In memory of T. A. Stephenson

The Chemistry of Tetraphenylcyclopentadienone Complexes of Ruthenium and Rhodium: the *X*-Ray Crystal Structure of $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$ †

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$[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**) and $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**) react with L-(−)-α-methylbenzylamine to give the tetraphenylcyclopentadienone complexes $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\{NH_2CH(Me)Ph\}]$ and $[Rh(\eta^4\text{-}C_5Ph_4O)Cl\{NH_2CH(Me)Ph\}]$ respectively; trimethylamine *N*-oxide also reacts with complex (**1**) to give the amine adduct $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2(NMe_3)]$ (**5**). Complexes (**2**) and (**5**) oxidatively add HX to give the corresponding hydroxytetraphenylcyclopentadienyl complexes $[\{M(\eta^5\text{-}C_5Ph_4OH)(L)X\}_n]$ [M = Ru, L = $(CO)_2$, X = Cl, $OC(O)CF_3$, or OC(O)Me, *n* = 1; M = Rh, X = L = Cl, *n* = 2]; all these compounds readily reductively eliminate HX, the ease of this reaction increasing in the order of X and M listed. Methyl iodide also oxidatively adds to (**5**) to give the stable complex $[Ru(\eta^5\text{-}C_5Ph_4OMe)(CO)_2I]$. The acyl chlorides RC(O)Cl similarly oxidatively add to complexes (**1**) and (**2**) to give the corresponding ester complexes $[M\{\eta^5\text{-}C_5Ph_4OC(O)R\}(L)Cl]_n$ [M = Ru, L = $(CO)_2$, *n* = 1, R = Me; M = Rh, L = Cl, *n* = 2, R = Me or (−)CH(OMe)Ph]; the complex $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$ also reacts with RC(O)Cl to give $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)R\}(CO)_2Cl]$ [R = Me or (−)CH(OMe)Ph (**14**)]. The *X*-ray structure of (**14**) is reported; the crystals are orthorhombic, space group $P2_12_12_1$ (no. 19) with *a* = 24.58(3), *b* = 14.518(13), *c* = 9.299(4) Å, and *Z* = 4. The structure was solved *via* the heavy-atom method and refined to *R* = 0.0541 using 1 425 independent reflections. Carbonylation of $[\{Rh(\eta^5\text{-}C_5Ph_4OC(O)R^*)Cl_2\}_2]$ in the presence of zinc gives $[Rh\{\eta^5\text{-}C_5Ph_4OC(O)R^*\}(CO)_2]$ and complex (**14**) undergoes carbonyl substitution with triphenylphosphine to give the two diastereoisomers of $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)R^*\}(CO)(PPh_3)Cl]$ [R* = (−)CH(OMe)Ph]. The use of $[Rh\{\eta^5\text{-}C_5Ph_4OC(O)R^*\}(CO)_2]$ and $[\{Rh(\eta^5\text{-}C_5Ph_4OC(O)R^*\}Cl_2\}_2]$ [R* = (−)CH(OMe)Ph] as asymmetric hydroformylation and hydrogenation catalysts respectively is briefly discussed. I.r., ^1H, ^{13}C, and ^{31}P n.m.r. spectroscopic data are presented.

One of the outstanding successes in recent years has been the use of chiral phosphine ligands in catalytic asymmetric synthesis.[1] A characteristic of the more effective ligands such as $Ph_2PCH(Me)CH(Me)PPh_2$ (chiraphos), is that they contain bis-(diarylphosphino) groups and it has been demonstrated that such phosphines are effective, despite the remoteness of the chiral centres from the metal, because the rigid chiral backbone orientates the aryl substituents on the phosphorus in a chiral array about the metal.[2] We are currently trying to mimic this effect using a cyclopentadienyl ligand containing four phenyl groups and a chiral substituent, R*. *X*-Ray structures of arylcyclopentadienyl compounds indicate that all four phenyl rings could not be coplanar[3–9] and their disymmetric orientation could therefore be governed by a suitable choice of the chiral substituent R*. Such chiral ligands could prove to be valuable alternatives to chiral phosphine ligands in catalytic asymmetric synthesis given that chiral phosphine ligands are often only successful with a limited type of substrate[1] and given the fact that cyclopentadienyl compounds catalyse a wide range of reactions including hydrogenation,[10] hydroformylation,[11] isomerisation,[12] polymerisation,[13] and oxidation[14] of alkenes.

In this paper we describe our initial investigations of the chemistry of the readily available tetraphenylcyclopentadienone complexes $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**) and $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**).[15,16] Although primarily directed towards exploring methods of introducing chiral substituents into the five-membered ring, these studies highlight several interesting features of the general chemistry of these compounds and their derivatives. The reactions studied are summarised in the Scheme. These results have added significance given the recent interest in the catalytic properties of tetraphenylcyclopentadienone complexes[9] and in perarylcyclopentadienyl metal complexes in general.[17]

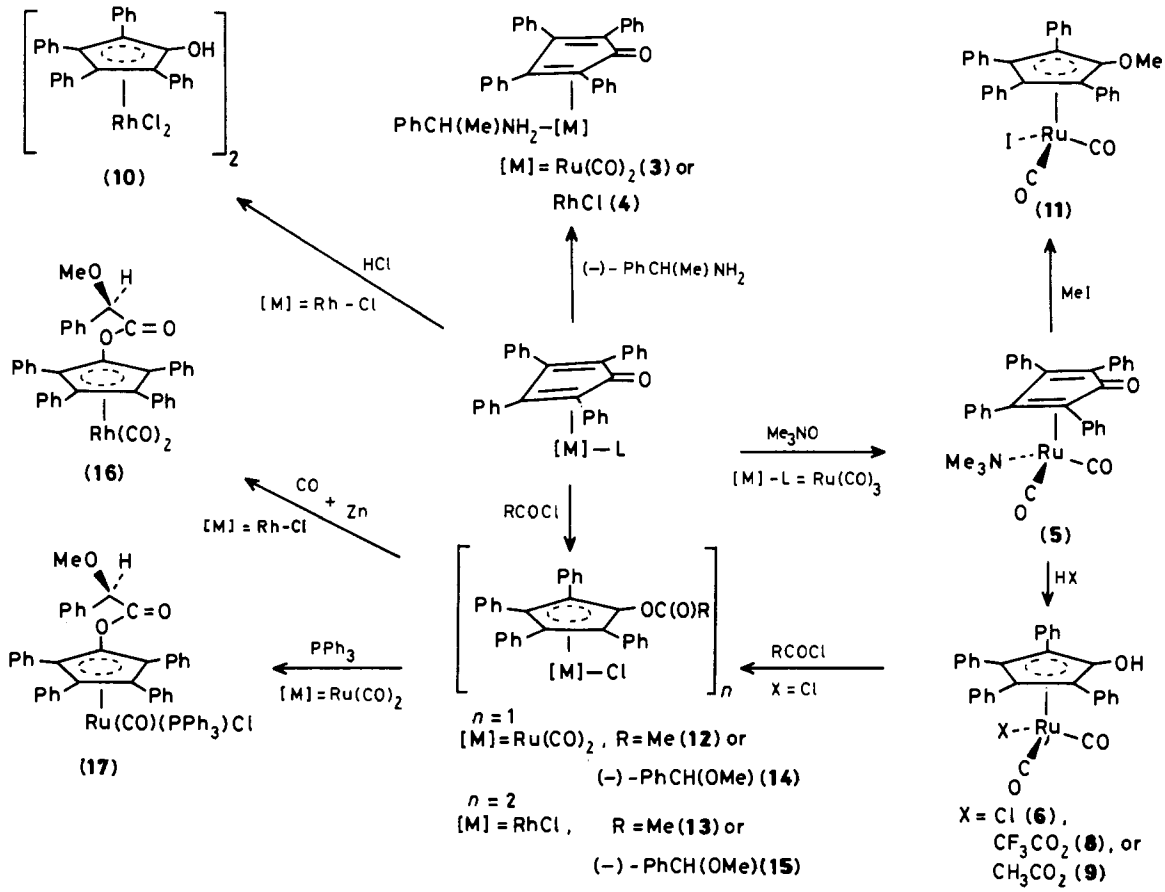
Results and Discussion

Reaction with Amines.—Schiff bases are readily formed between unco-ordinated cyclopentadienones and amines[18] and one such Schiff base co-ordinated to iron is known, *i.e.* $[Fe(\eta^4\text{-}C_5Ph_4NC_6H_4NMe_2\text{-}p)(CO)_3]$.[19] However, this latter was not prepared from the corresponding cyclopentadienone complex but by complexing the preformed Schiff base. We were interested to see if a chiral group could be directly introduced into the five-membered ring by forming a Schiff base from a chiral amine and a metal–cyclopentadienone complex.

† Dicarbonylchloro[η^5-1-D-(−)methoxy(phenyl)acetoxy-2,3,4,5-tetraphenylcyclopentadienyl]ruthenium(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: atm = 101 325 N m^{-2}.



Scheme. [M] = $Ru(CO)_2$, L = CO (**1**) or [M] = Rh–Cl, L = $Rh(\eta^4\text{-}C_5Ph_4O)Cl$ (**2**)

Rather than form a Schiff-base complex, L-(−)-α-methylbenzylamine reacted with $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**) to displace a carbonyl ligand and give $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\{NH_2CH(Me)Ph\}]$ (**3**). The nature of the product is evident from its i.r. spectrum which contains two metal–carbonyl stretching frequencies in contrast to that of the starting complex (**1**) which exhibits three such frequencies. Confirmation of the formulation comes from elemental analysis, the mass spectrum, and also the ^1H n.m.r. spectrum which shows the two diastereotopic N–H protons at δ 2.55 and 3.10 p.p.m. (Table 1). A surprising feature of the i.r. spectrum is that ν_{CO} of the cyclopentadienone ligand is shifted from 1 640 cm^{-1} to 1 600 cm^{-1} upon conversion of (**1**) to (**3**). In addition, in the ^{13}C n.m.r. spectrum of (**3**) the CO signal for the C_5Ph_4O ligand occurs at relatively high field, *i.e.* δ 142.0 p.p.m. and the other ring-carbon signals appear at δ 103.4—100.3 p.p.m. (Table 2). This is significantly different from that of (**1**) which exhibits a carbonyl signal at δ 173.8 p.p.m. and ring-carbon signals at δ 82.0 and 107.7 p.p.m. These spectral features suggest that whereas the C_5Ph_4O ligand is bonded as an η^4-cyclopentadienone in (**1**) it has significant cyclopentadienyl character in complex (**3**) with concomitant reduction in the C=O bond order. This could be aided by hydrogen bonding between the oxygen and the NH_2 group of the amine.

The corresponding reaction of L-(−)-α-methylbenzylamine with $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**) also failed to yield a Schiff-base complex and again resulted in ligand substitution at the metal to give, in this case, $[Rh(\eta^4\text{-}C_5Ph_4O)Cl\{NH_2CH(Me)Ph\}]$ (**4**). This was confirmed by elemental analysis, molecular weight determination by osmometry, and by the ^1H n.m.r. spectrum which contains the two diastereotopic N–H proton signals at δ 3.50 and 3.00 p.p.m. In contrast to the ruthenium complex (**3**) discussed above, the rhodium complex (**4**) exhibited ν_{CO} for the cyclopentadienone ligand at 1 634 cm^{-1}, very close to that of the precursor $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (1 640 cm^{-1}). The reason for this contrasting behaviour is not clear. Unfortunately, complex (**4**) proved too insoluble for ^{13}C n.m.r. studies.

Reaction with Me_3NO.—It has been reported that $[Fe(\eta^4\text{-}C_5H_4O)(CO)_3]$ may be converted to $[\{Fe(\eta^4\text{-}C_5H_4O)(CO)_2\}_2]$ either thermally or by reaction with molecular oxygen or peroxide.[20] Further, this dimeric complex is very reactive and readily oxidatively adds hydrogen halides HX to give the hydroxycyclopentadienyl complexes $[Fe(\eta^5\text{-}C_5H_4OH)(CO)_2X]$, a useful precursor to other substituted cyclopentadienyl complexes. This appeared to be an attractive route to introduce chiral substituents into a tetraphenylcyclopentadienyl ligand and therefore attempts were made to convert $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**) into the corresponding dimer $[\{Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\}_2]$ using the thermal procedure described for the corresponding iron complex; however, this appeared only to lead to extensive decomposition. Trimethylamine *N*-oxide has proved to be a successful reagent for decarbonylation[21] and therefore this was treated with (**1**) but, rather than the anticipated dimer the product was $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2(NMe_3)]$ (**5**). Microanalysis and ^1H n.m.r. spectroscopy fully support this formulation. Also, the i.r. spectrum of (**5**) is very similar to that of $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\{NH_2CH(Me)Ph\}]$ (**3**) in that it contains two metal carbonyl bands and a relatively low ν_{CO} for the C_5Ph_4O ligand, *i.e.* 1 590

Table 1. ^1H N.m.r data (δ/p.p.m.; recorded in $CDCl_3$ unless specified)

Complex	Ph	Me or OMe	Other
(3) $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\{(-)NH_2CH(Me)Ph\}]$	7.55 (4 H, d, J = 7) 7.25—6.95 (21 H, m)	1.21 (3 H, d, J = 7)	3.20 (CH, q) 3.10 (NH, br s), 2.55 (NH, br s)
(4) $[Rh(\eta^4\text{-}C_5Ph_4O)Cl\{(-)NH_2CH(Me)Ph\}]$	7.78 (3 H, br s) 7.45—6.95 (22 H, m)	1.47 (3 H, d, J = 8)	4.60 (CH, q) 3.50—3.00 (NH_2, br)
(5) $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2(NMe_3)]$	7.67 (3 H, d, J = 7) 7.52 (1 H, br s) 7.21—6.95 (16 H, m)	2.40 (9 H, s)	
(6) $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$	7.40—6.80 (20 H, m)		4.65 (OH, s)
(8) $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2\{OC(O)CF_3\}]$[a]	7.60—7.00 (20 H, m)		
(9) $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2\{OC(O)Me\}]$	7.50—6.50 (20 H, m)		4.55 (OH, s)
(10) $[\{Rh(\eta^5\text{-}C_5Ph_4OH)Cl_2\}_2]$[b]	7.85 (4 H, d, J = 7) 7.47—7.05 (16 H, m)		3.8 (OH, br s)
(11) $[Ru(\eta^5\text{-}C_5Ph_4OMe)(CO)_2I]$	7.60—6.80 (20 H, m)	3.47 (3 H, s)	
(12) $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)Me\}(CO)_2Cl]$	7.45—7.00 (20 H, m)	2.00 (3 H, s)	
(13) $[Rh\{\eta^5\text{-}C_5Ph_4OC(O)Me\}Cl_2\}_2]$	7.85—7.00 (20 H, m)	2.06 (3 H, s)	
(14) $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$	7.37—6.82 (25 H, m)	3.12 (3 H, s)	4.65 (CH, s)
(15) $[\{Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}Cl_2\}_2]$[b]	7.80 (4 H, d, J = 7) 7.56 (1 H, s) 7.40—7.00 (20 H, m)	3.35 (3 H, s)	3.52 (CH, s)
(16) $[Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2]$	7.20—6.75 (25 H, m)	3.31 (3 H, s)	3.50 (CH, s)
(17) $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)(PPh_3)Cl]$	7.40—6.56 (40 H, m)	2.99 (s), 2.95 (s) (3 H)	3.91 (s), 3.59 (s) (CH)

[a] Recorded in CF_3CO_2H, OH not observed. [b] Recorded in $[^2H_6]$acetone.

Table 2. $^{13}C\text{-}\{^1H\}$ N.m.r. data (δ/p.p.m.; recorded in $CDCl_3$ unless specified)

Complex	Ph	C_5 Ring	Ru–CO	Other
(1) $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$	133.0—127.9	107.7, 82.0 173.8 (CO)	194.3	
(3) $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\{(-)NH_2CH(Me)Ph\}]$	132.0—125.8	103.4, 103.1 101.5, 100.3 142.0 (CO)	200.1	24.5 (Me) 59.6 (CH)
(5) $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2(NMe_3)]$	133.4—125.9	102.9, 81.8 167.0 (CO)	201.1	58.0 (Me)
(6) $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$	133.3—125.9	102.9, 89.5 146.3 (COH)	188.0	
(8) $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2\{OC(O)CF_3\}]$[a]	132.0—127.6	102.9, 81.8 143.7 (COH)	196.9	
(11) $[Ru(\eta^5\text{-}C_5Ph_4OMe)(CO)_2I]$	132.0—127.6	101.7, 87.8 145.8 (*C*OMe)	197.2	62.8 (OMe)
(12) $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)Me\}(CO)_2Cl]$[b]	132.1—127.8	105.0, 95.2 135.6 (CO_2*C*Me)	213.7	51.2 (Me) 168.2 (CO_2)
(14) $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$	132.0—127.2	105.4 (2C) 94.6, 94.9 134.3 (COR)	195.8	57.5 (OMe) 81.9 (CH) 168.1 (CO_2)
(17) $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)(PPh_3)Cl]$	133.3—127.5	105.5—101.0[c] 99.0—92.4[c] 134.3, 133.9 (COR)	*d*	57.6 (OMe) 81.7, 81.3 (CH) 170.1 (CO_2)

[a] Recorded in CF_3CO_2H. [b] Recorded in $[^2H_2]$dichloromethane. [c] Broad due to overlapping signals of diastereoisomers and ^{31}P coupling. [d] Not observed.

cm^{-1}. Curiously, however, despite this low value the ^{13}C n.m.r. spectrum of the C_5Ph_4O ligand in (**5**) resembles that of $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**) rather than the 'cyclopentadienyl-like' $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\{NH_2CH(Me)Ph\}]$ (**3**) (Table 2).

Oxidative Addition Reactions.—Complex (**5**) proved to be extremely reactive and to undergo oxidative addition reactions readily with concomitant loss of trimethylamine. For example, within minutes of bubbling hydrogen chloride through a light petroleum solution of (**5**), $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$ (**6**) precipitated out quantitatively. A clear indication that a hydroxycyclopentadienyl complex is formed comes from monitoring the i.r. spectrum of the reaction. The ketonic ν_{CO} stretch at 1 590 cm^{-1} present in the spectrum of $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2(NMe_3)]$ (**5**) is replaced by bands at 1 460 and 1 440 cm^{-1} together with bands at 2 995 and 2 820 cm^{-1}; similar absorptions have been reported for $\nu_{C\text{-}OH}$ and $\nu_{O\text{-}H}$ in $[Co(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5Ph_4OH)]BF_4$.[22] Also, in keeping with the product being a hydroxycyclopentadienyl complex, the ^{13}C n.m.r. spectrum of (**6**) contained a signal at δ 146.3 characteristic of a C–OH group; this contrasts with the spectrum of the starting complex (**5**) which contains a CO signal at δ 167.0. Other workers have reported a similar ^{13}C n.m.r. shift for the C–OH group in (**6**) although no preparative or other spectroscopic details for this compound were given.[9]

Complex (**6**) proved to be unstable and satisfactory elemental

analysis could not be obtained. Within 4 h at room temperature a chloroform solution was completely converted to a compound whose i.r. spectrum contained metal carbonyl bands at 2 010 and 1 965 cm^{-1}. We suggest that this compound is $[\{Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\}_2]$ (**7**), produced by loss of hydrogen chloride from (**6**). Mays and co-workers[23] have recently determined the *X*-ray structure of genuine $[\{Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\}_2]$ and the i.r. spectrum reported is identical to that of (**7**). The i.r. spectrum of (**7**) is different to that of the unstable compound previously formulated as $[\{Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2\}_2]$[24] and recently shown to be $[\{Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2H\}_2]$ containing a bridging hydride and a hydrogen-bonded oxygen atom.[9] However, the elemental analysis of (**7**) always showed the presence of variable traces of nitrogen (0.6—1.2%) suggesting incomplete removal of trimethylamine or, more probably, trimethylammonium chloride from the original $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$ (**6**). Attempts to chromatograph either of the complexes (**6**) or (**7**) resulted in decomposition. Thus, the exact nature of (**7**) remains unsubstantiated.

Analogous oxidative addition to $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_2(NMe_3)]$ (**5**) occurred with both trifluoroacetic acid and acetic acid to give $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2\{OC(O)CF_3\}]$ (**8**) and $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2\{OC(O)Me\}]$ (**9**) respectively. These compounds proved to be even more unstable than the corresponding chloro-complex, especially complex (**9**) which in solution lost acetic acid within minutes to give (**7**). Complex $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**) appeared to undergo similar oxidative addition reactions. Thus, bubbling hydrogen chloride through a chloroform solution of (**2**) for 30 min gave a yellow precipitate, believed to be $[\{Rh(\eta^5\text{-}C_5Ph_4OH)Cl_2\}_2]$ (**10**). Consistent with this proposal the i.r. spectrum of the freshly precipitated product exhibited a strong band in the region 3 200—3 000 cm^{-1} characteristic of a hydrogen-bonded hydroxy group. However, (**10**) was so unstable that even attempts to remove solvent from the compound by suction regenerated the brown complex $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**).

Methyl iodide also oxidatively added to (**5**) to give $[Ru(\eta^5\text{-}C_5Ph_4OMe)(CO)_2I]$ (**11**). In contrast to the reactions discussed above this oxidative addition reaction was not reversible and the stable product (**11**) was characterized by elemental analysis, i.r., ^1H, and ^{13}C n.m.r. spectroscopy. The most significant spectroscopic features of the methoxytetraphenylcyclopentadienyl ligand were ν_{CO} at 1 490 cm^{-1} and, in the ^{13}C n.m.r. spectrum, the COMe signals at δ 145.8 and 62.8 p.p.m. Attempts oxidatively to add menthyl chloride to (**5**) in an analogous manner and thus introduce a chiral substituent onto the five-membered ring were unsuccessful.

Acetyl chloride oxidatively added to $[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**) to give the corresponding acetoxytetraphenylcyclopentadienyl complex $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)Me\}(CO)_2Cl]$ (**12**); again this compound was stable and showed no tendency to undergo reductive elimination. A standard way of preparing acetato esters of alcohols is to react the alcohol with acetyl chloride and complex (**12**) can indeed be prepared by the reaction between acetyl chloride and complex $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$ (**6**). The rhodium complex $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**) also oxidatively added acetyl chloride but, in contrast to the ruthenium complex (**12**) discussed above, the product $[\{Rh\{\eta^5\text{-}C_5Ph_4OC(O)Me\}Cl_2\}_2]$ (**13**), readily reverted to the original complex within hours at room temperature. The i.r. spectra of (**12**) and (**13**) contain ν_{CO} bands at 1 710 and 1 330 cm^{-1} and 1 790 and 1 400 cm^{-1} respectively; a ν_{CO} band at 1 789 cm^{-1} has been reported for the analogous compound $[Fe\{\eta^5\text{-}C_5H_4OC(O)Me\}(CO)_2Cl]$.[20]

The successful preparation of the esters (**12**) and (**13**) immediately suggested a method of introducing a chiral substituent into the cyclopentadienyl ring by analogous reactions using a chiral acid chloride. Hence, (−)methoxy(phenyl)acetyl chloride was treated with $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$ (**6**) to give the chiral ester complex $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$ (**14**). Similarly, when a benzene solution of $[\{Rh(\eta^4\text{-}C_5Ph_4O)Cl\}_2]$ (**2**) was refluxed with (−)methoxy(phenyl)acetyl chloride the chiral ester complex $[\{Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}Cl_2\}_2]$ (**15**) precipitated out. Unlike the corresponding rhodium–acetoxy complex (**13**) this latter complex was quite stable and showed no tendency to undergo reductive elimination; the reason for this marked difference in stability is not understood.

Comparison of the metal carbonyl stretching frequencies in the two ruthenium ester complexes (**12**) and (**14**) reveals that they are virtually identical but *ca.* 20 cm^{-1} higher than the corresponding bands in $[Ru(\eta^5\text{-}C_5Ph_4OH)(CO)_2Cl]$ (**6**). This suggests that the ester function is withdrawing significant electron density from the ruthenium. There are, it may be noted, significant differences between the ester absorbances of (**12**) and (**14**) but this is not uncommon in esters since such bands are rarely pure C–O stretching frequencies. The rhodium ester complex (**15**) proved to be too insoluble for ^{13}C n.m.r. spectroscopy but the ^{13}C n.m.r. spectrum of the corresponding ruthenium complex $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$ (**14**) is given in Table 2. It should be noted that this spectrum shows no evidence for the presence of diastereoisomers suggesting that the chiral centre in the ester function is too remote to lock the phenyl substituents on the cyclopentadienyl ring into a chiral array. This was confirmed by the *X*-ray structure determination of (**14**).

X-Ray Structure of $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$ (**14**).—The structure is illustrated in the Figure, together with the atom labelling used in the Tables. Selected geometric parameters, with estimated standard deviations are given in Table 3.

The molecule has a piano-stool geometry around the ruthenium with a chlorine and two carbonyl ligands in the basal sites: there is disorder of the chlorine and one of the carbonyl ligands between the two sites, with a small, but statistically significant preference for one conformer. The cyclopentadienyl ligand is substituted with four phenyl groups, which adopt a 'propeller' conformation with angles of 61, 54, 60, and 41° respectively between their normals and the normal to the mean plane through atoms C(1), C(2), C(4), and C(5). The remaining site is occupied by a bulky ester function which contains a carbon atom, C(31), the chirality of which was confirmed by anomalous scattering results. The only significantly short intramolecular contacts are between the substituent phenyl groups on the cyclopentadienyl ring, and there are none from these phenyl substituents to either the phenyl of the ester group or to the basal ligands. It is clear therefore that although the 'propeller' of phenyl substituents has a different conformation from that of related molecules, *e.g.* $[Mn(\eta^5\text{-}C_5Ph_4OSnPh_3)(CO)_3]$,[3] this is determined by crystal packing forces rather than by the chirality of the remote ester function.

It is interesting that whereas the phenyl ring-substituents are displaced from the mean ring plane in a direction away from the ruthenium the oxygen of the ester function is slightly displaced towards the metal. The bond lengths within the cyclopentadienyl ring, although rather long, are acceptable within estimated standard deviations. The ring is not precisely planar; atom C(3) is displaced 0.13 Å out of the plane through the remaining four atoms in a direction towards the ruthenium. Atom C(3) is positioned almost exactly *trans* to the site of highest chlorine occupancy. It is tempting to suggest that, since chlorine is, if anything, a π-electron donor and carbonyl is a strong π-acceptor, the opportunities for back donation to the cyclopentadienyl ring will be greater *trans* to chlorine rather than *trans* to the more competitive carbonyl ligands. This shows

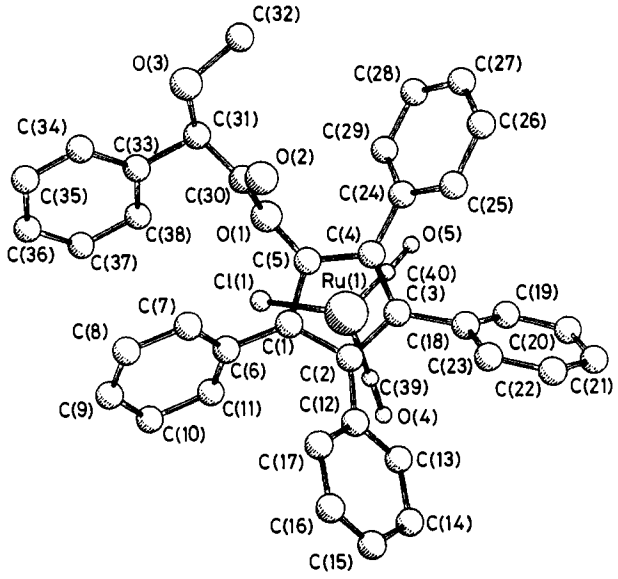


Figure. The molecular structure of $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$ (**14**) with atom labelling. The disorder component of higher occupancy is shown

itself in the out-of-plane displacement of atom C(3) to give a shorter ruthenium–carbon distance: the high estimated standard deviations, and the associated disorder problems, do not permit the detection of any bond localisation towards a 'diene' type geometry which might result. Such bond localisation has been observed in similar molecules in which the π-bonding characteristics of the *trans* ligands lack cylindrical symmetry, for example in $[Ru(\eta^5\text{-}C_5Me_4Et)(CO)_2Br]$.[25]

Reactions of $\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph$ *Complexes.*—$[\{Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}Cl_2\}_2]$ (**15**) like other substituted cyclopentadienyl rhodium complexes[26] reacts with carbon monoxide in the presence of zinc to give the corresponding dicarbonyl complex $[Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2]$ (**16**). Although air-sensitive, this compound was otherwise quite stable.

Triphenylphosphine reacted with complex (**14**) to displace a carbonyl ligand to give $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)(PPh_3)Cl]$ (**17**). This complex contains a chiral ruthenium centre in addition to the chiral ester function. The formation of diastereoisomers is clearly evident in the ^1H, ^{13}C, and ^{31}P n.m.r. spectra (Tables 1 and 2) and integration of the ^{31}P and ^1H spectra showed the diastereoisomeric excess to be 22%. This compares with a diastereoisomeric excess of 6% obtained when the chiral ruthenium centre in $[Ru\{\eta^5\text{-}C_5H_4\text{-}(+)\text{-}C_{10}H_{19}\}(CO)(PPh_3)Cl]$ [$C_{10}H_{19}$ = neomenthyl (*c*-2-isopropyl-*t*-5-methylcyclohexan-*r*-1-yl)] is formed by an analogous carbonyl displacement reaction.[27] This would seem to suggest that although the chiral centre is remote from the metal, the $\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph$ ligand has considerably greater stereochemical influence than the $\eta^5\text{-}C_5H_4\text{-}(+)\text{-}C_{10}H_{19}$ ligand especially when one considers that the neomenthyl complex was prepared at a temperature 10 °C below that of (**17**). Initial experiments indicate, however, that the $\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph$ ligand is a rather ineffective ligand when used in catalytic asymmetric synthesis. Thus, $[Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2]$ (**16**) catalyses the hydroformylation of vinyl acetate to give 2-acetoxypropanal with 3% enantiomeric excess (e.e.) and $[\{Rh\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}Cl_2\}_2]$ (**15**) catalyses the hydrogenation of (*Z*)-methyl α-acetamidocinnamate to give 6% e.e. *N*-acetyl-D-phenylalanine methyl ester. Clearly, the chiral substituent in the above complexes is too remote to lock the phenyl substituents into a chiral array and our present work is directed towards the synthesis of more effective ligands in which the chiral substituent is joined directly to the tetraphenylcyclopentadienyl ring.

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations, and shortest intramolecular contacts (Å) for $[Ru\{\eta^5\text{-}C_5Ph_4OC(O)CH(OMe)Ph\}(CO)_2Cl]$ (**14**)

Ru(1)–Cl(1)	2.444(8)	Ru(1)–Cl(2)	2.477(13)
Ru(1)–C(40)	1.88(4)	Ru(1)–C(41)	1.87(5)
C(40)–O(5)	1.08(4)	C(41)–O(6)	1.11(6)
Ru(1)–C(39)	1.934(21)	C(39)–O(4)	1.076(27)
Ru(1)–C(1)	2.246(19)	C(1)–C(2)	1.519(26)
Ru(1)–C(2)	2.297(18)	C(2)–C(3)	1.467(25)
Ru(1)–C(3)	2.202(18)	C(3)–C(4)	1.387(25)
Ru(1)–C(4)	2.292(18)	C(4)–C(5)	1.436(27)
Ru(1)–C(5)	2.224(20)	C(5)–C(1)	1.431(28)
C(5)–O(1)	1.370(24)	C(30)–C(31)	1.500(27)
O(1)–C(30)	1.370(23)	C(31)–O(3)	1.349(22)
C(30)–O(2)	1.195(25)	O(3)–C(32)	1.494(28)
C(6) · · · C(17)	3.24	C(13) · · · C(23)	3.27
C(11) · · · C(12)	3.50	C(18) · · · C(25)	3.08
C(12) · · · C(23)	3.23	C(7) · · · C(30)	3.46
C(13) · · · C(18)	3.33	C(29) · · · C(30)	3.50
C(39)–Ru(1)–Cl(1)	90.6(7)	C(5)–C(1)–C(2)	105.4(16)
C(39)–Ru(1)–Cl(2)	84.7(7)	C(1)–C(2)–C(3)	105.0(15)
C(39)–Ru(1)–C(40)	84.5(13)	C(2)–C(3)–C(4)	110.3(15)
C(39)–Ru(1)–C(41)	93.7(18)	C(3)–C(4)–C(5)	107.9(16)
Cl(1)–Ru(1)–C(40)	88.6(12)	C(4)–C(5)–C(1)	110.6(17)
Cl(2)–Ru(1)–C(41)	87.2(17)	C(5)–O(1)–C(30)	119.1(15)
Ru(1)–C(39)–O(4)	174.9(19)	O(1)–C(30)–O(2)	123.7(18)
Ru(1)–C(40)–O(5)	170(3)	O(1)–C(30)–C(31)	111.1(16)
Ru(1)–C(41)–O(6)	170(5)	O(2)–C(30)–C(31)	125.1(18)

Experimental

Microanalyses were carried out by the University of Sheffield Microanalytical Laboratory. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R-34 (220 MHz) spectrometer using $SiMe_4$ as an internal reference. Carbon-13 and ^{31}P n.m.r. spectra were recorded on a JEOL PFT-100 n.m.r. spectrometer using $SiMe_4$ as an internal reference (for ^{13}C) and H_3PO_4 as external reference (for ^{31}P) respectively. Molecular weights were determined osmometrically in chloroform and i.r. spectra were measured on a PE-157G spectrometer. All reactions were carried out under an atmosphere of nitrogen although the compounds were subsequently found not to be particularly air-sensitive.

$[Ru(\eta^4\text{-}C_5Ph_4O)(CO)_3]$ (**1**)[15] and D-(−)methoxy(phenyl)-acetyl chloride[28] were prepared as previously described.

Di-μ-chloro-bis[(η⁴-*tetraphenylcyclopentadienone*)*rhodium*-(I)] (**2**).—This complex was prepared by a modification of the method previously described.[16] Tetraphenylcyclopentadienone (1.05 g, 3 mmol) and $[\{Rh(C_2H_4)_2Cl\}_2]$ (0.5 g, 1.25 mmol) were refluxed in benzene (50 cm^3) under nitrogen for 48 h. The solution was then concentrated on a rotary evaporator to *ca.* 5 cm^3 and then chromatographed on a silica column (20 cm) using dichloromethane–ethanol (9:1) as eluant. Removal of the solvent *in vacuo* gave the product in the form of dark red crystals (0.84 g, 60%), m.p. 320—322 °C (decomp.) [lit.,[16] 316—318 °C (decomp.)]. I.r. (Nujol); ν_{CO} at 1 640s cm^{-1}.

Dicarbonyl[L-α-*methylbenzylamine*](η⁴-*tetraphenylcyclopentadienone*)*ruthenium* (**3**).—A solution of $[Ru(\eta^4\text{-}C_5Ph_4O)$-

$(CO)_3$] (570 mg, 1 mmol) and L-(−)-α-methylbenzylamine (121 mg, 1 mmol) was refluxed in dry benzene (60 cm^3) under nitrogen for 24 h to give a bright yellow solution. Solvent was removed *in vacuo* to leave yellow crystals which were recrystallised from diethyl ether to give the pure yellow product (603 mg, 89%), m.p. 80—82 °C (decomp.) [Found: C, 69.5; H, 4.7; N, 2.2%; *M*, 663. $C_{39}H_{31}NO_3Ru$ requires C, 70.8; H, 4.7; N, 2.1%; *M*, 663). I.r. (KBr): ν_{CO} at 2 008s, 1 960s, and 1 600s; ν_{NH} at 3 200w cm^{-1}.

Chloro[L-(−)-α-*methylbenzylamine*](η⁴-*tetraphenylcyclopentadienone*)*rhodium*(I) (**4**).—A mixture of [{Rh(η⁴-C_5Ph_4O)Cl}$_2$] (300 mg, 0.287 mmol) and L-(−)-α-methylbenzylamine (90 mg, 743 mmol) was refluxed in dry benzene (30 cm^3) under nitrogen for 48 h. Upon cooling the brown product crystallised out; this was filtered off and dried *in vacuo* (280 mg, 76%) [Found: C, 69.2; H, 4.9; Cl, 6.6; N, 2.0%; *M*($CHCl_3$), 639. $C_{37}H_{31}ClNORh$ requires C, 69.0; H, 4.9; Cl, 5.5; N, 2.2%; *M*, 644]. I.r. (Nujol): ν_{CO} at 1 634s cm^{-1}.

Dicarbonyl(η⁴-*tetraphenylcyclopentadienone*)(*trimethylamine*)*ruthenium* (**5**).—A mixture of [Ru(η⁴-C_5Ph_4O)$(CO)_3$] (150 mg, 0.26 mmol) and trimethylamine *N*-oxide (50 mg, 0.67 mmol) was refluxed under nitrogen in dry benzene (50 cm^3) for 24 h to give a dark green solution. The solvent was removed *in vacuo* to give the product in the form of green crystals (125 mg, 77%), m.p. 172—175 °C (Found: C, 67.2; H, 5.2; N, 2.3. $C_{34}H_{29}NO_3Ru$ requires C, 67.9; H, 4.9; N, 2.3%). I.r. ($CHCl_3$): ν_{CO} at 2 005s, 1 953s, and 1 590s cm^{-1}.

Dicarbonylchloro(η⁵-1-*hydroxy*-2,3,4,5-*tetraphenylcyclopentadienyl*)*ruthenium*(II) (**6**).—[Ru(η⁴-C_5Ph_4O)$(CO)_2$-(NMe_3)] (130 mg, 0.216 mmol) was dissolved in light petroleum (b.p. 40—60 °C, 50 cm^3) and hydrogen chloride gas was bubbled through the solution. The yellow product immediately precipitated from the solution together with trimethylammonium chloride. When precipitation was complete the product was extracted into diethyl ether (3 × 10 cm^3); removal of the diethyl ether *in vacuo* gave yellow unstable crystals which were characterised by i.r., ^1H, and ^{13}C n.m.r. spectroscopy (105 mg, 68%). I.r. ($CHCl_3$): ν_{CO} at 2 039s and 1 990s, ν_{OH} at 2 995s and 2 820s, ν_{C-OH} at 1 460w and 1 440m cm^{-1}.

Dicarbonyl(η⁵-1-*hydroxy*-2,3,4,5-*tetraphenylcyclopentadienyl*)*trifluoroacetatoruthenium*(II) (**8**).—[Ru(η⁴-C_5Ph_4O)-$(CO)_2(NMe_3)$] (100 mg, 0.167 mmol) was dissolved in trifluoroacetic acid (20 cm^3) and the solution refluxed for 20 h. The trifluoroacetic acid was then removed on a rotary evaporator to leave unstable brown crystals which were characterised by i.r., ^1H, and ^{13}C n.m.r. spectroscopy. I.r. ($CHCl_3$): ν_{CO} at 2 040s and 2 000s, ν_{OH} at 2 970s and 2 880s, ν_{OCO} at 1 690s and 1 465s cm^{-1}.

Acetatodicarbonyl(η⁵-1-*hydroxy*-2,3,4,5-*tetraphenylcyclopentadienyl*)*ruthenium*(II) (**9**).—[Ru(η⁴-C_5Ph_4O)$(CO)_2$-(NMe_3)] (100 mg, 0.167 mmol) was dissolved in acetic acid (50 cm^3) and the solution refluxed for 1 week. The product was isolated and characterised spectroscopically as described above for the trifluoroacetato analogue. I.r. ($CHCl_3$); ν_{CO} at 2 050s and 1 985s, ν_{OH} 3 000—2 800m, ν_{OCO} at 1 730s and 1 450s cm^{-1}.

Di-μ-*chloro-bis*[*chloro*(η⁵-1-*hydroxy*-2,3,4,5-*tetraphenylcyclopentadienyl*)*rhodium*(III)] (**10**).—Hydrogen chloride gas was bubbled through a solution of [{Rh(η⁵-C_5Ph_4O)Cl}$_2$] (250 mg, 0.239 mmol) in chloroform (10 cm^3) at 5 °C. After 10 min the precipitate of yellow crystals formed was filtered off and washed with diethyl ether (2 × 5 cm^3) (110 mg, 41%). Attempts to dry the compound further by suction resulted in loss of hydrogen chloride and regeneration of the original tetraphenylcyclopentadienone complex. The product was therefore characterised by i.r. and n.m.r. spectroscopy. I.r. (Nujol); ν_{OH} at 3 200—3 000br cm^{-1}.

Dicarbonyliodo(η⁵-1-*methoxy*-2,3,4,5-*tetraphenylcyclopentadienyl*)*ruthenium*(II) (**11**).—[Ru(η⁴-C_5Ph_4O)$(CO)_2(NMe_3)$] (200 mg, 0.333 mmol) and an excess of methyl iodide (2 cm^3) were refluxed under nitrogen in dry benzene for 24 h; the green solution turned brown. Removal of the solvent *in vacuo* yielded a brown solid which crystallised from diethyl ether as brown crystals (325 mg, 78%) (Found: C, 56.4; H, 3.4; I, 18.4. $C_{32}H_{23}IO_3Ru$ requires C, 56.2; H, 3.4; I, 18.6%). I.r. ($CHCl_3$); ν_{CO} at 2 020s and 1 998s, ν_{COMe} at 1 490s cm^{-1}.

(η⁵-1-*Acetoxy*-2,3,4,5-*tetraphenylcyclopentadienyl*)-*dicarbonylchlororuthenium*(II) (**12**).—(*i*) [Ru(η⁴-C_5Ph_4O)-$(CO)_3$] (200 mg, 0.351 mmol) was dissolved in acetyl chloride (10 cm^3) and refluxed for 4 h. The acetyl chloride was then removed on the rotary evaporator and the yellow residue crystallised from chloroform–diethyl ether (150 mg, 69%) (Found: C, 62.9; H, 3.8; Cl, 6.2. $C_{33}H_{23}ClO_4Ru$ requires C, 63.9; H, 3.7; Cl, 5.7%). I.r. ($CHCl_3$): ν_{CO} at 2 060s, 2 008s, and 1 710s; ν_{C-O} at 1 330s cm^{-1}.

(*ii*) [Ru(η⁴-C_5Ph_4O)$(CO)_3$] (120 mg, 0.208 mmol) and acetyl chloride (2 cm^3) were refluxed for 5 h under nitrogen in hexane (40 cm^3); on cooling the product crystallised out. It was filtered off, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo* (95 mg, 76%).

(*iii*) [Ru(η⁵-C_5Ph_4OH)$(CO)_2Cl$] (100 mg, 0.173 mmol) was dissolved in acetyl chloride (10 cm^3) and refluxed for 8 h. The acetyl chloride was then removed on the rotary evaporator to give the product in the form of yellow crystals (70 mg, 65%).

Dicarbonylchloro[η⁵-1-D-(−)*methoxy*(*phenyl*)*acetoxy*-2,3,4,5-*tetraphenylcyclopentadienyl*]*ruthenium*(II) (**14**).—D-(−)-Methoxy(phenyl)acetyl chloride (100 mg, 0.542 mmol) and [Ru(η⁵-C_5Ph_4OH)$(CO)_2Cl$] (300 mg, 0.519 mmol) were refluxed under nitrogen in hexane (60 cm^3) for 16 h. Upon cooling a green solid crystallised out; this was filtered off, recrystallised from chloroform–diethyl ether and dried *in vacuo* (240 mg, 67%) (Found: C, 65.4; H, 3.9; Cl, 5.2. $C_{40}H_{29}ClO_5Ru$ requires C, 66.1; H, 4.0; Cl, 4.9%). I.r. ($CHCl_3$): ν_{CO} at 2 060s and 2 010s, ν_{OCO} at 1 785s and 1 360s cm^{-1}.

Di-μ-*chloro-bis*[*chloro*{η⁵-1-D-(−)*methoxy*(*phenyl*)*acetoxy*-2,3,4,5-*tetraphenylcyclopentadienyl*}*rhodium*(III)] (**15**).—[{Rh-(η⁴-C_5Ph_4O)Cl}$_2$] (522 mg, 0.5 mmol) and D-(−)methoxy-(phenyl)acetyl chloride (254 mg, 1.375 mmol) were refluxed under nitrogen in benzene (70 cm^3) for 18 h. The solution was then concentrated on a rotary evaporator to *ca.* 15 cm^3 and the brown crystalline precipitate filtered off and dried *in vacuo* (385 mg, 54%) (Found: C, 65.1; H, 4.0; Cl, 8.6. $C_{76}H_{58}Cl_4O_6Rh_2$ requires C, 64.5; H, 4.1; Cl, 10.0%). I.r. (Nujol): ν_{OCO} at 1 790s and 1 400s cm^{-1}.

Dicarbonyl[η⁵-1-D-(−)*methoxy*(*phenyl*)*acetoxy*-2,3,4,5-*tetraphenylcyclopentadienyl*]*rhodium*(I) (**16**).—Carbon monoxide was bubbled for 3 h through a well stirred suspension of [{Rh{η⁵-$C_5Ph_4OC(O)CH(OMe)Ph$}Cl_2}$_2$] (300 mg, 0.433 mmol) and zinc dust (60 mg, 0.918 mmol) in methanol (50 cm^3) at 65 °C. The solution was then filtered and the solution slowly concentrated *in vacuo* to 5 cm^3. The brown crystals formed were filtered off and dried (210 mg, 70%) (Found: C, 69.2; H, 4.3. $C_{40}H_{29}O_5Rh$ requires C, 69.4; H, 4.2%). I.r. ($CHCl_3$): ν_{CO} at 2 035s, 1 922s, and 1 660m cm^{-1}.

Carbonylchloro[η⁵-1-D-(−)*methoxy*(*phenyl*)*acetoxy*-2,3,4,5-*tetraphenylcyclopentadienyl*](*triphenylphosphine*)*ruthenium*(II) (**17**).—A solution of [Ru{η⁵-$C_5Ph_4OC(O)CH(OMe)Ph$}-

Table 4. Atomic positional parameters with estimated standard deviations for [Ru{η^5-$C_5Ph_4OC(O)CH(OMe)Ph$}$(CO)_2Cl$] (**14**)*

Atom	*X/a*	*Y/b*	*Z/c*
Ru(1)	0.103 92(6)	0.224 79(12)	0.089 43(19)
O(1)	0.217 9(4)	0.133 5(9)	0.140 4(14)
O(2)	0.251 3(6)	0.056 1(11)	0.332 3(16)
O(3)	0.339 1(5)	0.002 8(9)	0.169 7(17)
O(4)	0.015 9(6)	0.363 3(11)	0.029 0(19)
C(1)	0.161 7(6)	0.247 0(13)	0.273 3(24)
C(2)	0.104 5(8)	0.242 5(12)	0.334 8(16)
C(3)	0.083 5(7)	0.152 3(12)	0.290 3(20)
C(4)	0.124 7(6)	0.099 8(12)	0.229 8(21)
C(5)	0.171 2(8)	0.158 3(14)	0.210 9(24)
C(6)	0.202 4(7)	0.321 6(14)	0.296 6(22)
C(7)	0.246 7(8)	0.300 6(12)	0.374 3(22)
C(8)	0.283 9(10)	0.367 9(17)	0.402 8(37)
C(9)	0.275 9(8)	0.455 2(17)	0.350 9(28)
C(10)	0.230 2(10)	0.478 5(17)	0.276 2(30)
C(11)	0.191 8(7)	0.406 4(14)	0.245 9(30)
C(12)	0.080 1(6)	0.311 7(12)	0.425 6(26)
C(13)	0.026 2(6)	0.340 7(14)	0.404 7(27)
C(14)	0.002 0(8)	0.398 9(15)	0.508 5(29)
C(15)	0.035 4(10)	0.427 8(15)	0.623 7(29)
C(16)	0.084 2(10)	0.398 1(20)	0.639 2(28)
C(17)	0.110 1(8)	0.341 3(14)	0.543 2(24)
C(18)	0.030 1(8)	0.115 6(14)	0.339 5(22)
C(19)	−0.011 1(7)	0.090 8(15)	0.239 6(22)
C(20)	−0.061 0(9)	0.061 3(17)	0.285 5(30)
C(21)	−0.075 3(7)	0.062 5(14)	0.428 2(29)
C(22)	−0.033 2(10)	0.089 5(17)	0.533 5(26)
C(23)	0.015 6(9)	0.121 4(15)	0.480 0(29)
C(24)	0.123 6(6)	0.001 2(14)	0.192 1(23)
C(25)	0.099 7(7)	−0.058 1(13)	0.291 6(19)
C(26)	0.104 2(9)	−0.155 0(13)	0.270 7(23)
C(27)	0.125 3(7)	−0.188 6(16)	0.146 1(26)
C(28)	0.148 4(8)	−0.131 9(17)	0.044 8(25)
C(29)	0.147 8(6)	−0.034 5(13)	0.065 1(24)
C(30)	0.257 4(6)	0.086 3(15)	0.213 8(25)
C(31)	0.306 5(7)	0.070 9(13)	0.121 3(18)
C(32)	0.315 0(9)	−0.090 8(16)	0.150 8(30)
C(33)	0.338 7(7)	0.159 5(14)	0.112 1(23)
C(34)	0.391 2(9)	0.164 9(17)	0.177 5(21)
C(35)	0.420 5(11)	0.244 5(20)	0.166 9(33)
C(36)	0.398 1(12)	0.324 2(16)	0.103 0(35)
C(37)	0.348 2(10)	0.321 9(20)	0.038 2(34)
C(38)	0.315 8(7)	0.239 7(15)	0.042 1(24)
C(39)	0.048 2(8)	0.314 3(15)	0.044 4(23)
Cl(1)	0.166 5(3)	0.299 5(5)	−0.078 2(10)
Cl(2)	0.062 7(5)	0.133 8(8)	−0.107 8(17)
O(5)	0.059 4(9)	0.110(2)	−0.144(3)
O(6)	0.176 1(12)	0.295(2)	−0.142(4)
C(40)	0.074 7(14)	0.159(3)	−0.066(4)
C(41)	0.152 6(19)	0.271(4)	−0.047(5)

* Atoms Cl(2), O(6), and C(41) are the chlorine and carbonyl ligand of lower occupancy.

$(CO)_2Cl$] (200 mg, 0.275 mmol) and triphenylphosphine (79 mg, 0.30 mmol) in toluene (50 cm^3) was refluxed under nitrogen for 24 h. The solvent was removed *in vacuo*; ^1H and ^{31}P n.m.r. analysis of the crude product showed that the diastereoisomeric ratio was 39:61. Recrystallisation of the crude material from dichloromethane–hexane gave yellow crystals (180 mg, 68%) (Found: C, 70.9; H, 4.6; Cl, 3.7. $C_{57}H_{44}ClO_4PRu$ requires C, 71.3; H, 4.6; Cl, 3.7%). I.r. ($CHCl_3$): ν_{CO} at 1 968s and 1 775s cm^{-1}; ^{31}P-{^1H} n.m.r. ($CDCl_3$); δ, 48.20 and 48.01 p.p.m.

Structure Determination of [Ru{η^5-$C_5Ph_4OC(O)CH(OMe)Ph$}$(CO)_2Cl$] (**14**).—*Crystal data.* $C_{40}H_{29}ClO_5Ru$, M = 762.12, crystallises from chloroform–diethyl ether as pale yellow needles, crystal dimensions 0.35 × 0.15 × 0.11 mm, orthorhombic, a = 24.58(3), b = 14.518(13), c = 9.299(4) Å, U = 3 315(5) Å^3, D_m = 1.45, Z = 4, D_c = 1.455 g cm^{-3}, space group $P2_12_12_1$ (no. 19), Mo-K_α radiation (λ = 0.710 69 Å), μ(Mo-K_α) = 5.87 cm^{-1}, F(000) = 1 480.

Three-dimensional X-ray diffraction data were collected in the range 6.5 < 2θ < 50° on a Stoe Stadi-2 diffractometer by the ω-scan method. The 1 425 independent reflections for which $I/\sigma(I) > 3.0$ were corrected for Lorentz and polarisation effects, but not for absorption. The structure was solved by standard Patterson and Fourier techniques and refined by block-diagonal least-squares methods. Hydrogen atoms were detected and placed in calculated positions [C–H 0.98 Å, C–C–H (methyl) 112°]; their contributions were included in structure factor calculations (B = 8.0 Å^2) but no refinement of positional parameters was permitted. The chlorine and a carbonyl group were disordered over two sites and the occupancy factor was optimised to 0.61:0.39; the positional parameters of overlapping atoms were refined in alternate cycles. Refinement converged at R 0.0541 with allowance for anisotropic thermal motion of all non-hydrogen atoms, with the exception of those of the disordered carbonyl group for which isotropic thermal parameters were refined, and for the anomalous scattering of ruthenium and chlorine. Table 4 lists the atomic positional parameters with estimated standard deviations. Scattering factors were taken from ref. 29; unit weights were used throughout the refinement and computer programs formed part of the Sheffield X-ray system.

Catalytic Studies.—(*i*) *Z*-Methyl α-acetamidocinnamate (50 mg, 0.228 mmol), [{Rh{η^5-$C_5Ph_4OC(O)CH(OMe)Ph$}Cl_2}$_2$] (**15**) (3 mg, 0.002 mmol), freshly distilled propan-2-ol (20 cm^3), and a magnetic stirrer bar were placed in a glass liner inside a steel autoclave (130-cm^3 volume). The autoclave was sealed, flushed out with hydrogen several times, and then pressurised with hydrogen to 50 atm; stirring was commenced and the autoclave heated in an oil-bath at 50 ± 1 °C for 2 d. ^1H N.m.r. analysis of the product showed that complete reduction to *N*-acetylphenylalanine had occurred and the enantiomeric excess was shown to be 6 ± 0.5% (D) by g.l.c. analysis using a chiral support (*i.e.* a 5 ft column packed with 3% *N*-lauroyl-L-valine-t-butylamide on 100/120 Supelcoport).

(*ii*) Vinyl acetate (2 cm^3, 21.7 mmol), [Rh{η^5-$C_5Ph_4OC(O)CH(OMe)Ph$}$(CO)_2$] (**16**) (7 mg, 0.01 mmol), and a magnetic stirrer bar were placed in a glass liner inside a steel autoclave (130-cm^3 volume). The autoclave was sealed, flushed out with carbon monoxide several times and then pressurised with H_2 + CO (1:1) to 100 atm; stirring was commenced and the autoclave heated in an oil-bath at 50 ± 1 °C for 2 d. The reaction mixture was diluted with light petroleum (b.p. 40—60 °C, 10 cm^3) and passed down a short silica column (5 cm) to remove the catalyst. Solvent was removed and ^1H n.m.r. analysis of the product showed that complete conversion to 2-acetoxypropanal had taken place; using the chiral reagent tris[3-(trifluoroacetyl)bornan-2-onato]europium(III) the enantiomeric excess was determined to be 3%. A similar e.e. was obtained using a mixture of [{Rh{η^5-$C_5Ph_4OC(O)CH(OMe)Ph$}Cl_2}$_2$] and zinc as the catalyst.

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