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## The stereochemical and kinetic consequences of binding a pentaphenylcyclopentadienyl ligand. Crystal structure of $\text{Ru}(\text{C}_5\text{Ph}_5)(\text{CO})(\text{PPh}_3)\text{Br}$

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### Abstract

The reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{C}_5\text{Ph}_5\text{Br}$  yields  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$  (**1**), which reacts with phosphorus donor ligands to give  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\text{LBr}$  (**2**:  $\text{L} = \text{PPh}_3$ ; **3**:  $\text{L} = \text{P}(\text{OMe})_3$ ; **4**:  $\text{L} = \text{P}(\text{OPh})_3$ ). A limited kinetic study has revealed that these carbonyl replacement reactions occur via a dissociative mechanism at a rate significantly faster than those for  $\text{Ru}(\text{Cp}')(\text{CO})_2\text{Br}$  ( $\text{Cp}' = \text{C}_5\text{H}_5$  or  $\text{C}_5\text{Me}_4\text{Et}$ ). The crystal structure of **2** is reported, and reveals that the triphenylphosphine ligand extends into the region occupied by the pentaphenyl propeller, forcing this propeller into an unsymmetrical chiral array. This chiral array complexed to a chiral ruthenium atom gives rise to diastereoisomers which can be seen in the  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra of **2**.

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### Introduction

Since the characterisation of ferrocene in 1951 [1] the cyclopentadienyl ligand has played a major role in the development of organometallic chemistry. In the last twenty years the use of peralkylcyclopentadienyl ligands has become popular as chemists have come to appreciate the beneficial effects on the physical and chemical properties which can arise from modification of the cyclopentadienyl ligand in this way [2]. More recently, several complexes containing peraryl-cyclopentadienyl ligands have been prepared [3–9]; if such ligands are to become widely used then the chemical and kinetic consequences of complexing such ligands to metals should be clearly understood. Since we described some years ago a comparative kinetic study of the substitution reactions of the complexes  $\text{Ru}(\text{Cp}')(\text{CO})_2\text{Br}$  where  $\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$  or  $\text{Cp}' = \eta^5\text{-C}_5\text{Me}_4\text{Et}$  [10], it seemed timely to extend this to encompass the kinetic behaviour of the complex  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$ . In the course of this study we have observed an interesting steric phenomenon which should have general implica-

tions for the usefulness of perarylcylopentadienyl ligands in organometallic chemistry.

## Results and discussion

### *Synthetic studies*

$\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$  (**1**) was prepared by refluxing a solution of bromopentaphenylcyclopentadiene and  $\text{Ru}_3(\text{CO})_{12}$  in tetrahydrofuran; a similar procedure has been described previously [4,9]. The product is a yellow air-stable, crystalline solid, and although it has been suggested that pentaphenylcyclopentadienyl-complexes tend to be rather insoluble [4] the solubility of  $\text{Ru}(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Br}$  ( $\text{R} = \text{Ph}$ ) in common organic solvents is comparable with that of  $\text{R} = \text{H}$  or  $\text{R} = \text{Me}$ . It has also been reported [9] that carbonyl substitution of **1** by  $\text{PPh}_3$  could not be brought about thermally, whereas we found that the reaction occurred readily in refluxing xylene. However, the product  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PPh}_3)\text{Br}$  is not stable in solution in the absence of an excess of  $\text{PPh}_3$  and, for example, when carbon monoxide is bubbled through the solution the triphenylphosphine ligand is readily displaced to regenerate complex **1**. Thus, if in the reaction of **1** with  $\text{PPh}_3$  the carbon monoxide is not swept out of the solution by vigorous refluxing or by purging with a flow of nitrogen then the carbonyl displacement reaction does not proceed; this presumably explains the previous failure to bring about this reaction. Other phosphorus-donor ligands displace carbon monoxide from **1** to give the corresponding monosubstituted derivative  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\text{LBr}$  (**3**:  $\text{L} = \text{P}(\text{OMe})_3$ ; **4**:  $\text{L} = \text{P}(\text{OPh})_3$ ). After the completion of this work it was reported that **2**, **4** and similar compounds could be prepared under reflux by chemically removing the liberated carbon monoxide with  $\text{Me}_3\text{NO}$  [9].

The IR spectrum of  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Br}$  shows a carbonyl band at  $1983\text{ cm}^{-1}$  ( $\text{CS}_2$ ); this compares with a value of  $1990\text{ cm}^{-1}$  for the corresponding cyclopentadienyl analogue [11], and is at a significantly higher frequency than the band at  $1970\text{ cm}^{-1}$  observed for the corresponding ethyltetramethylcyclopentadienyl complex, suggesting that whereas peralkylcyclopentadienyl ligands are strong electron donor ligands the electronic influence of  $\text{C}_5\text{Ph}_5$  is comparable to that of  $\text{C}_5\text{H}_5$ .

Although the complexes  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})\text{LBr}$  ( $\text{L} = \text{PPh}_3$  or  $\text{P}(\text{OMe})_3$ ) have been prepared previously their NMR spectra were not reported. The spectra of the trimethyl and triphenyl phosphite complexes are unremarkable (see Experimental), but this is not the case for the triphenylphosphine complex. The  $^{31}\text{P}$  NMR spectrum of the latter shows two peaks of equal intensity at  $\delta$  39.44 and 39.99; similarly, in the  $^{13}\text{C}$  NMR spectrum the carbonyl ligand gives rise to two doublets at  $\delta$  206.3 ( $J(\text{P}-\text{C})$  25.5 Hz) and  $\delta$  206.2 ( $J(\text{P}-\text{C})$  26.6 Hz). In order to gain an insight into the origins of these unusual features the crystal structure of  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PPh}_3)\text{Br}$  was determined.

### *Description of structure*

The molecular structure is illustrated in Fig. 1. Table 1 gives selected bond lengths and angles with estimated standard deviations and Table 2 lists atomic coordinates with estimated standard deviations.

The molecule consists of a ruthenium(II) ion symmetrically coordinated by a *pentahapto*-pentaphenylcyclopentadienyl ligand (deviation of ruthenium from mean

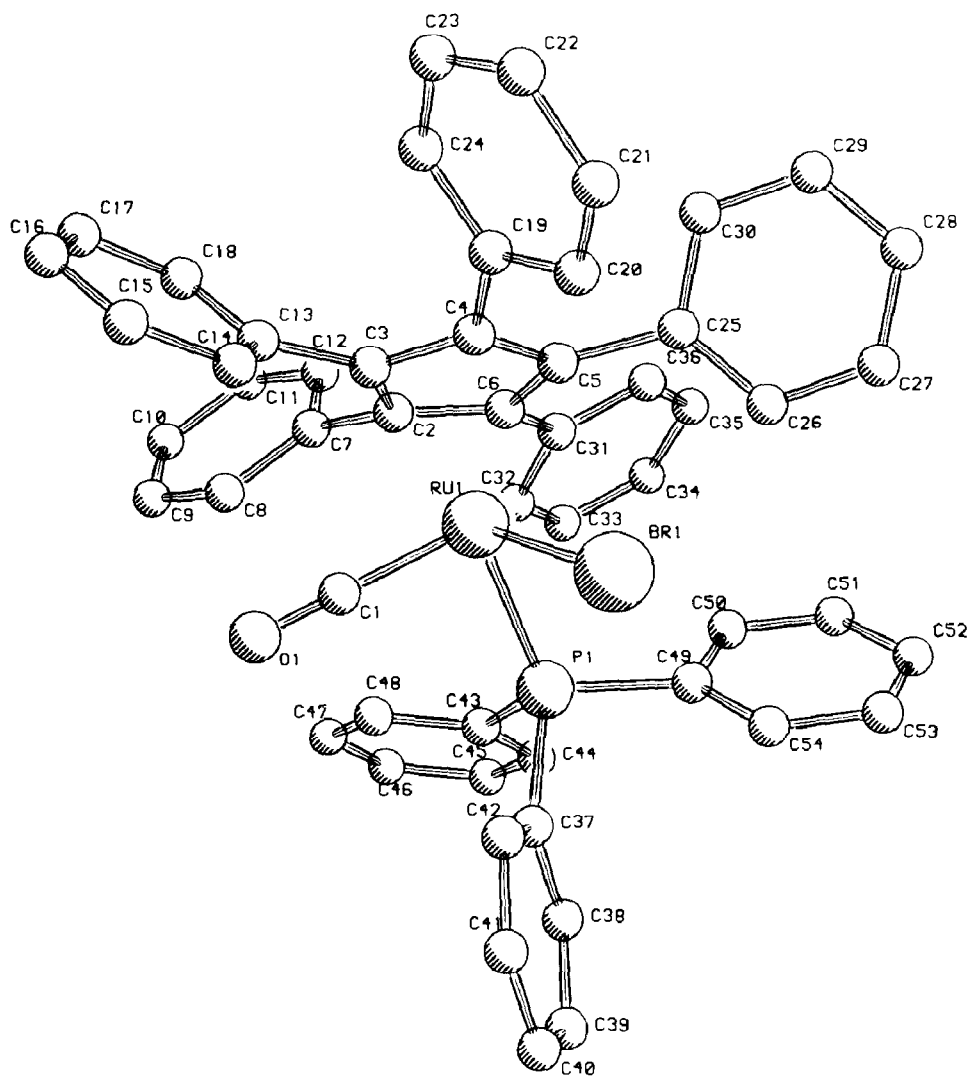


Fig. 1. The molecular structure of  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PPh}_3)\text{Br}$  (**2**) with atom labelling.

cyclopentadienyl plane 1.93 Å). The remaining three ligands are a triphenylphosphine (r.m.s. deviations of the phenyl groups 0.028, 0.005, 0.014 Å), a bromine, and a carbonyl; these last two are disordered equally between two sites. The mean Ru–C distance is 2.277 Å, and this compares with values of 2.219 and 2.229 Å in  $\text{Ru}(\text{C}_5\text{H}_5)(\text{CO})_2\text{Br}$  and  $\text{Ru}(\text{C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$  [12], respectively. Thus, as the bulk of the five-membered ring increases the ruthenium atom is forced further away. The phenyl groups are all essentially planar (r.m.s. deviations 0.007, 0.010, 0.016, 0.014, 0.019 Å) and, as observed in the structures of other pentaphenylcyclopentadienyl metal complexes, the phenyl groups are twisted in a propeller manner from the plane of the cyclopentadienyl plane. However, the most striking feature of this structure, compared to that of other pentaphenylcyclopentadienyl metal complexes, is that the phenyl propeller is less symmetrical. For example, in  $\text{Co}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2$  [5] the angles between the Cp plane and the phenyl rings range from 50.4 to 68.2°,

Table 1

Selected bond lengths (Å) and angles (°), with estimated standard deviations and shortest intramolecular contact (Å) for Ru( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>)(CO)(PPh<sub>3</sub>)Br (**2**)

Ru(1)–Br(1)	2.569(4)	Ru(1)–Br(1a)	2.558(4)
Ru(1)–P(1)	2.359(2)	Ru(1)–C(1)	1.913(26)
Ru(1)–C(1a)	1.910(28)	Ru(1)–C(2)	2.269(12)
Ru(1)–C(3)	2.262(11)	Ru(1)–C(4)	2.276(11)
Ru(1)–C(5)	2.292(12)	Ru(1)–C(6)	2.288(12)
P(1)–C(37)	1.861(12)	P(1)–C(43)	1.823(13)
P(1)–C(49)	1.844(14)	O(1)–C(1)	1.166(33)
O(1a)–C(1a)	1.160(36)	C–C(cp)	1.420
C(2)–C(7)	1.506(14)	C(3)–C(13)	1.517(14)
C(4)–C(19)	1.485(12)	C(5)–C(25)	1.511(15)
C(6)–C(31)	1.500(13)	C(32)···C(44)	3.43
Br(1)–Ru(1)–P(1)	84.4(1)	Br(1)–Ru(1)–C(1)	93.6(8)
P(1)–Ru(1)–C(1)	90.3(5)	Br(1a)–Ru(1)–P(1)	87.8(1)
Br(1a)–Ru(1)–C(1a)	92.0(8)	P(1)–Ru(1)–C(1a)	85.1(8)
Ru(1)–P(1)–C(37)	118.2(3)	Ru(1)–P(1)–C(43)	116.7(4)
C(37)–P(1)–C(43)	98.7(6)	Ru(1)–P(1)–C(49)	111.8(4)
C(37)–P(1)–C(49)	102.5(7)	C(43)–P(1)–C(49)	107.3(5)
Ru(1)–C(1)–O(1)	170.8(22)	Ru(1)–C(1a)–O(1a)	177.4(24)
C(3)–C(2)–C(7)	122.8(5)	C(6)–C(2)–C(7)	126.3(5)
C(2)–C(3)–C(13)	129.6(6)	C(4)–C(3)–C(13)	122.0(5)
C(3)–C(4)–C(19)	124.7(5)	C(5)–C(4)–C(19)	125.9(5)
C(4)–C(5)–C(25)	120.4(5)	C(6)–C(5)–C(25)	131.5(5)
C(2)–C(6)–C(31)	127.8(8)	C(5)–C(6)–C(31)	123.5(8)
C–C–C(cp)	108.0		

with an average value of 55.8°; in contrast, the corresponding angles in **2** are 56, 53, 53, 66 and 26°. The reason for the distortion is that the triphenylphosphine ligand extends into the region occupied by the cyclopentadienyl phenyl propeller. Thus in order to avoid contact the C(31)–C(36) phenyl-ring is tilted away from the triphenylphosphine ligand, resulting in the low propeller angle of 26°. This brings the shortest contact between the carbon atoms of the triphenylphosphine and the pentaphenylcyclopentadienyl ligand to 3.43 Å, the distance between C(32) and C(44), which is marginally shorter than the Van der Waals diameter of carbon.

The propeller arrangement shown for the C<sub>5</sub>Ph<sub>5</sub> ligand is a chiral array, as is the phenyl arrangement around the triphenylphosphine ligand. Obviously these may equally exist in the opposite chiral forms and presumably do so in 50% of the crystalline sample. Also both forms of the chiral ruthenium centre are present in the single crystal, as evidenced by the 1/1 disorder of the carbonyl and bromine ligands. Given the need for the phenyl rings of the C<sub>5</sub>Ph<sub>5</sub> ligand not only to avoid contact between each other but also to avoid contact with the triphenylphosphine ligand, rotation of these rings is clearly restricted. This would explain the doubling seen in the NMR spectra of this compound. Thus, on the NMR timescale, the compound exists as a mixture of diastereoisomers with a chiral centre at the ruthenium atom and additional chirality due to the C<sub>5</sub>Ph<sub>5</sub> propeller. In keeping with this explanation, the less bulky ligands P(OMe)<sub>3</sub> and P(OPh)<sub>3</sub> would not be expected to significantly restrict the rotation of the C<sub>5</sub>Ph<sub>5</sub> propeller, and hence the NMR spectra of the complexes Ru( $\eta^5$ -C<sub>5</sub>Ph<sub>5</sub>)(CO)LBr (L = P(OPh)<sub>3</sub> or P(OMe)<sub>3</sub>)

Table 2

Atom coordinates ( $\times 10^4$ ) and temperature factors ( $\text{\AA}^2 \times 10^3$ )

Atom	x	y	z	$U_{eq}^a$
Ru(1)	-104(1)	0	1055(1)	26(1)
Br(1)	852(3)	1105(2)	291(3)	55(1)
Br(1a)	1103(3)	-1009(2)	337(3)	36(1)
P(1)	-1786(2)	3(3)	-884(2)	36(1)
O(1)	1548(20)	-1169(10)	331(19)	81(4)
O(1a)	1221(22)	1210(10)	67(21)	81(4)
C(1)	946(24)	-686(14)	540(15)	63(3)
C(1a)	746(18)	742(12)	443(31)	63(3)
C(2)	-608(9)	-646(5)	2468(10)	28(5)
C(3)	783(9)	-439(5)	2950(10)	38(5)
C(4)	843(9)	333(5)	3019(10)	25(3)
C(5)	-510(9)	603(5)	2579(10)	39(6)
C(6)	-1407(9)	-2(5)	2239(10)	32(3)
C(7)	-1090(11)	-1405(6)	2587(9)	30(4)
C(8)	-663(14)	-1994(7)	2076(12)	44(5)
C(9)	-1061(15)	-2686(7)	2233(11)	49(5)
C(10)	-1860(16)	-2820(9)	2876(13)	60(6)
C(11)	-2298(14)	-2230(9)	3383(14)	62(6)
C(12)	-1928(12)	-1538(7)	3219(10)	45(5)
C(13)	2045(11)	-909(7)	3461(9)	35(4)
C(14)	3179(12)	-774(7)	3187(11)	43(5)
C(15)	4386(13)	-1131(8)	3807(14)	61(6)
C(16)	4427(15)	-1602(7)	4641(13)	59(6)
C(17)	3331(15)	-1780(8)	4927(14)	66(6)
C(18)	2083(14)	-1415(8)	4324(11)	53(5)
C(19)	2082(10)	759(5)	3688(9)	28(4)
C(20)	2473(15)	1407(8)	3242(11)	57(6)
C(21)	3638(17)	1766(9)	3931(13)	71(7)
C(22)	4436(14)	1561(7)	5093(10)	56(5)
C(23)	4014(15)	955(9)	5544(13)	71(6)
C(24)	2868(14)	568(7)	4852(10)	51(5)
C(25)	-781(11)	1411(7)	2588(11)	39(4)
C(26)	-1337(13)	1851(7)	1606(12)	41(5)
C(27)	-1504(15)	2578(9)	1724(13)	67(6)
C(28)	-1068(18)	2885(9)	2873(20)	89(9)
C(29)	-539(16)	2448(9)	3863(14)	76(7)
C(30)	-422(17)	1741(8)	3724(13)	67(7)
C(31)	-2921(9)	59(10)	1896(9)	37(4)
C(32)	-3755(13)	-498(8)	1205(11)	48(5)
C(33)	-5162(12)	-429(8)	847(13)	60(6)
C(34)	-5740(13)	164(13)	1129(14)	80(9)
C(35)	-4949(16)	700(10)	1848(16)	74(8)
C(36)	-3522(13)	638(8)	2247(12)	54(6)
C(37)	-1227(11)	-72(9)	-2198(8)	38(4)
C(38)	-2252(15)	-133(10)	-3330(11)	60(6)
C(39)	-1873(20)	-78(17)	-4358(12)	94(9)
C(40)	-555(19)	-22(18)	-4258(14)	96(9)
C(41)	448(18)	18(18)	-3156(13)	89(8)
C(42)	101(12)	37(12)	-2129(10)	55(5)
C(43)	-3003(11)	-746(7)	-1244(9)	36(4)
C(44)	-4381(14)	-694(9)	-1811(12)	58(6)
C(45)	-5222(16)	-1268(9)	-1991(16)	80(8)
C(46)	-4692(17)	-1930(10)	-1611(15)	69(7)

Table 2 (continued)

Atom	x	y	z	$U_{eq}^a$
C(47)	-3368(17)	-2033(9)	-1044(15)	77(8)
C(48)	-2506(13)	-1444(7)	-869(12)	52(5)
C(49)	-2772(11)	857(7)	-1196(10)	42(4)
C(50)	-3852(12)	966(8)	-816(10)	47(5)
C(51)	-4517(16)	1640(10)	-942(14)	73(7)
C(52)	-4071(17)	2207(8)	-1528(15)	72(7)
C(53)	-2990(16)	2088(9)	-1906(14)	69(7)
C(54)	-2385(12)	1429(7)	-1791(11)	47(5)

<sup>a</sup> Equivalent isotropic  $U$  defined as one third of the trace of the orthogonalised  $U_{ij}$  tensor, except for O(1), O(1a), C(1), C(1a) and C(4).

are unremarkable. In fact, even at  $-70^\circ\text{C}$  the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})[\text{P}(\text{OPh})_3]\text{Br}$  contains only one signal.

Attempts to study the restricted rotation in  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})(\text{PPh}_3)\text{Br}$  by variable-temperature NMR spectroscopy were frustrated by the instability of **2** in solution at elevated temperatures in the absence of an excess of  $\text{PPh}_3$ .

### Kinetic studies

As stated earlier, carbonyl displacement from the complex  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$  is severely inhibited by carbon monoxide. Thus attempts to follow such reactions in a closed thermostatted infrared cell were unsuccessful. Reaction did take place when the reactants were placed in a thermostatted reaction flask and a stream of nitrogen was bubbled through the solution to purge any carbon monoxide formed. Inevitably such a procedure results in some solvent loss despite the use of the high boiling solvent diglyme. It was also found that whereas triphenylphosphine gave reproducible results, the rate of reaction with ligands such as trimethyl phosphite was very dependent upon the actual sample of ligands used; such behaviour has been noted previously, and it has been ascribed to traces of phosphates that catalyse substitution of metal carbonyl complexes [13]. We have also reported that substitution reactions of the analogous  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}$  complex with phosphites in non-polar solvents tend to take place via a radical mechanism [10]; in the case of **1** there is probably an even greater propensity towards radical reactions, given that the  $\text{C}_5\text{Ph}_5$ -ligand has been shown to stabilize paramagnetic complexes [7].

Because of such difficulties only a limited kinetic study was carried out, but despite this some clear conclusions can be drawn from the results obtained (Table 3). The rates of reaction were independent of the ligand concentration, and thus carbonyl replacement in  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$  takes place via a dissociative mechanism, as was found for  $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}$  and  $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$  [10]. The pentaphenyl-complex is also significantly more reactive than these last complexes; at  $112.1^\circ\text{C}$  the approximate relative rates for the complexes  $\text{Ru}(\text{Cp}')(\text{CO})_2\text{Br}$  are 1/14/20 for  $\text{Cp}' = \text{C}_5\text{H}_5$ ,  $\text{C}_5\text{Me}_4\text{Et}$  and  $\text{C}_5\text{Ph}_5$ , respectively. Whilst it is not surprising that bulky ligands promote a dissociative process, one would normally expect a simple dissociative process in a relatively non-interacting solvent to have a positive  $\Delta S^\ddagger$ . Inspection of the activation parameters (Table 4) reveals a steady decrease in the activation entropy as the bulk of the  $\text{Cp}'$  ligand increases, with a negative entropy of activation for the pentaphenyl derivative. However, similar

Table 3

Rates of reaction of  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$  with phosphorus donor ligands in diglyme

Temp. (° C)	ligand	[ligand] (M)	$10^5 k_{\text{obsd.}}$ (s <sup>-1</sup> )
84.6	PPh <sub>3</sub>	0.088	2.3
		0.183	2.5
		0.233	3.0
		0.381	2.3
98.8	PPh <sub>3</sub>	0.106	13.0
		0.137	11.0
		0.158	13.6
		0.328	10.9
		0.153	13.5
107.3	P(OPh) <sub>3</sub>	0.343	13.3
		0.093	24.1
		0.264	23.4
112.1	PPh <sub>3</sub>	0.373	24.8
		0.149	37.6
		0.223	37.4
		0.301	37.9

Table 4

Activation parameters for carbonyl replacement reactions in diglyme

Complex	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$\Delta S^*$ (J K <sup>-1</sup> mol <sup>-1</sup> )
$\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})_2\text{Br}$	108.9 ± 4.2	-28 ± 8
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}^a$	132.0 ± 2.6	27 ± 6
$\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Br}^a$	155.9 ± 3.9	67 ± 8

<sup>a</sup> Data from ref. 10.

negative entropies of activation have been observed for other dissociative reactions involving bulky ligands, e.g. in substitution reactions of complexes of the type  $\text{Mo}(\text{CO})_4\text{L}_2$  (L = phosphine or phosphite) [14]. Such negative entropy terms imply a gross reorganization in the transition state.

The enhanced lability of the pentaphenyl derivative compared to that of the  $\text{C}_5\text{H}_5$  or  $\text{C}_5\text{Me}_4\text{Et}$  analogues derives from a more favourable activation enthalpy term. Since there is no evidence that the ruthenium-carbonyl bond is weaker in  $\text{Ru}(\text{Cp}')(\text{CO})_2\text{Br}$  ( $\text{Cp}' = \text{C}_5\text{Me}_4\text{Et}$  or  $\text{C}_5\text{Ph}_5$ ), this implies that the substituted Cp' ligands are able to stabilize the transition state to a greater extent than the  $\text{C}_5\text{H}_5$  ligand.

## Conclusions

It might have been expected that the steric bulk of the pentaphenylcyclopentadienyl ligand would result in the  $\text{C}_5\text{Ph}_5$  complexes being less reactive than their  $\text{C}_5\text{H}_5$  analogues, whereas in fact the opposite is true for the dissociative process studied; this is probably a general effect, given that the majority of 18-electron

organometallic complexes react via a dissociative mechanism. As expected, the steric bulk of the pentaphenylcyclopentadienyl ligand does limit the nature of the other ligands which can simultaneously complex to the metal to form a stable compound. The observation that appropriate bulky ligands on the metal can influence the orientation and chirality of the pentaphenyl propeller is interesting, and may also find applications in enantioselective synthesis. For example, chiral bis(di-arylphosphine) ligands are effective ligands in enantioselective synthesis despite the fact that the chiral centre(s) in the ligand is (are) often some distance from the metal; this has been ascribed to the fact that chiral backbone of the ligand fixes the orientation of the P(aryl)<sub>2</sub> moieties in a chiral array about the metal [15]. One might therefore envisage that a suitable bulky chiral ligand attached to a pentaphenylcyclopentadienyl catalyst or reagent would also direct the orientation of the chiral-pentaphenyl array, with consequent beneficial effects upon the enantioselectivity.

## Experimental

### General procedures

Proton and <sup>13</sup>C spectra were recorded on a Bruker AM-250 FTNMR spectrometer. The chemical shifts for the <sup>31</sup>P NMR spectra were measured from 85% H<sub>3</sub>PO<sub>4</sub> (downfield positive) with a Bruker UP-80SY FTNMR spectrometer. 2-Methoxyethyl ether was dried by distillation from calcium hydride, xylene by distillation from sodium, and tetrahydrofuran over sodium benzophenone; all solvents were freshly distilled before use. Reactions were carried out under nitrogen, although the compounds were subsequently found not to be particularly air-sensitive.

*Bromodicarbonyl(η<sup>5</sup>-pentaphenylcyclopentadienyl)ruthenium, Ru(η<sup>5</sup>-C<sub>5</sub>Ph<sub>5</sub>)(CO)<sub>2</sub>Br (1).* A solution of bromopentaphenylcyclopentadiene [16] (4 g, 7.62 mmol) and Ru<sub>3</sub>(CO)<sub>12</sub> (1.62 g, 2.54 mmol) in thf (75 cm<sup>3</sup>) was refluxed under nitrogen for 16 h then allowed to cool. The solvent was removed in vacuo and the orange residue chromatographed on alumina; the product was eluted with chloroform-petroleum ether (b.p. 40–60 °C) (1/1), and removal of the solvent gave orange crystals (2.44 g, 47%) (Found: C, 65.9; H, 3.9. C<sub>37</sub>H<sub>25</sub>BrO<sub>2</sub>Ru calcd.: C, 65.1; H, 3.7%). δ<sub>C</sub> (63 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 196.7 (s, CO), 132.4–126.3 (Ph), 106.5 (s, C<sub>5</sub>Ph<sub>5</sub>).

*Bromocarbonyl(η<sup>5</sup>-pentaphenylcyclopentadienyl)(triphenylphosphine)ruthenium, Ru(η<sup>5</sup>-C<sub>5</sub>Ph<sub>5</sub>)(CO)(PPh<sub>3</sub>)Br (2).* A mixture of Ru(η<sup>5</sup>-C<sub>5</sub>Ph<sub>5</sub>)(CO)<sub>2</sub>Br (0.26 g, 0.380 mmol) and triphenylphosphine (0.11 g, 0.420 mmol) in xylene (100 cm<sup>3</sup>) was refluxed under nitrogen for 15 h then allowed to cool. The solvent was removed in vacuo and the red residue chromatographed on alumina; the product was eluted with chloroform-petroleum ether (b.p. 40–60 °C) (1/1), and removal of the solvent gave red micro-crystals (0.237 g, 68%). Recrystallisation from diethylether/pentane gave red blocks suitable for X-ray crystallography. δ<sub>C</sub> (63 MHz, CDCl<sub>3</sub>, SiMe<sub>4</sub>) 206.3 (d, J(PC) 25.3 Hz, CO), 206.2 (d, J(PC) 26.6 Hz, CO), 135.0–127.1 (Ph), 103.3 (s, C<sub>5</sub>Ph<sub>5</sub>); δ<sub>P</sub> (32.4 Mz, CDCl<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>) 39.99, 39.44 (PPh<sub>3</sub>).

*Bromocarbonyl(η<sup>5</sup>-pentaphenylcyclopentadienyl)(trimethyl phosphite)ruthenium, Ru(η<sup>5</sup>-C<sub>5</sub>Ph<sub>5</sub>)(CO)[P(OMe)<sub>3</sub>]Br (3).* A solution of Ru(η<sup>5</sup>-C<sub>5</sub>Ph<sub>5</sub>)(CO)<sub>2</sub>Br (0.24 g, 0.352 mmol) and trimethyl phosphite (0.05 g, 0.40 mmol) in 2-methoxyethyl ether (70 cm<sup>3</sup>) was kept at 140 °C for 4 h as a stream of nitrogen was slowly bubbled through the solution. Work up as above gave the product (3) as a yellow crystalline solid (0.083 g, 31%) (Found: C, 61.0; H, 4.7; Br, 10.4. C<sub>39</sub>H<sub>34</sub>BrO<sub>4</sub>PRu calcd.: C,



60.2; H, 4.4; Br, 10.3%).  $\delta_{\text{H}}$  (250 MHz,  $\text{CDCl}_3$ ,  $\text{SiMe}_4$ ) 7.2–6.9 (25H, m, Ph) and 3.70 (9H, d,  $J(\text{PH})$  10 Hz, OMe)  $\delta_{\text{C}}$  (63 MHz,  $\text{CDCl}_3$ ,  $\text{SiMe}_4$ ) 203.6 (d,  $J(\text{PC})$  33.7 Hz, CO), 133.0–126.5 (Ph), 103.8 (d,  $J(\text{PC})$  2.9 Hz,  $\text{C}_5\text{Ph}_5$ ), 54.1 (d,  $J(\text{PC})$  7.5 Hz);  $\delta_{\text{P}}$  (32.4 Mz,  $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$ ) 135.4.

*Bromocarbonyl*( $\eta^5$ -pentaphenylcyclopentadienyl)(triphenyl phosphite)ruthenium,  $\text{Ru}(\eta^5\text{-C}_5\text{Ph}_5)(\text{CO})[\text{P}(\text{OPh})_3]\text{Br}$  (**4**). This was isolated as yellow crystals by a procedure analogous to that described for **3** (42%).  $\delta_{\text{C}}$  (63 MHz,  $\text{CDCl}_3$ ,  $\text{SiMe}_4$ ) 201.8 (d,  $J(\text{PC})$  33 Hz, CO), 132.7–121 (Ph), 104.0 (d,  $J(\text{PC})$  3 Hz,  $\text{C}_5\text{Ph}_5$ );  $\delta_{\text{P}}$  (32.4 Mz,  $\text{CDCl}_3$ ,  $\text{H}_3\text{PO}_4$ ) 119.9;  $\nu(\text{CO})$  1979  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ).

### Kinetic studies

The general procedure described previously [10] was used but with the modification that a slow stream of nitrogen was bubbled through, rather than over, the solution in order to remove the displaced carbon monoxide from the reaction vessel. Reactions were monitored for at least 2.5 half-lives, and found to give good linear plots of  $\log[\log(T_{\infty}/T)]$  against time,  $t$ , where  $T$  and  $T_{\infty}$  are the transmittances of the reaction mixture at time  $t$  and at the end of the reaction, respectively. The slopes of these plots were computed by using a least-mean squares error analysis.

*Crystal data for bromocarbonyl*( $\eta^5$ -pentaphenylcyclopentadienyl)(triphenylphosphine)ruthenium;  $\text{C}_{54}\text{H}_{40}\text{BrOPRu}$ ,  $M = 916.86$ ; crystal dimensions  $0.40 \times 0.25 \times 0.15$  mm. Monoclinic,  $a$  10.509(5),  $b$  18.357(6),  $c$  11.909(10) Å,  $\beta$  110.76(6)°,  $U$  2148.4(24) Å<sup>3</sup>;  $D_{\text{c}}$  1.417  $\text{g cm}^{-3}$ ,  $Z = 2$ . Space group  $P2_1$  ( $C_2^2$ , No. 4); Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71069$  Å),  $\mu(\text{Mo-}K_{\alpha})$  13.52  $\text{cm}^{-1}$ ,  $F(000) = 931.88$ .

### Structure analysis and refinement

Three-dimensional X-ray data were collected at room temperature on a Nicolet R3 diffractometer in the range  $3.5 < 2\theta < 50^\circ$  by the omega scan method. The 3040 independent reflections for which  $|F|/\sigma(|F|) > 3.0$  were corrected for Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structure was solved by standard Patterson and Fourier techniques and refined by blocked cascade least squares methods. The cyclopentadienyl ring was constrained to possess  $D_{5h}$  symmetry. Hydrogen atoms were placed in calculated positions, and refined in riding mode, with isotropic thermal parameters related to those of the supporting carbon atoms. The carbonyl and bromine ligands were disordered equally between their two basal sites: the geometries of the carbonyl fragments were partially constrained during refinement, which converged at a final  $R = 0.0539$ , with allowance for anisotropic thermal motion of all non-hydrogen atoms, except for those of the disordered carbonyl groups, and of C(4). Complex scattering factors were taken from the program package SHELXTL [17], which, as implemented on the Nova 3 computer, was used throughout the structure solution and refinement. Unit weights were used throughout. The absolute configuration of the chosen crystal was that which gave the more successful refinement (by  $\Delta R$  0.1%).

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.

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