Chiral Cyclopentadienyl Catalysts. Part 3.[1] Synthesis and Reactions of (*S*)-1-(1-dimethylaminoethyl)-2-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)benzene; Crystal Structure of $[Rh\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}Cl_2]$†

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The synthesis of (*S*)-1-(1-dimethylaminoethyl)-2-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)benzene (HL) and its reactions with $[Ru_3(CO)_{12}]$ and $IrCl_3\cdot3H_2O$ have been performed. Compound HL also reacts with $RhCl_3\cdot3H_2O$ to give a mixture of $[Rh\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}Cl_2]$ **1** and $[\{Rh[\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\cdot HCl]Cl_2\}_2]$ **2**. A single-crystal X-ray diffraction study of **1** was carried out: the compound crystallises in the orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19) with $a = 8.691(6)$, $b = 15.803(15)$, $c = 13.840(10)$ Å and $Z = 4$; $R = 0.0657$. Interconversion between **1** and **2** can be effected readily using HCl or base respectively. Other aspects of the chemistry of **1** have been investigated including its conversion into $[Rh\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}(C_2H_4)_2]$ in which rotation of the co-ordinated ethene molecules has been estimated by ^1H NMR spectroscopy to have a free energy of activation ($\Delta G^{\ddagger}$) = 67.2 kJ mol^{-1}. In contrast to **1**, the methylated derivative $[Rh\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_3^+BF_4^-\}Cl_2]$ functions as a hydrogenation catalyst but with prochiral alkenes the optical yields were low (≤8% enantiomeric excess).

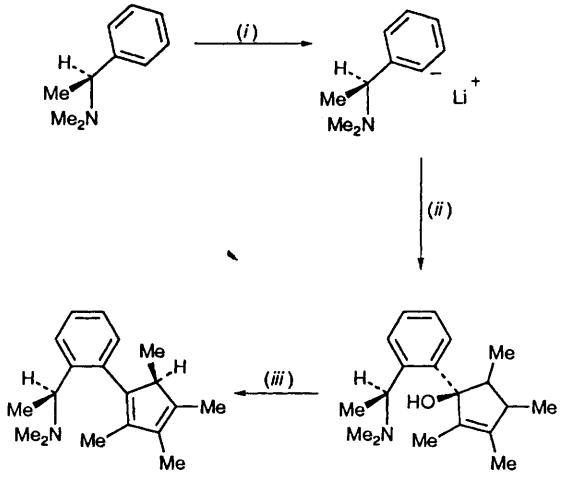
The use of chiral metal catalysts in enantioselective synthesis is now a mature science.[2] Although most applications involve the use of chiral chelating phosphines, ligands which contain additional pendant functional groups have considerable appeal since such groups may interact with appropriate functional groups in the substrate, thus increasing the rigidity of the catalyst–substrate intermediate with a concomitant increase in the optical yield. This strategy has been used with considerable success with various chiral ferrocenylphosphines.[3] As part of a programme to develop effective chiral cyclopentadienyl ligands for use in enantioselective synthesis, we have attempted to use this strategy by synthesising a cyclopentadienyl with a pendant amine function, namely (*S*)-1-(1-dimethylaminoethyl)-2-(2,3,4,5-tetramethylcyclopenta-1,3-dienyl)benzene $C_5Me_4H\text{-}\{C_6H_4[CH(Me)NMe_2]\text{-}2\}$ (HL). This compound, containing a hard nitrogen-donor atom linked to the soft cyclopentadiene function, is also of interest as a 'hybrid' ligand.[4,5] Such ligands normally bind to metals with one strong interaction coupled with one weak interaction; this feature has found applications in catalysis where there is the need readily to generate and maintain a free co-ordination site for substrate activation.[5b]

We report herein the synthesis of transition-metal complexes of HL and the chemistry and crystal structure of $[RhLCl_2]$.

Results and Discussion

The homochiral ligand HL was synthesised in 51% chemical yield by the convenient one-pot procedure outlined in Scheme 1.

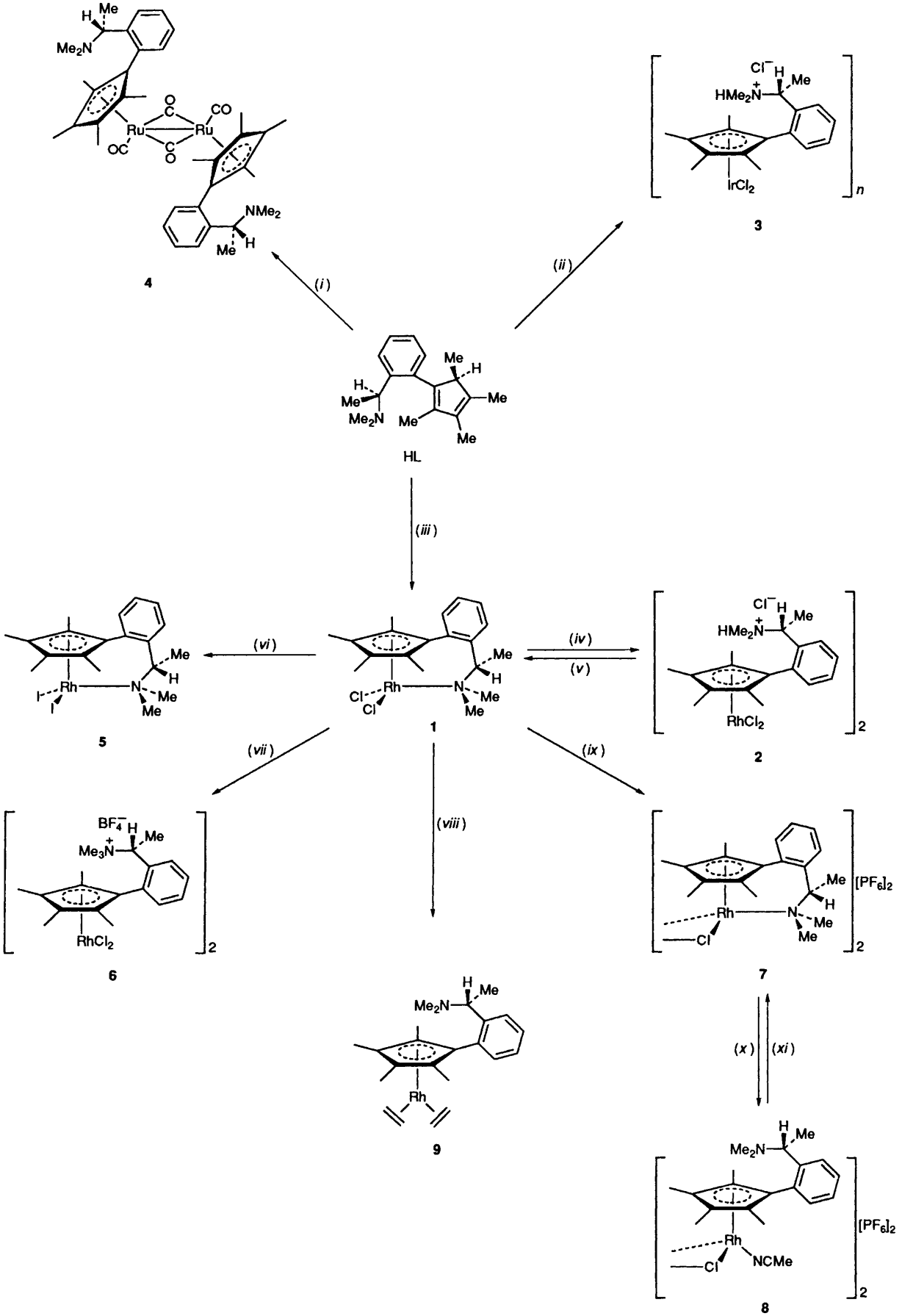
Complexation of HL *to Metals.*—The reactions investigated are outlined in Scheme 2. Heating HL with $RhCl_3\cdot3H_2O$ in methanol under reflux yielded a mixture of $[RhLCl_2]$ **1** and $[\{Rh(L\cdot HCl)Cl_2\}_2]$ **2** in approximately equal proportions; the latter complex was only appreciably soluble in water or extremely polar organic solvents such as alcohols so that the two complexes were readily separated. It was found that interconversion between **1** and **2** could be readily effected. Thus, treatment of a mixture of an aqueous solution of $[\{Rh(L\cdot HCl)Cl_2\}_2]$ and dichloromethane with saturated sodium carbonate solution resulted in the transfer of the deep red colour to the organic phase; separation and evaporation of the dichloromethane yielded $[RhLCl_2]$ **1**. Similarly, $[RhLCl_2]$ dissolved in dilute hydrochloric acid to give $[\{Rh(L\cdot HCl)Cl_2\}_2]$ **2**.



Scheme 1 Synthesis of HL. (*i*) LiBu; (*ii*) 2,3,4,5-tetramethylcyclopent-2-enone; (*iii*) H^+

A crystal structure study of complex **1** revealed that in the solid state the pendant chiral chain is co-ordinated to the rhodium *via* the nitrogen atom (Fig. 1). Evidence that this structure is maintained in solution comes from osmometry which confirms that **1** is monomeric. Also, the two diastereotopic *N*-methyl groups gave rise to two signals in the ^1H and ^{13}C NMR spectra but only one signal in the spectra of **2**.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: atm = 101 325 Pa.



Scheme 2 (*i*) $[Ru_3(CO)_{12}]$; (*ii*) $IrCl_3 \cdot 3H_2O$, MeOH, 65 °C, 48 h; (*iii*) $RhCl_3 \cdot 3H_2O$, MeOH, 65 °C, 48 h; (*iv*) HCl(aq); (*v*) Na_2CO_3 (aq); (*vi*) NaI, CH_2Cl_2–Me_2CO (2:1), 30 min; (*vii*) $Me_3O^+BF_4^-$; (*viii*) C_2H_4, Na_2CO_3, EtOH, 78 °C, 2 h; (*ix*) $AgPF_6$, CH_2Cl_2–Me_2CO (2:1), 2 h; (*x*) MeCN; (*xi*) heat or *in vacuo*

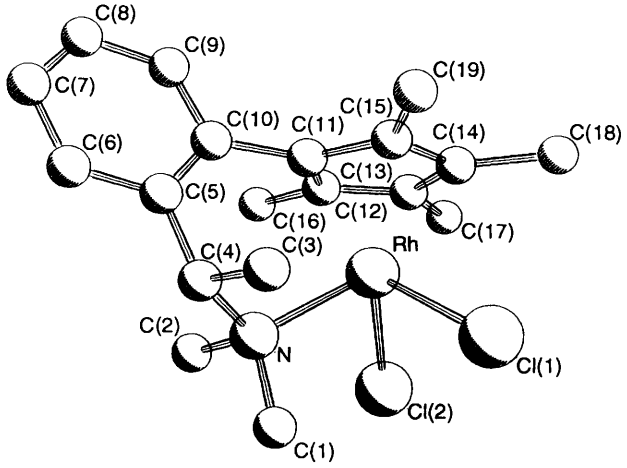


Fig. 1 Molecular structure of $[Rh\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}Cl_2]$ showing the atomic numbering scheme

Presumably this is a reflection of the greater degree of freedom of the unco-ordinated chiral sidechain of **2**.

A similar reaction between HL and $IrCl_3 \cdot 3H_2O$ yielded only an amorphous brown solid which analysed for $[\{Ir(L \cdot HCl)Cl_2\}_2]$ **3**. This could very well be polymeric since the solid proved to be insoluble in water or organic solvents and therefore no NMR data could be obtained to support this formulation.

Infrared spectroscopy suggested that the reaction pathway between HL and $[Ru_3(CO)_{12}]$ in refluxing heptane followed that established for cyclopentadiene.[6] Thus, in addition to a peak at 2063 cm^{-1} due to $[Ru_3(CO)_{12}]$, peaks at 1980 and 1975 cm^{-1} were initially observed to grow and then decay {*cf.* $[Ru(\eta^4\text{-}C_5H_6)(CO)_3]$, ν_{CO} 2062, 1998 and 1986 cm^{-1}} to be replaced by those at 2016 and 1958 cm^{-1} {*cf.* $[Ru(\eta^5\text{-}C_5H_5)(CO)_2H]$, ν_{CO} 2025 and 1966 cm^{-1}}. After 5 h these peaks were almost completely replaced by two new ones at 1938 and 1766 cm^{-1}; after exposure to air and an additional 1 h of reflux these remained the only peaks in the carbonyl region of the spectrum (*cf.* $[\{Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2\}_2]$, ν_{CO} 1937 and 1765 cm^{-1}).[7] Unfortunately, when the reaction was carried out on a preparative scale it was found that extensive decomposition occurred. A brown oil was isolated and, although the infrared and mass spectra were consistent with this being $[\{Ru(\eta^5\text{-}L)(CO)_2\}_2]$ **4**, further work was abandoned in view of the poor yield (4%).

Crystal Structure of $[RhLCl_2]$ **1**.—The molecular structure is illustrated in Fig. 1; Table 1 gives the final atomic coordinates, Table 2 selected bond lengths and angles with estimated standard deviations. The molecule comprises a dichlororhodium(III) unit which is bonded to a pentahapto-phenyltetramethylcyclopentadienyl ligand, the phenyl substituent of which is *ortho*-substituted with a pendant dimethylaminoethyl chain. The tertiary amino fragment co-ordinates to the rhodium in the remaining basal site of the overall 'piano-stool' conformation. The cyclopentadienyl ring is planar [root mean square (r.m.s.) deviation from plane 0.013 Å, deviation of rhodium from mean plane 1.763 Å]; the Rh–C bond distances are similar, with that to C(11), which carries the substituted phenyl group, being the shortest. The four methyl substituents on the five-membered ring all deviate from its mean plane in directions away from the metal by between 0.05 and 0.12 Å; this is a feature commonly observed in peralkylcyclopentadienyl compounds.[8] Atom C(10) of the phenyl group is displaced 0.02 Å from the cyclopentadienyl plane in a direction towards the rhodium. The phenyl ring itself is planar (r.m.s. deviation 0.023 Å) and is twisted with respect to the cyclopentadienyl plane by 77°. The angles between the three basal ligands are close to 90° and there is little sign of strain in the geometry of the amino-ethyl chain, although, in view of the constraints applied during refinement, further discussion of the geometry would not be justified.

There have been several reports of complexes bound to a cyclopentadienyl ligand with a pendant chelating phosphine[9] or alkene[10] function. To our knowledge, however, the only

Table 1 Atomic coordinates ($\times 10^4$) for $[Rh\{\eta^5\text{-}C_5Me_4C_6H_4CH(Me)NMe_2\}Cl_2]$ **1**

Atom	*x*	*y*	*z*
Rh	847(3)	627(2)	863(2)
Cl(1)	3410(11)	923(6)	272(7)
Cl(2)	961(13)	−782(5)	254(6)
N	1612(28)	148(16)	2245(20)
C(1)	3140(38)	−255(22)	2205(29)
C(2)	556(38)	−509(21)	2578(24)
C(3)	3050(36)	1449(20)	2781(25)
C(4)	1776(40)	828(22)	3050(28)
C(5)	207(42)	1209(24)	3290(20)
C(6)	48(38)	1389(20)	4268(22)
C(7)	−1255(35)	1808(23)	4593(31)
C(8)	−2399(47)	2028(24)	3941(24)
C(9)	−2190(42)	1855(22)	2971(26)
C(10)	−867(38)	1479(18)	2626(20)
C(11)	−763(37)	1393(15)	1520(18)
C(12)	−1571(28)	792(14)	980(16)
C(13)	−1147(34)	936(18)	21(18)
C(14)	−119(36)	1612(18)	−40(19)
C(15)	85(30)	1915(15)	899(18)
C(16)	−2741(38)	154(20)	1352(25)
C(17)	−1808(35)	419(18)	−821(26)
C(18)	579(38)	2018(18)	−940(24)
C(19)	1029(44)	2699(17)	1158(23)

Table 2 Bond lengths (Å) and angles (°) for complex **1**

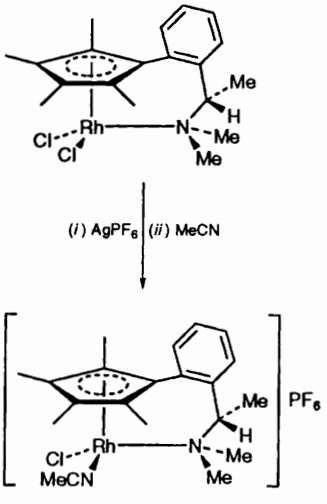
Rh–Cl(1)	2.419(10)	Rh–Cl(2)	2.383(9)
Rh–N	2.162(27)	Rh–C(11)	2.061(28)
Rh–C(12)	2.124(24)	Rh–C(13)	2.144(28)
Rh–C(14)	2.166(28)	Rh–C(15)	2.141(25)
N–C(1)	1.474(42)	N–C(2)	1.460(42)
N–C(4)	1.554(46)	C(3)–C(4)	1.525(47)
C(4)–C(5)	1.527(50)	C(5)–C(6)	1.391(42)
C(5)–C(10)	1.378(45)	C(6)–C(7)	1.387(47)
C(7)–C(8)	1.387(53)	C(8)–C(9)	1.383(49)
C(9)–C(10)	1.379(48)	C(10)–C(11)	1.540(38)
C(11)–C(12)	1.397(35)	C(11)–C(15)	1.400(37)
C(12)–C(13)	1.396(33)	C(12)–C(16)	1.521(40)
C(13)–C(14)	1.396(41)	C(13)–C(17)	1.535(42)
C(14)–C(15)	1.397(36)	C(14)–C(18)	1.526(42)
C(15)–C(19)	1.529(40)		
Cl(1)–Rh–Cl(2)	91.3(4)	Cl(1)–Rh–N	94.8(7)
Cl(2)–Rh–N	88.5(7)	Rh–N–C(1)	113.3(21)
Rh–N–C(2)	109.6(19)	C(1)–N–C(2)	105.7(25)
Rh–N–C(4)	114.9(20)	C(1)–N–C(4)	104.1(25)
C(2)–N–C(4)	108.9(25)	N–C(4)–C(3)	109.6(28)
N–C(4)–C(5)	110.3(26)	C(3)–C(4)–C(5)	116.6(29)
C(4)–C(5)–C(6)	112.4(29)	C(4)–C(5)–C(10)	125.6(28)
C(6)–C(5)–C(10)	121.2(32)	C(5)–C(6)–C(7)	119.7(33)
C(6)–C(7)–C(8)	119.6(36)	C(7)–C(8)–C(9)	119.3(36)
C(8)–C(9)–C(10)	122.0(33)	C(5)–C(10)–C(9)	117.9(28)
C(5)–C(10)–C(11)	126.6(28)	C(9)–C(10)–C(11)	115.5(28)
C(10)–C(11)–C(12)	124.2(24)	C(10)–C(11)–C(15)	126.0(24)
C(12)–C(11)–C(15)	109.7(22)	C(11)–C(12)–C(13)	105.3(22)
C(11)–C(12)–C(16)	127.3(23)	C(13)–C(12)–C(16)	127.3(24)
C(12)–C(13)–C(14)	110.6(23)	C(12)–C(13)–C(17)	122.4(25)
C(14)–C(13)–C(17)	126.9(24)	C(13)–C(14)–C(15)	106.6(23)
C(13)–C(14)–C(18)	128.8(24)	C(15)–C(14)–C(18)	124.4(26)
C(11)–C(15)–C(14)	107.6(23)	C(11)–C(15)–C(19)	128.0(23)
C(14)–C(15)–C(19)	124.3(24)		

other reported structures containing an intramolecularly co-ordinated amino function of a cyclopentadienyl side chain are those of $[Mo(\eta^5\text{-}C_5H_4CH_2CH_2NMe_2)(CO)_2X]^{n+}$ ($n = 0$, $X = I$[11] or $\eta^3\text{-}C_6H_9$[12]; $n = 1$, $X = PPh_3$[13]), although we note that the complexes $[M'\{\eta^5\text{-}C_5H_3(CMe_3)(SiMe_2NCMe_3)\}]$ [$M' = Fe(CO)_2$ or $TiCl_2$] containing a linked cyclopentadienylamido ligand have also been synthesised.[14]

The Chemistry of $[RhLCl_2]$ **1**.—Quaternisation of the amine group in complex **1** was attempted by stirring a dichloromethane solution of $[RhLCl_2]$ with an excess of iodomethane. After 3 d the solution had darkened considerably and so the solvent was removed and the residue examined by ^1H NMR spectroscopy. This showed approximately three times the number of peaks found in the spectrum of $[RhLCl_2]$ **1** and it was reasoned that partial halide exchange at the rhodium had occurred. The mixture was therefore stirred with sodium iodide in acetone to complete the replacement of the rhodium–chloride bonds and this did indeed yield pure $[RhLI_2]$ **5**; the same product could be obtained more conveniently by treating **1** directly with sodium iodide in an acetone–dichloromethane mixture. The ^1H and ^{13}C NMR spectra of $[RhLI_2]$ **5** (Experimental section) were similar to those of the corresponding chloro-compound except that the difference in the chemical shifts was generally considerably greater for **5**, containing the larger iodide ligands. For example, in the ^1H spectrum the NMe signals differ by δ 0.29 compared with only δ 0.04 for the chloride **1**.

A successful quaternisation of the amine function was achieved by treating $[RhLCl_2]$ with $Me_3O^+BF_4^-$ to yield $[\{Rh(L{\cdot}MeBF_4)Cl_2\}_2]$ **6**. That methylation of the Rh–NMe_2 function has occurred is apparent in the ^1H and ^{13}C NMR spectra where the unco-ordinated NMe_3^+ group gives rise to one signal; this contrasts with the two signals observed for the Rh–NMe_2 function in $[RhLCl_2]$ **1**.

Since a prime objective in this work was to develop catalysts capable of inducing asymmetry it seemed appropriate to attempt to generate a second chiral centre located at the rhodium metal atom and to determine the effectiveness of the HL ligand in directing the stereoselectivity of such a reaction. With this in mind reaction (1) was attempted. On reaction of



(1)

$[RhLCl_2]$ **1** with 1 equivalent of $AgPF_6$ and then with acetonitrile a yellow solid was obtained which was dried *in vacuo*. The ^1H NMR spectrum revealed that the product contained no acetonitrile and elemental analysis was consistent with the formulation $[\{RhL(Cl)\}_2]^{2+}2PF_6^-$ which we suggest has the chloride-bridged structure **7** (Scheme 2). Supporting evidence for this comes from the ^1H NMR spectrum which contains two signals for the NMe_2 group, a feature which appears to be diagnostic of a N-co-ordinated L ligand (see above). An identical product was obtained when $[RhLCl_2]$ **1** was treated with 1 equivalent of $AgPF_6$ alone.

Further investigation revealed that $[\{RhL(Cl)\}_2]^{2+}2PF_6^-$ **7** underwent a reversible addition reaction with acetonitrile. Thus, when it was dissolved in either neat acetonitrile or in a mixture with dichloromethane an acetonitrile adduct $[\{RhL(Cl)(NCMe)\}_2]^{2+}2PF_6^-$ **8** was formed. After removing the solvent on a rotary evaporator *without heating* a ^1H NMR spectrum was recorded and this contained a signal at δ 2.40 which integrated for 3 H, consistent with co-ordinated MeCN. Significantly, only one signal was observed for the NMe_2 group suggesting that acetonitrile reacts with **7** to displace the co-ordinated NMe_2 function. When the acetonitrile adduct was dried under high vacuum, ^1H NMR spectroscopy revealed that the acetonitrile ligand had been lost to regenerate **7**. The cycle of addition and removal of acetonitrile could be repeated several times without any signs of side-reactions or decomposition.

When the acetonitrile adduct $[\{RhL(Cl)(NCMe)\}_2]^{2+}2PF_6^-$ **8** was heated at 65 °C in CD_3CN for 48 h there was no change in the signal of the co-ordinated acetonitrile in the ^1H NMR spectrum indicating that exchange of acetonitrile was slow. Clearly, therefore, the rhodium–acetonitrile bond is not inherently weak and the driving force for the facile loss of MeCN when **8** is heated must be the chelation of the pendant NMe_2 group. In a polar solvent such as acetonitrile the amine group will interact strongly with the solvent, stabilising the 'pendant chain' form of the ligand L.

Under reducing conditions (*i.e.* Na_2CO_3 in refluxing ethanol) ethene reacts with $[\{Rh(L{\cdot}HCl)Cl_2\}_2]$ **2** to give $[Rh(\eta^5\text{-}L)(\eta^2\text{-}C_2H_4)_2]$ **9**. The ^1H NMR spectrum of this compound revealed that the ethene ligands were rotating rapidly at ambient temperature. From a variable-temperature study the coalescence temperature was found to be 335 K and using the method of Cramer and Mrowca[15] the activation energy for alkene rotation ($\Delta G^{\ddagger}$) was estimated at 67.2 ± 1.0 kJ mol^{-1}. Not surprisingly this lies between the values found for $[Rh(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)_2]$ (71.5 ± 0.84 kJ mol^{-1})[16] and $[Rh(\eta^5\text{-}C_5H_4Ph)(\eta^2\text{-}C_2H_4)_2]$ (61.8 ± 1.0 kJ mol^{-1}).[17]

Catalytic Studies.—In contrast to the related complexes $[\{Rh(\eta^5\text{-}C_5Me_4R)Cl_2\}_2]$ (R = Me[18] or menthyl[1b]), the complex with R = $C_6H_4CH(Me)NMe_2$ (*i.e.* **1**) did not catalyse the hydrogenation of alkenes at 5 atm pressure and 50 °C. The former dimeric complexes can readily generate the necessary free co-ordination site by dissociation into monomers; presumably, the lack of catalytic activity of the monomer **1** stems from the fact that the chelated amine function does not readily dissociate. In support of this proposal it was found that the quaternary ammonium salt $[\{Rh(L{\cdot}MeBF_4)Cl_2\}_2]$ **6** catalysed the hydrogenation of methyl α-acetamidocinnamate. Interestingly, whereas previous catalysts of the type $[\{Rh(\eta^5\text{-}C_5Me_4R)Cl_2\}_2]$ (R = Me[18] or menthyl[1b]) had been found to be active only in the presence of base, *e.g.* NEt_3, no dramatic effect of base was observed. Thus, after 24 h, 66% reduction of $PhCH{=}C(NHCOMe)CO_2Me$ was achieved in the absence of base whereas a maximum of 84% reduction was found with a triethylamine to catalyst ratio of 10:1. Further, under the same conditions in the absence of base, total reduction of the free acid $PhCH{=}C(NHCOMe)CO_2R$ (R = H) occurred.

The optical yields obtained in the above reductions were disappointingly low. The only encouraging result was that whereas the ester $PhCH{=}C(NHCOMe)CO_2Me$ was hydrogenated in ≤1% enantiomeric excess (e.e.) the free acid gave *N*-acetyl-(*S*)-phenylalanine in 8% e.e. suggesting that the chiral pendant ammonium function of the catalyst did indeed interact with an appropriate functional group (*i.e.* CO_2H) in the substrate. In support of this the optical yield dropped to zero in the presence of an excess of triethylamine.

It was found that, when heated under reflux in ethanol with Na_2CO_3, $[RhLCl_2]$ **1** catalysed double-bond isomerisation;

thus, hex-1-ene was isomerised to a 3:1 mixture of *trans*- and *cis*-hex-2-ene (catalyst turnover rate *ca.* 12 h^{-1}).

Experimental

Microanalytical data were obtained by the University of Sheffield Microanalytical service. Proton and ^{13}C NMR spectra were recorded on Perkin-Elmer R-34 (220 MHz) and Bruker AM 250 spectrometers respectively using $SiMe_4$ as an internal reference, IR spectra on a PE-157G spectrometer. All reactions were carried out under an atmosphere of nitrogen although the compounds were subsequently found not to be air-sensitive.

Syntheses.—1-(1-*Dimethylaminoethyl*)-2-(2,3,4,5-*tetramethylcyclopenta*-1,3-*dienyl*)*benzene* (HL). (*S*)-*N*,*N*-Dimethyl-1-phenylethylamine was prepared in 60% yield by the literature method.[19] A thoroughly degassed solution of this compound (10 g) in anhydrous diethyl ether (150 cm^3) was treated with butyllithium (2.6 mol dm^{-3} in hexane, 25 cm^3) under argon. The mixture was heated under reflux for 30 h with stirring, then cooled to room temperature. 2,3,4,5-Tetramethylcyclopent-2-enone[20] (11.0 g) was added dropwise over 30 min so as to bring the solution to a gentle reflux and the mixture was then heated under reflux for 2 h. The solution was cooled in an ice-bath and hydrochloric acid (4 mol dm^{-3}, 100 cm^3) was carefully added. It was then concentrated at reduced pressure to give a red syrup which was redissolved in water (100 cm^3) and the pH adjusted to 10 by addition of 10 mol dm^{-3} sodium hydroxide solution. The product then separated as a yellow oil, which was removed and the aqueous layer extracted with diethyl ether (3 × 50 cm^3). The combined organic phase was dried over anhydrous $MgSO_4$, filtered then concentrated on a rotary evaporator and finally vacuum distilled to yield a viscous oil (9.8 g, 51%), b.p. 141–147 °C (3 mmHg ≈ 400 Pa), α(589.3 nm, 20 °C) −44.8° (neat). Analysis by gas chromatography–mass spectrometry (GC–MS) showed only the three double-bond isomers of the cyclopentadiene, at *m*/*z* 269 (M^+). $\delta_H(CDCl_3)$ 7.60–7.45 (1 H, m, aryl), 7.35–7.10 (2 H, m, aryl), 7.05–6.85 (1 H, m, aryl), 3.15 (1 H, q, *J* = 6 Hz) and 2.23–0.82 (22 H, m, overlapping signals of isomers). IR 3053w, 3010w, 2950s, 2918s, 2845m, 2804m, 2759m, 2722vw, 1695m (br), 1645w (br), 1480m, 1458 (sh), 1449m, 1440m, 1376m, 1364m, 1335w (br), 1269w, 1253w, 1200w, 1150m, 1072m, 1035m, 949m and 755s cm^{-1} (neat).

$[RhLCl_2]$ **1** *and* $[\{Rh(\eta^5\text{-L}\cdot HCl)Cl_2\}_2]$ **2**. With the aid of a motorised syringe pump a solution of HL (2.5 g, 9.28 mmol) in methanol (40 cm^3) was added, under nitrogen, over a period of 36 h to a well stirred, refluxing solution of $RhCl_3\cdot 3H_2O$ (2.0 g, 7.60 mmol) in methanol (250 cm^3). Reflux was continued for 12 h then an insoluble residue (*ca.* 100 mg) was filtered off and the filtrate evaporated to dryness. The solid remaining was extracted with dichloromethane (50 cm^3), approximately half dissolved. The residue was recrystallised from methanol–diethyl ether to give dark red cubic crystals of $[\{Rh(\eta^5\text{-L}\cdot HCl)Cl_2\}_2]$ **2** (1.22 g, 33.5%) (Found: C, 47.2; H, 5.7; Cl, 22.3; N, 2.9. $C_{38}H_{54}Cl_6N_2Rh_2$ requires C, 47.7; H, 5.7; Cl, 22.2; N, 2.9%). $\delta_H(D_2O)$ 8.35 (2 H, m, NH^+), 7.89–7.48 (8 H, m, aryl), 4.10 [2 H, q, *J* 7 Hz, C*H*(Me)], 2.72 (12 H, s, NMe_2), 1.82 (s), 1.79 (s), 1.66 (s), 1.62 (s) (24 H, 4Me) and 1.80 [6 H, d, CH(*Me*)].

The dichloromethane extract from above was concentrated to 5 cm^3, an equal volume of acetone was added, and the solvent slowly evaporated under nitrogen, to yield red needles of $[RhLCl_2]$ **1** (1.6 g, 47.6%) [Found: C, 51.0; H, 5.8; Cl, 16.2; N, 3.1%; *M* ($CHCl_3$) 466. $C_{19}H_{26}Cl_2NRh$ requires C, 51.6; H, 5.9; Cl, 16.0; N, 3.2%; *M* 442]; $\delta_H(CDCl_3)$ 7.45 (3 H, m, aryl), 7.28 (1 H, m, aryl), 3.51 [1 H, q, *J* = 6 Hz, C*H*(Me)], 2.74 (s), 2.70 (s) (6 H, NMe_2), 1.78 (s), 1.72 (s), 1.48 (s), 1.35 (s) (12 H, 4-Me) and 1.70 [3 H, d, *J* = 6 Hz, CH(*Me*)]; $\delta(^{13}C\text{-}\{^1H\})$ ($CDCl_3$) 144.2 (s), 123.3 (s) (2 C, C_{aryl}), 130.2 (s), 130.1 (s), 129.7 (s), 128.5 (s) (4 C, CH_{aryl}), 104.5 [1 C, d, *J*(RhC) 7, C_5Me_4], 95.9 [1 C, d, *J*(RhC) 10, C_5Me_4], 95.3 [1 C, d, *J*(RhC) 7, C_5Me_4], 90.1 [1 C, d, *J*(RhC) 9, C_5Me_4], 83.6 [1 C, d, *J*(RhC) 10 Hz, C_5Me_4], 74.4 [1 C, s, *C*H(Me)], 54.3 (s), 50.1 (s) (2 C, NMe_2), 22.3 [1 C, s, CH(*Me*)], 10.1 (s), 9.6 (s), 9.4 (s) and 8.6 (s) (4Me).

$[\{Ir(\eta^5\text{-L}\cdot HCl)Cl_2\}_2]$ **3**. The compound $IrCl_3\cdot 3H_2O$ (760 mg, 2.2 mmol) was heated under reflux in methanol (40 cm^3) under nitrogen. A solution of HL (650 mg, 2.4 mmol) in methanol (10 cm^3) was added over 24 h, and the reflux continued for 24 h. The mixture was cooled and the residue (30 mg) filtered off. Concentration of the filtrate afforded a brown oil, and upon redissolving this in methanol it began to form a solid precipitate. This was accelerated by cooling to 5 °C and adding diethyl ether. A highly insoluble brown solid was obtained (580 mg, 46%) (Found: C, 40.9; H, 5.1; Cl, 18.8; N, 2.3. $C_{38}H_{54}Cl_6Ir_2N_2$ requires C, 40.2; H, 4.8; Cl, 18.7; N, 2.5%). Treatment with sodium carbonate solution and dichloromethane did not convert this into a soluble product.

$[\{Ru(\eta^5\text{-L})(CO)_2\}_2]$ **4**. The compounds HL (114 mg, 0.42 mmol) and $[Ru_3(CO)_{12}]$ (83 mg, 0.13 mmol) were dissolved on warming in heptane (6 cm^3) and the solution was heated at reflux under nitrogen. Samples were periodically withdrawn so that their IR spectra could be checked. The reflux was continued for 5 h under nitrogen, then for 1 h exposed to the atmosphere. After cooling, the product was filtered off and the black residue extracted with heptane. The combined filtrates were evaporated to dryness to give $[\{Ru(\eta^5\text{-L})(CO)_2\}_2]$ as a deep brown oil (15 mg, 4%). This was identified as the desired product by its infrared and mass spectra (Found: *m*/*z* 851, M^+. Calc. for $C_{42}H_{52}N_2O_4Ru_2$: 851).

$[RhLI_2]$ **5**. The complex $[RhLCl_2]$ (100 mg, 0.23 mmol) was treated with an excess of sodium iodide (200 mg) in dichloromethane–acetone (2:1). After 30 min solvent was removed and the residue extracted into dichloromethane. The extract was recrystallised from dichloromethane–diethyl ether to give dark needles of $[RhLI_2]$ **5** (115 mg, 82%) (Found: C, 36.4; H, 4.1; I, 40.5; N, 2.2. $C_{19}H_{26}I_2NRh$ requires C, 36.5; H, 4.2; I, 40.6; N, 2.2%). $\delta_H(CDCl_3)$ 7.47–7.20 (4 H, m, aryl), 3.14 [1 H, q, *J* = 8, C*H*(Me)], 3.06 (s), 2.78 (s) (6 H, NMe_2), 2.24 (s), 1.99 (s), 1.77 (s), 1.52 (s) (12 H, 4Me) and 1.69 [3 H, d, *J* = 8 Hz, CH(*Me*)]; $\delta(^{13}C\text{-}\{^1H\})$ ($CDCl_3$) 143.5 (s), 123.2 (s) (2 C, C_{aryl}), 130.1 (s), 130.0 (s), 129.3 (s), 128.6 (s) (4 C, CH_{aryl}), 102.2 [1 C, d, *J*(RhC) 7, C_5Me_4], 97.5 [1 C, d, *J*(RhC) 8, C_5Me_4], 94.2 [1 C, d, *J*(RhC) 7, C_5Me_4], 92.8 [1 C, d, *J*(RhC) 8, C_5Me_4], 88.6 [1 C, d, *J*(RhC) 8 Hz, C_5Me_4], 75.1 [1 C, s, *C*H(Me)], 58.2 (s), 57.0 (s) (2 C, NMe_2), 23.7 [1 C, s, CH(*Me*)], 14.2 (s), 13.1 (s), 10.8 (s) and 9.6 (s) (4Me).

$[\{Rh(\eta^5\text{-L}\cdot MeBF_4)Cl_2\}_2]$ **6**. The complex $[RhLCl_2]$ (440 mg, 1.0 mmol) was dissolved in dichloromethane (20 cm^3) and treated with $Me_3O\cdot BF_4$ (150 mg, 1.0 mmol) for 3 h. The resulting dark red solution was filtered and reduced to half volume. Addition of diethyl ether gave orange crystals, which were filtered off and washed with chloroform. (Yield 310 mg, 60%) (Found: C, 44.0; H, 5.1; Cl, 12.8; N, 2.4. $C_{40}H_{58}B_2Cl_4F_8N_2Rh_2$ requires C, 44.1; H, 5.4; Cl, 13.0; N, 2.6%). $\delta_H[D_2O\text{–}(CD_3)_2CO]$ 8.25 (1 H, m, aryl), 7.79–7.30 (3 H, m, aryl), 3.99 [1 H, q, *J* = 6, C*H*(Me)], 2.70 (9 H, s, NMe_3), 1.75 (s), 1.71 (s), 1.56 (s), 1.52 (s) (12 H, 4Me) and 1.65 [3 H, d, *J* = 6 Hz, CH(*Me*)]; $\delta(^{13}C\text{-}\{^1H\})$ [D_2O–$(CD_3)_2CO$] 129.1 (s), 119.5 (s) (2 C, C_{aryl}), 127.8 (s), 125.4 (s) 123.3 (s), 120.0 (s) (4 C, CH_{aryl}), 98.1 [1 C, d, *J*(RhC) 7, C_5Me_4], 95.3 [1 C, d, *J*(RhC) 7, C_5Me_4], 92.5 [1 C, d, *J*(RhC) 7, C_5Me_4], 87.4 [1 C, d, *J*(RhC) 7, C_5Me_4], 86.6 [1 C, d, *J*(RhC) 7 Hz, C_5Me_4], 56.1 [1 C, s, *C*H(Me)], 34.6 (s, 3 C, NMe_3), 12.1 [1 C, s, CH(*Me*)], 3.9 (s), 3.2 (s), 2.4 (s) and 2.1 (s) (4Me).

$[\{RhL(Cl)\}_2]^{2+}2PF_6^-$ **7** *and* $[\{RhL(Cl)(NCMe)\}_2]^{2+}2PF_6^-$ **8**. The complex $[RhLCl_2]$ (200 mg, 0.45 mmol) was vigorously stirred in dichloromethane (20 cm^3) as a solution of $AgPF_6$ (114 mg, 0.45 mmol) in acetone (10 cm^3) was added dropwise. The mixture was stirred for an additional 2 h under nitrogen, then the solvent was removed to give a dark yellow solid. This was extracted into dichloromethane, and purified by filtering first through cotton-wool, then through a 5 cm cellulose

column. The bright yellow product was recrystallised from dichloromethane–diethyl ether to give $[\{RhL(Cl)\}_2]^{2+}2PF_6^-$ **7** (210 mg, 87%) (Found: C, 41.0; H, 4.6; N, 2.6. $C_{38}H_{52}Cl_2F_{12}N_2P_2Rh_2$ requires C, 41.3; H, 4.7; N, 2.5%). $\delta_H[(CD_3)_2CO]$ 7.71–7.52 (8 H, m, aryl), 3.96 [2 H, q, J = 6, C*H*(Me)], 2.76 (s), 2.64 (s) (12 H, NMe_2), 1.86 (s), 1.80 (s), 1.48 (s), 1.33 (s) (24 H, 4Me) and 1.70 [6 H, d, J = 6 Hz, CH(*Me*)]; $\delta(^{13}C\text{-}\{^1H\})$ $[(CD_3)_2CO]$ 143.6 (s), 123.3(s) (2 C, C_{aryl}), 130.2 (s), 130.1 (s), 129.7 (s), 128.5 (s) (8 C, CH_{aryl}), 104.5 [2 C, d, J(RhC) 7, C_5Me_4], 95.9 [2 C, d, J(RhC) 10, C_5Me_4], 95.3 [2 C, d, J(RhC) 7, C_5Me_4], 90.1 [2 C, d, J(RhC) 9, C_5Me_4], 83.6 [2 C, d, J(RhC) 10 Hz, C_5Me_4], 74.4 [2 C, s, *C*H(Me)], 54.3 (s), 50.1 (s) (4 C, NMe_2), 22.3 [2 C, s, CH(*Me*)], 10.1 (s), 9.6 (s), 9.4 (s) and 8.6 (s) (8Me).

A small amount (40 mg) of this compound was dissolved in dichloromethane (10 cm^3) to which acetonitrile (2 cm^3) was added. After stirring for 15 min the solvent was removed using a rotary evaporator *without applying heat*. After 20 min the product appeared quite dry; examination by ^1H NMR spectroscopy then showed it to be $[\{RhL(Cl)(NCMe)\}_2]^{2+}2PF_6^-$ **8**. $\delta_H[(CD_3)_2CO]$ 7.74–7.49 (8 H, m, aryl), 3.90 [2 H, q, J = 5, C*H*(Me)], 2.70 (s, 12 H, NMe_2), 2.39 (s, 6 H, 2MeCN), 1.84 (s), 1.79 (s), 1.55 (s), 1.33 (s) (24 H, 8Me) and 1.67 [6 H, d, J = 5 Hz, CH(*Me*)]. This acetonitrile adduct **8** when left *in vacuo*, even without warming, reverted completely to **7** within 24 h.

$[Rh(\eta^5\text{-}L)(\eta^2\text{-}C_2H_4)_2]$ **9**. Ethene was bubbled for 2 h through a refluxing mixture of ethanol (40 cm^3), $[\{Rh(L\cdot HCl)Cl_2\}_2]$ (320 mg, 0.334 mmol) and Na_2CO_3 (180 mg, 1.70 mmol). During this time the colour changed from orange-red to olive-green. The solution was allowed to cool, filtered and the filtrate taken to dryness using a rotary evaporator. The residue was extracted with ether (3 × 15 cm^3) and the combined ether washings reduced to 20 cm^3; on standing yellow crystals of $[Rh(\eta^5\text{-}L)(\eta^2\text{-}C_2H_4)_2]$ slowly crystallised, and were collected and dried *in vacuo* (225 mg, 79%) (Found: C, 64.0; H, 8.0; N, 3.2. $C_{23}H_{34}NRh$ requires C, 64.6; H, 8.0; N, 3.3%). $\delta_H(CDCl_3)$ 8.04 (1 H, dd, J = 8, 1.5, aryl), 7.48 (1 H, dd, J = 7.5, 1.5, aryl), 7.32 (1 H, dt, J = 7.5, 1.5, aryl), 7.21 (1 H, dt, J = 8, 1.5, aryl), 3.05 [1 H, q, J = 6.5, C*H*(Me)], 2.10 (s, 6 H, NMe_2), 2.00 (s), 1.95 (s), 1.24 (s), 1.21 (s) (12 H, 4Me), 1.86 (dd, br), 1.43 (dd, br) [8 H, J = 11, J(RhH) = 2, $2C_2H_4$] and 1.23 [3 H, d, J = 6.5 Hz, CH(*Me*)]; $\delta(^{13}C\text{-}\{^1H\})$ ($CDCl_3$) 145.5 (1 C, d, J = 3, C_{aryl}), 132.4 (s, 1 C, C_{aryl}), 138.7 (s), 127.8 (s), 126.0 (s). 125.8 (s) (4 C, CH_{aryl}), 109.5 [1 C, d, J(RhC) 6, C_5Me_4], 98.4 [1 C, d, J(RhC) 5, C_5Me_4], 98.3 [1 C, d, J(RhC) 4, C_5Me_4], 95.8 [1 C, d, J(RhC) 4, C_5Me_4], 95.7 [1 C, d, J(RhC) 4, C_5Me_4], 61.9 [1 C, s, *C*H(Me)], 44.8 [2 C, d, J(RhC) 14, C_2H_4], 44.7 [2 C, d, J(RhC) 14 Hz, C_2H_4], 43.8 (s, 2 C, NMe_2), 21.5 [1 C, s, CH(*Me*)], 10.2 (s), 10.0 (s), 9.1 (s) and 8.9 (s) (4Me).

Catalytic Studies.—The hydrogenation reactions were carried out in a Fischer–Porter apparatus at 50 ± 1 °C and an initial hydrogen pressure of 5 atm. The solvent was either propan-2-ol or acetone–water (1:1) and a substrate concentration of 0.125 mol dm^{-3} with a substrate:catalyst ratio of 50:1 was used. After the reaction, solvent was removed and the extent of reaction determined by ^1H NMR spectroscopy. The residue was then redissolved in acetone–water (4:1) and the catalyst removed using an ion-exchange resin (BDH Zerolit 325). After 8–12 h the solution was colourless, and the hydrogenation product was taken up in acetone (2.0 cm^3) for polarimetry measurements.

X-Ray Crystal Structure Determination of $[RhLCl_2]$ **1**.—Suitable crystals of complex **1** were grown by slow evaporation under nitrogen of a solution in acetone–dichloromethane (1:1). The crystals formed as very thin, elongated red plates; crystal dimensions 0.35 × 0.09 × 0.01 mm.

Crystal data. $C_{19}H_{26}Cl_2NRh$, M = 442.23, orthorhombic, space group $P2_12_12_1$ (D_2^4, no. 19), a = 8.691(6), b = 15.803(15), c = 13.840(10) Å, U = 1900.8(26) $Å^3$, Z = 4, D_c = 1.545 g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 11.67 cm^{-1}, $F(000)$ = 903.90.

Structure analysis and refinement. Three-dimensional, room-temperature X-ray data were collected in the range 3.5 < 2θ < 55° on a Nicolet R3 diffractometer by the ω-scan method. The 742 independent reflections (of 2614 measured) for which $|F|/\sigma(|F|) > 6.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of seven azimuthal scans (minimum and maximum transmission coefficients 0.731 and 0.857). The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. In view of the limited quantity of data, it was necessary to impose geometric constraints of bond-length equivalence within each of the cyclopentadienyl and phenyl rings, and for the six carbon–methyl and two nitrogen–methyl fragments. Hydrogen atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting atom. Refinement converged at a final R 0.0657 (112 parameters, final mean and maximum δ/σ 0.000 and 0.001 respectively), with allowance for the thermal anisotropy of rhodium and chlorines only. The enantiomeric form of the space group could not be unambiguously determined (ΔR 0.0002). A final difference electron-density synthesis showed minimum and maximum values of −0.75 and +0.77 e $Å^{-3}$. Complex scattering factors were taken from ref. 21 and from the program package SHELXTL[22] as implemented on a Data General Nova 3 computer. Unit weights were used throughout. Table 1 lists atomic positional parameters with estimated standard deviations.

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

Acknowledgements

We record our sincere thanks to the SERC for a studentship (to P. A. S.), to Johnson Matthey for the generous loan of ruthenium trichloride (to C. W.) and to the Royal Society and the SERC for funds for the X-ray and computing equipment.

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Received 1*st December* 1993; *Paper* 3/07110C