 9.6, 9.2 ($C_5\mathit{Me}_4$).

The residue remaining after the ether extraction was dissolved in a minimum of dichloromethane and, on slow addition of diethyl ether an orange solid precipitated out. This was filtered off and dried to give $[Rh\{\eta^5\text{-}C_5Me_4H\}Cl_2]_2$ (**5**) (50 mg, 5%). Found: C, 37.0; H, 4.9; Cl, 23.7. $C_{18}H_{26}Cl_4Rh_2$ calc.: C, 36.6; H, 4.4; Cl, 24.0%. δ_H (250 MHz, $CDCl_3$, $SiMe_4$): 5.01 (1H), 1.68 (6H), 1.62 (6H).

Di-μ-iododiiodobis(η^5-menthyltetramethylcyclopentadienyl)dirhodium, $[Rh\{\eta^5\text{-}C_5Me_4menthyl\}I_2]_2$ (6)

Sodium iodide (500 mg, 3.3 mmol) was stirred with $[Rh\{\eta^5\text{-}C_5Me_4menthyl\}Cl_2]_2$ (100 mg, 0.12 mmol) in acetone (25 cm^3) for 1 h. Solvent was removed on the rotary evaporator and the product extracted into dichloromethane. An equal volume of ether was added and slow evaporation of this mixture afforded dark purple microcrystals of $[Rh\{\eta^5\text{-}C_5Me_4menthyl\}I_2]_2$ (**6**) (120 mg, 85%). Found: C, 37.9; H, 5.1; I, 40.0. $C_{38}H_{62}I_4Rh_2$ calc.: C, 37.0; H, 5.1; I, 41.2%. δ_H (250 MHz, $CDCl_3$, $SiMe_4$): 2.28 s, 2.19 s, 2.04 s, 1.95 s (Me_4), 2.40 (1H, m, H(10)), 2.14–0.99 (9H, m), 0.94 (3H, d, J 6 Hz), 0.82 (3H, d, J 7 Hz, Me), 0.66 (3H, d, J 7 Hz, Me). δ_C (63 MHz, $CDCl_3$, $SiMe_4$): 101.1 (d, J(Rh–C) 8 Hz), 99.1 (d, J(Rh–C) 9 Hz), 98.5 (d, J(Rh–C) 9 Hz), 96.3 (d, J(Rh–C) 9 Hz), 93.7 (d, J(Rh–C) 9 Hz), C_5Me_4); 45.5 (C11), 44.5 (C15), 37.1 (C10), 34.9 (C13), 33.5 (C14), 28.2 (C16). 25.2 (C12); 22.0, 21.9, 16.1, 3Me; 14.6, 14.1, 11.1, 10.5 ($C_5\mathit{Me}_4$).

Di-μ-iododiiodobis(η^5-neomenthylcyclopentadienyl)dirhodium, $[Rh\{\eta^5\text{-}C_5H_4neomenthyl\}I_2]_2$ (7)

This dark purple solid was prepared in 89% yield by a similar procedure. δ_H (250 MHz, $CDCl_3$, $SiMe_4$): 5.38 m, 5.61 m, 5.57 m, 5.40 m ($C_5\mathit{H}_4$), 3.07 (m, H(10)), 2.43 (m, 1H), 1.80–1.00 (m, 8H), 0.94 (d, $J = 6$ Hz, Me), 0.90 (d, $J = 6$ Hz, Me), 0.75 (d, $J = 6$ Hz, Me). δ_C (63 MHz, $CDCl_3$, $SiMe_4$): 108.4 (d, J(Rh–C), 7.5 Hz), 88.3 (d, J(Rh–C) 7 Hz), 87.7 (d, J(Rh–C) 6 Hz), 83.2 (d, J(Rh–C) 7 Hz), 80.2 (d, J(Rh–C)

7.5 Hz) C_5H_4; 48.1 (C7), 41.3 (C11), 35.3 (C9), 35.0 (C6), 29.5 (C10), 28.4 (C12), 24.7 (C8); 22.3, 22.0, 20.6, 3Me.

Catalytic studies

Hydrogenation of itaconic acid at 5 atm H_2 pressure and 50 °C was carried out in a Fischer–Porter apparatus using a substrate concentration of 125 mmolar in propan-2-ol and a substrate : catalyst ratio of 50 : 1. Reduction was complete within 24 h as indicated by ^{1}H NMR. Solvent was then removed *in vacuo* and the product was separated from the chiral catalyst by extracting into water; removal of the water *in vacuo* gave pure methylsuccinic acid. The optical yield was determined by polarimetry, comparing the observed rotation with the literature value [14]. Other substrates were hydrogenated using a similar procedure but in the presence of Et_3N (62.5 mmol).

Crystal data

$[Rh\{C_5H_4(neomenthyl)\}Cl_2]_2$; $C_{30}H_{46}Cl_4Rh_2$; $M = 754.32$; crystallizes from dichloromethane/methanol as red, platey needles; crystal dimensions $0.09 \times 0.15 \times 0.15$ mm. Triclinic, $a = 31.095(19)$, $b = 7.115(4)$, $c = 7.109(4)$ Å, $\alpha = 91.734(2)$, $\beta = 96.993(4)$, $\gamma = 88.143(2)°$, $U = 1560(2)$ Å^3; $Z = 2$, $D_c = 1.606$ g cm^{-3}; space group $P\bar{1}$ (C_1, No. 1); Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 14.06 cm^{-1}, $F(000) = 768$.

Crystals of **4** were obtained by serendipity from an unsuccessful attempt to prepare $[Rh\{C_5Me_4(menthyl)\}Cl_2(PPh_3)]$; the reaction mixture of triphenylphosphine and **4** in THF was put aside and as the solvent evaporated red needles formed; one of these ($0.09 \times 0.65 \times 0.10$ mm) was selected. The X-ray analysis revealed that the lattice contains triphenylphosphine oxide in addition to **4**; however, there are no significant intermolecular contacts between the two sets of molecules to influence the bond lengths or bond angles of **4**.

$[Rh\{C_5Me_4(menthyl)\}Cl_2]_2 \cdot 2[(C_6H_5)_3PO]$; $C_{74}H_{92}Cl_4P_2O_2Rh_2$; $M = 1423.11$. Monoclinic, $a = 14.405(13)$, $b = 9.344(5)$, $c = 25.387(26)$ Å, $\beta = 95.75(8)°$, $U = 3400$ Å^3; $Z = 2$, $D_c = 1.390$ g cm^{-3}; space group $P2_1$ (C_2^2, No. 4); Mo-K_α radiation ($\lambda = 0.71069$ Å), μ(Mo-K_α) = 7.26 cm^{-1}, $F(000) = 1480$.

Structure analysis and refinement

Three-dimensional X-ray diffraction data for **3** were collected in the range $6.5 < 2\theta < 50°$ on a Stoe Stadi-2 diffractometer by the omega-scan method. The 4794 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects. The structure was solved by standard Patterson and Fourier techniques for the Rh_2Cl_4 core in space group $P\bar{1}$ and a structure in $P\bar{1}$ was gradually revealed, but the value of R would not fall to much less than 0.20. It slowly became clear that each of the two chemically equivalent but crystallographically independent molecules in the unit cell was disordered by a rotation of about 36 ° of each cyclopentadienyl ligand about the metal-to-centroid axis, resulting in an approximate relative translation of the two components of each neomenthyl group of about 1 Å. When this disorder was taken into account, the value of R dramatically reduced and the structure was refined with constraints on each neomenthyl group (in bond lengths (1.54 Å), bond angles (109.5 °) and torsion angles (60 and 180 °)) and on each cyclopentadienyl group (D_{5h} symmetry with C–C 1.42 Å), and

on the bond lengths and angles which link these two constrained ring fragments. The structure was refined by block-cascade least-squares methods. Hydrogen atoms were not located or positioned, since the model already almost exceeded the capacity of the computer program. Refinement converged at R 0.0494 with allowance for anisotropic thermal motion of rhodium and chlorine atoms only: all carbon atoms were given a common isotropic thermal parameter which was not refined; allowance was made for the anomalous scattering of rhodium and chlorine. The different intermolecular environments of the two molecules showed them not to be related by any undetected symmetry.

Three-dimensional X-ray diffraction data for **4** were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet $R3m$ diffractometer by the ω-scan method. The 4232 independent reflections (of 7123 measured) for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were placed in calculated positions (C–H 0.95 Å); their contributions were included in structure factor calculations ($B = 7.0$ Å^2) but no refinement of positional parameters was permitted. Refinement converged at $R = 0.0390$ with allowance for anisotropic thermal motion of all non-hydrogen atoms and for the anomalous scattering of rhodium, phosphorus and chlorine. The structure was fully ordered.

The absolute configurations of the two crystal structures were defined by the known chirality at the menthyl and neomenthyl groups, and was confirmed by the marginally lower values of R for the reported structures. Scattering factors were taken from reference 15 and unit weights were used throughout the refinement; computer programs were SHELXTL as implemented on the Nova 3 computer, and those of the Sheffield X-ray system.

A full listing of bond lengths and bond angles with estimated standard deviations, tables of observed structure amplitudes, calculated structure factors, anisotropic thermal vibrational parameters with estimated standard deviations and predicted hydrogen atom positional parameters are available from the authors.

Acknowledgements

We wish to record our sincere thanks to the S.E.R.C. for a studentship (to P.A.S.), to N.A.T.O. for financial assistance, to Johnson Matthey for the generous loan of ruthenium trichloride (to C.W.), and to the S.E.R.C. and the Royal Society for funds for the X-ray and computing equipment.

References

1 (a) H. Brunner, Synthesis, (1988) 645; (b) J.M. Brown, Platinum Metals Rev., 31 (1987) 137; (c) J. Halpern, in J.D. Morrison (Ed.), Asymmetric Synthesis, Vol. 5, Academic Press, Orlando, FL, 1985, p. 41 and references therein.

2 (a) Y. Gao, R.M. Hanson, J.M. Klunder, S.Y. Ko, H. Masamune and K.B. Sharpless, J. Am. Chem. Soc., 109 (1987) 5765; (b) H.B. Kagan, Phosphorus Sulfur, 27 (1986) 127.

3 (a) H. Brunner and H. Fisch, J. Organomet. Chem., 335 (1987) 15; (b) G. Zassinovich and G. Mestroni, J. Mol. Catal., 42 (1987) 81.

4 M.J. Russell, C. White and P.M. Maitlis, J. Chem. Soc., Chem. Commun., (1977) 427.

5 E. Cesarotti, A. Fusi, R. Ugo and G.M. Zanderighi, J. Mol. Catal., 4 (1978) 205.

6 (a) D.G. Ballard, A. Courtis, J. Holton, J. McMeeking and R.J. Pearce, J. Chem. Soc., Chem. Commun., (1974) 2737; (b) S.J. McLain, J. Sancho and R. Schrock, J. Am. Chem. Soc., 101 (1979) 5451; J.A. Ewen, J. Am. Chem. Soc., 106 (1984) 6355.
7 J.E. Lyons, Tetrahedron Lett., (1974) 2737.
8 (a) E. Cesarotti, R. Ugo and H.B. Kagan, Angew. Chem., Int. Ed. Engl., 18 (1979) 10; (b) E. Cesarotti, R. Ugo and V. Vitiello, J. Mol. Catal., 12 (1981) 63.
9 (a) N.A. Bailey, V.S. Jassal, R. Vefghi and C. White, J. Chem. Soc., Dalton Trans., (1987) 2815; (b) R.L. Halterman and K.P.C. Vollhardt, Tetrahedron Lett., (1986) 1461; (c) S. Couturier, G. Tainturier and B. Gautheron, J. Organomet. Chem., 195 (1980) 291; (d) G. Erker and A.H. van der Zeijden, Angew. Chem., Int. Ed. Engl., 29 (1990) 512.
10 P. Pino, P. Cioni and J.J. Wei, J. Am. Chem. Soc., 109 (1987) 6189.
11 R.L. Halterman, K.P.C. Vollhardt, M.E. Welker, D. Blaser and R. Boese, J. Am. Chem. Soc., 109 (1987) 8105.
12 E. Cesarotti, H.B. Kagan, R. Goddard and C. Kruger, J. Organomet. Chem., 162 (1978) 297.
13 G. Schmitt and S. Ozman, Chem. Z., 100 (1976) 143.
14 R. Rossi, Gazz. Chem. Ital., 98 (1968) 1391.
15 International Tables for X-ray Crystallography, Vol. 4, Kynoch Press, Birmingham, 1974.