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Polyhedron 23 (2004) 2695–2707
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Synthesis and characterisation of $[(\eta^6\text{-cymene})Ru(L)X_2]$ compounds: single crystal X-ray structure of $[(\eta^6\text{-cymene})Ru(P\{OPh\}_3)Cl_2]$ at 203 K

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Received 16 April 2004; accepted 11 June 2004
Available online 6 August 2004

Dedicated to Malcolm Green on his retirement; thank you for teaching me that chemistry should be fun and that the "suck it and see" approach is the most fun of all

Abstract

Treatment of the chloro bridged dimer $\{[(\eta^6\text{-cymene})RuCl]_2(\mu\text{-}Cl)_2\}$ (**1**) with the donor molecules $P(OPh)_3$, $P(OMe)_3$, PPh_3, PMe_3, CO, SMe_2, CN^tBu and CNTos in hot hexane causes bridge splitting reactions that produce the monomeric compounds $[(\eta^6\text{-cymene})Ru(L)Cl_2]$, (**4**)–(**11**), respectively. Use of the chiral isonitrile *S*(−)-α-methylbenzylisonitrile produced the corresponding complex **12**. The diiodo analogues, **13**–**15**, were prepared similarly from $\{[(\eta^6\text{-cymene})RuI]_2(\mu\text{-}I)_2\}$ (**3**) for $P(OPh)_3$, $P(OMe)_3$ and PPh_3, respectively. Insertion of tin(II) chloride into both metal–chlorine bonds was observed for $[(\eta^6\text{-cymene})Ru(P\{OMe\}_3)Cl_2]$ (**5**), while only monosubstitution was observed for $[(\eta^6\text{-cymene})Ru(PPh_3)Cl_2]$ (**6**). Halide abstraction in the presence of a substrate reaction has been used to prepare some selected cationic compounds which contain an asymmetric ligand environment. Reaction of $\{[(\eta^6\text{-cymene})RuCl]_2(\mu\text{-}Cl)_2\}$ with 1,2-bis(diphenylphosphino)-ethane under ionising conditions produced the cation $[(\eta^6\text{-cymene})Ru(dppe)Cl]PF_6$ (**20**). Selected compounds have been examined by $\{^{13}C\text{–}^1H\}$ heteronuclear correlation and $\{^1H\text{–}^1H\}$ COSY and NOESY experiments. The structure of $[(\eta^6\text{-cymene})Ru(P\{OPh\}_3)Cl_2]\cdot CH_2Cl_2$ (**4**) has been determined at −70 °C.

Keywords: Cymene; Ruthenium; X-ray

1. Introduction

The chemistry of $(\eta^6$-arene)ruthenium half-sandwich systems has been explored to a lesser extent than that of the isoelectronic $(\eta^5$-cyclopentadienyl)ruthenium systems. This is probably due to the requirement for 1,3- or 1,4-cyclohexadienes as ligand precursors; these are normally obtained by Birch reduction of the appropriate arene. However the diene precursor to $(\eta^6$-cymene)ruthenium compounds, (*R*)-α-Phellandrene, (5-isopropyl-2-methyl-1,3-cyclo-hexadiene) is commercially available and thus the bulk of the reported chemistry to date is of complexes of this arene ligand [1,2]. Other arene ligands such as mesitylene and hexamethylbenzene have generally been introduced by high temperature ligand exchange using the cymene dimer **1** and the free arene.

We have a developing interest in metal complexes which contain chiral at metal centres and/or chiral ligands. The present work describes the development of reaction chemistry designed to generate racemic $(\eta^6$-cymene)ruthenium complexes with an asymmetric ligand environment. These complexes have been examined

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doi:10.1016/j.poly.2004.06.016

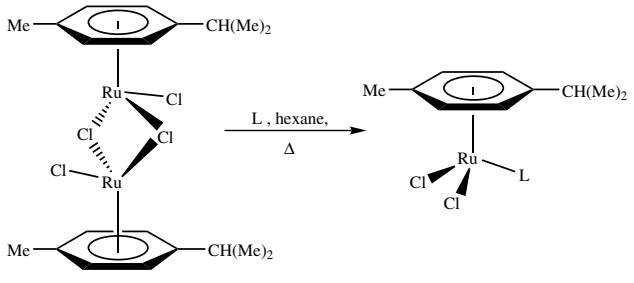
by NMR spectroscopy in order to investigate the chemical shift differentiation of the arene ring substituents.

Some of the compounds prepared have been reported previously; **4** and **6** [3–5], **5** and **7** [6], and **10** and **11** [7]. We have improved yields in some cases and provided fuller spectroscopic data in all these cases.

2. Results and discussion

Treatment of a suspension of red {[(η^6-cymene)RuCl]$_2$(μ-Cl)$_2$} (**1**) in hexane with triphenylphosphite, trimethylphosphite, triphenylphosphine or trimethylphosphine under reflux for several hours gave orange or red-orange suspensions of the monomeric compounds [(η^6-cymene)Ru(L)Cl$_2$], (**4**) to (**7**), respectively. The salmon-pink carbonyl compound **8** was prepared from the dimer starting material by stirring the hexane suspension under carbon monoxide (150 psig) for 2 h at 50 °C. An increase in the reaction time to 12 h resulted in the isolation of a small quantity of bright yellow crystals which contained two sharp infrared absorptions at 2080 and 2023 cm^{-1}. This is probably [(η^6-cymene)Ru(CO)$_2$Cl]Cl and was not investigated further. Similarly reactions with dimethylsulfide (SMe$_2$), *tert*-butylisonitrile (CN^{t}Bu) and *p*-toluenesulfonylmethylisonitrile (CNTos), gave the hexane insoluble compounds **9** to **11**, respectively (see Scheme 1).

Subsequent crystallisation of the precipitated products in each case from dichloromethane/petroleum ether provided crystalline products which were used for spectroscopic characterisation. The infrared spectra of **8**, **10** and **11** contain inter alia sharp absorptions at 2042 (ν_{CO}), 2133 (ν_{CN}) and 2162 cm^{-1} (ν_{CN}), indicating only a small degree of π-backbonding from the metal centre to the ligand π^* orbitals in the isonitrile complexes; the free ligand stretching frequencies being 2143, 2131 and 2150 cm^{-1}, respectively.



(1)

(4) P(OPh)$_3$
(5) P(OMe)$_3$
(6) PPh$_3$
(7) PMe$_3$
(8) CO
(9) SMe$_2$
(10) CN^{t}Bu
(11) CNTos

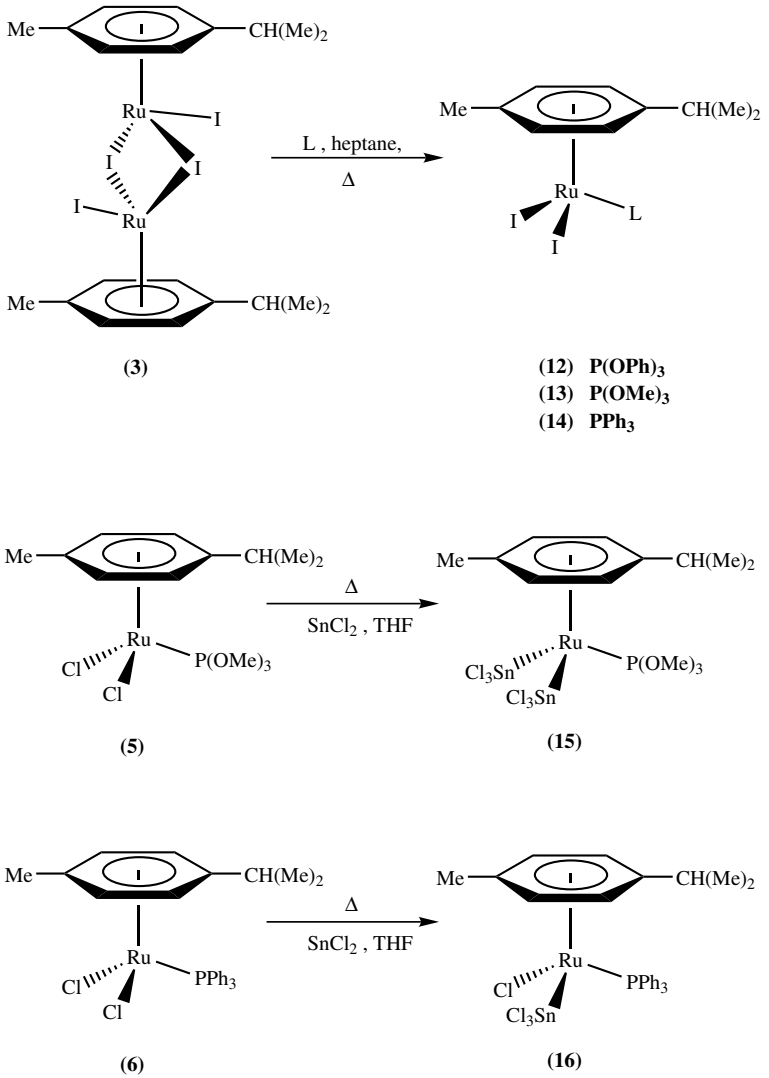
Scheme 1.

The diiodo complexes **12**, **13** and **14** were prepared similarly from {[(η^6-cymene)RuI]$_2$(μ-I)$_2$} (**3**) and the ligands in hot heptane solution (see Scheme 2). Treatment of the red dichloro complex **6** with an excess of sodium iodide in moist acetone also produced the purple diiodo complex **14** in 80% yield.

Reaction of anhydrous stannous chloride with **5** in tetrahydrofuran under reflux led to insertion into both ruthenium–chlorine bonds producing orange [(η^6-cymene)Ru(P{OMe}$_3$)(SnCl$_3$)$_2$)] (**15**). The poor solubility of this compound required long acquisition times to obtain NMR spectra and did not allow observation of tin satellites in the ^{31}P{^{1}H} spectrum. The ring protons on the cymene ligand of these complexes formally constitute an AA′BB′ spin system, but in all of the complexes **4**–**15** and the dimer starting materials **1**–**3** they appear as the more simple [AB]$_2$ spin system with J_{AB} being approximately 6 Hz. This is an expected result of both a very small value of $^5J_{HH}$ and rapid ring rotation relative to the [MX$_2$L] fragment; adoption of a static structure like that found in the solid state for [(η^6-cymene)Ru(P{OPh}$_3$)Cl$_2$] (**4**) (vide infra) must lead to two isolated [AB] spin systems. The ring substituent chemical shifts are collected in Table 1, and they do not suggest any correlation with ligand (L) donor or acceptor properties. The ring proton chemical shift differentiation ($\Delta\delta$) is largest for compounds **4**, **11** and **14**, zero for complex **7**, and similar to that of the dimer precursor for the other complexes. The nature of the three ligands is such that the ring protons are differentiated in all rotational conformations but it is likely that there may be some shielding process involving the ring current from a spatially close pendant phenyl ring. A complete assignment of the cymene ring protons in **6** and **12** was made possible by obtaining both COSY and NOESY spectra and demonstrates that the protons *ortho* to the isopropyl substituent (H$_{2,6}$,) are to low-field of those *ortho* to the methyl substituent (H$_{3,5}$). The assignments made in Table 1 assume that this is generally the case for these compounds.

Heteronuclear correlation spectra (^{13}C–^{1}H) were obtained for selected compounds to establish if there was a pattern which would facilitate assignment of the cymene ring chemical shifts for future compounds. Table 2 is a compilation of these data. It is clear from the values of $\Delta(\delta^{13}C)$ that the relative assignment of ^{13}C NMR chemical shifts for the ring methine groups is not predictable; in the free *p*-cymene ligand the chemical shifts are δ 126.3 and δ 129.0 for C$_{2,6}$ and C$_{3,5}$, respectively, while the ^{1}H NMR chemical shifts are isochronous at δ 7.32 [8].

Replacement of one of the two chloro ligands in the symmetrical compounds **4** to **11** would produce compounds which contain an asymmetric centre rendering



(3)

(12) $P(OPh)_3$
(13) $P(OMe)_3$
(14) PPh_3

(5)

(15)

(6)

(16)

Scheme 2.

all the cymene ring protons inequivalent and also differentiating the isopropyl methyl groups. Such a product would be obtained as a racemic mixture under most reaction conditions and in the Schemes 3–5 only one enantiomer is drawn for clarity.

A valuable synthetic target would be to prepare neutral molecules of the type [(η^6-cymene)Ru(L)(Cl)X] where X is a different halogen; differing metal–halogen bond strengths in subsequent reactions could be exploited. All efforts to replace one chloro ligand with a bromo, cyano or iodo ligand using sodium or potassium salts failed, variation of stoichiometry, solvent, reaction time and temperature gave only mixtures of the symmetrical product, starting material and trace amounts of the required product. Later work with analogues containing more heavily substituted arene ligands has proved more successful [9]. Reaction of [(η^6-cymene)Ru(PPh_3)Cl_2] (**6**) with stannous chloride in tetrahydrofuran gave the orange complex [(η^6-cymene)Ru(PPh_3)($SnCl_3$)(Cl)] (**16**) (see Scheme 2), whose ^{1}H NMR spectrum contained an [AB] system (δ_A 6.11, δ_B 6.01) and two doublets (δ 5.29, 4.95) for the cymene ring protons. The isopropyl group methyl resonances occur as two doublets at δ 1.21, 1.14. The nature of the three ligands is such that the ring protons are differentiated in all rotational conformations but it is likely that the major conformation is one which has a pair of protons in a similar environment and the other pair more strongly differentiated, such as in Fig. 1.

In contrast to **15**, the greater solubility of **16** allowed the observation of the tin satellites in the $^{31}P\{^1H\}$ NMR spectrum; the values of $^2J(^{119}Sn–^{31}P)$ and $^2J(^{117}Sn–^{31}P)$ being 704 and 671 Hz, respectively.

Treatment of the dimer **1** with the chiral isonitrile ligand *S*(−)-α-methylbenzylisonitrile under the conditions used for compounds **10** and **11** gave red microcrystalline **17** (see Scheme 3). The cymene ring protons are all differentiated in the ^{1}H NMR spectrum of **17** as expected when a chiral centre is introduced. The remoteness of

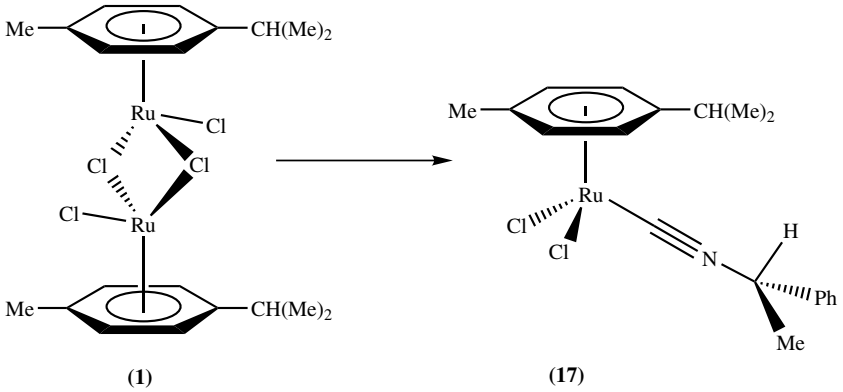
Table 1
^{1}H NMR chemical shifts for the compounds {[(η^6-cymene)RuX]$_2$(μ-X)$_2$} (**1**)–(**3**) and [(η^6-cymene)Ru(L)X$_2$] (**4**)–(**15**)

L	X		$H_{2,6}$	$H_{3,5}$	$\Delta\delta$	Me	$CHMe_2$	$CHMe_2$
	Cl	**1**	5.44	5.30	0.14	2.12	1.24	2.90
	Br	**2**	5.63	5.48	0.15	2.25	1.28	2.78
	I	**3**	5.51	5.41	0.10	2.33	1.22	2.98
$P(OPh)_3$	Cl	**4**	5.39	5.07	0.32	1.80	1.16	2.70
$P(OMe)_3$	Cl	**5**	5.52	5.38	0.14	2.15	1.22	2.90
PPh_3	Cl	**6**	5.17	4.97	0.20	1.84	1.07	2.83
PMe_3	Cl	**7**	5.39	5.39	0.00	2.02	1.18	2.81
CO	Cl	**8**	5.94	5.79	0.15	2.35	1.30	2.87
SMe_2	Cl	**9**[a]	5.61	5.43	0.18	2.18	1.31	2.92
CN^tBu	Cl	**10**	5.53	5.37	0.16	2.26	1.27	2.80
CNTos	Cl	**11**	5.72	5.40	0.32	2.30	1.29	2.92
$P(OPh)_3$	I	**12**	5.32	5.17	0.15	2.11	1.13	3.07
$P(OMe)_3$	I	**13**	5.56	5.38	0.18	2.39	1.23	3.22
PPh_3	I	**14**	5.42	4.90	0.52	1.94	1.06	3.42
$P(OMe)_3$	$SnCl_3$	**15**[b]	6.18	6.02	0.16	2.47	1.30	2.99

Other compounds in $CDCl_3$.
[a] $(CD_3)_2CO$.
[b] CD_2Cl_2.

Table 2
^{13}C–^{1}H correlation data for selected compounds in $CDCl_3$

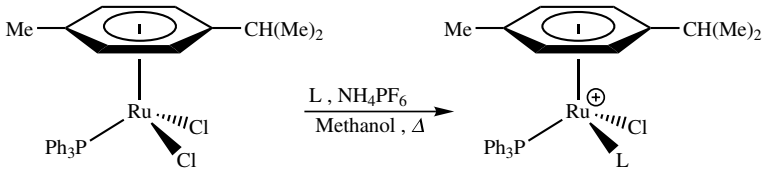
		$H_{2,6}$	$H_{3,5}$	$C_{2,6}$	$C_{3,5}$	$\Delta(\delta^{13}C)$
{[(η^6-cymene)RuCl]$_2$(μ-Cl)$_2$}	**1**	5.44	5.30	81.20	80.50	0.70
{[(η^6-cymene)RuBrl]$_2$(μ-Br)$_2$}	**2**	5.63	5.48	78.54	78.68	−0.14
{[(η^6-cymene)RuI]$_2$(μ-I)$_2$}	**3**	5.51	5.41	82.02	82.51	−0.49
[(η^6-cymene)Ru(P{OPh}$_3$)(Cl)$_2$]	**4**	5.39	5.07	88.60	88.90	−0.30
[(η^6-cymene)Ru(P{OPh}$_3$)(I)$_2$]	**12**	5.32	5.17	87.85	90.33	−2.48
[(η^6-cymene)Ru(P{OMe}$_3$)(Cl)$_2$]	**5**	5.52	5.38	88.80	89.10	−0.30
[(η^6-cymene)Ru(P{OMe}$_3$)(I)$_2$]	**13**	5.56	5.38	89.31	89.31	0.00
[(η^6-cymene)Ru(PPh_3)(Cl)$_2$]	**6**	5.17	4.97	87.20	89.00	−1.80
[(η^6-cymene)Ru(PPh_3)(I)$_2$]	**14**	5.42	4.90	88.70	88.60	0.10



Scheme 3.

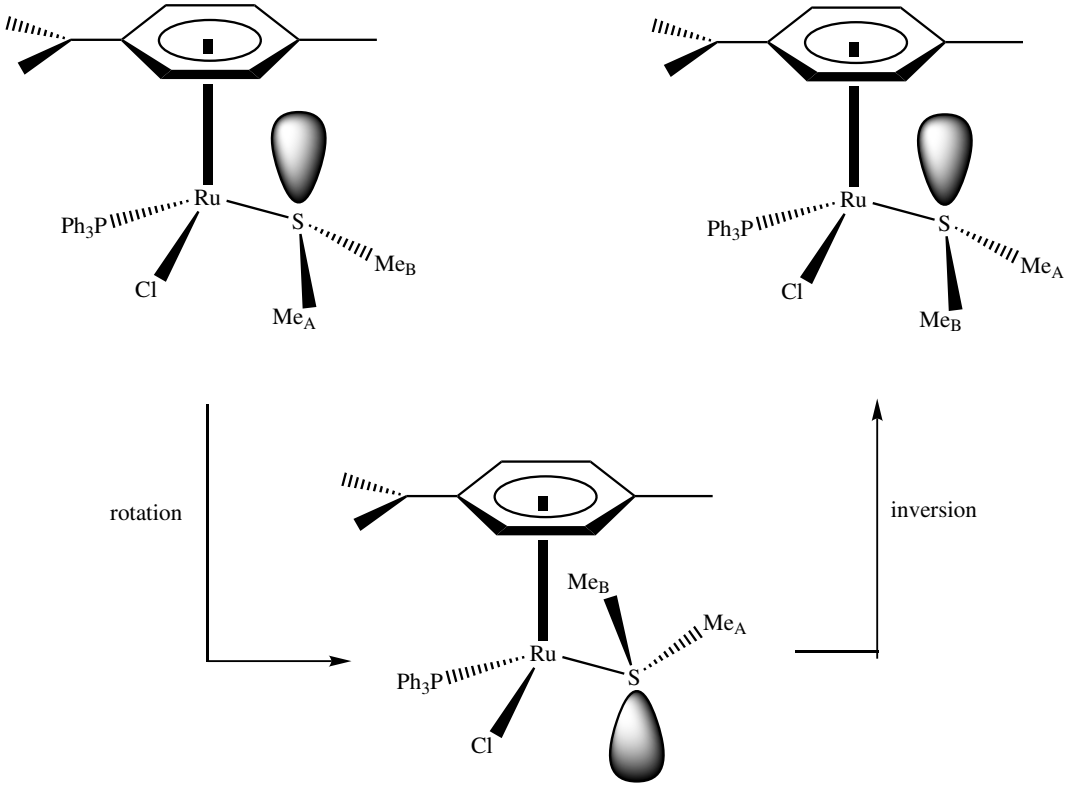
the chiral centre from the cymene ring protons induces an equivalence of only 0.02 ppm between the positionally related pairs. The heteronuclear correlation spectrum (^{13}C–^{1}H) established the ((δ_H, δ_C) pairings (5.56, 87.9), (5.54, 87.5), (5.40, 87.6) and (5.38, 87.4) establishing the effect of the remote chiral centre on the cymene ring carbon atoms.

Halide abstraction in the presence of a substrate can also be used to generate asymmetric metal centres; thus the reaction of **4** with dimethylsulfoxide in hot methanol



L = SMe_2 (**20**)
CNBu (**21**)
CNTos (**22**)
quinoline (**23**)

Scheme 4.



Scheme 5. Rotation–inversion process for the SMe_2 group in **20**.

solutions containing ammonium hexafluorophosphate produced bright yellow [(η^6-cymene)Ru(P{OPh}$_3$)(S{O}Me_2)(Cl)]PF_6 (**18**).

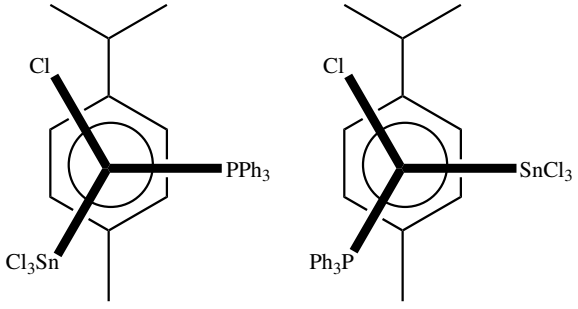


Fig. 1. Possible preferred conformations of **16**.

Similarly compound **5** could be transformed into the cation [(η^6-cymene)Ru(P{OMe}$_3$)(S{O}Me_2)(Cl)]PF_6 (**19**). The infrared spectra of **18** and **19** contained a weak band at 1124 and 1129 cm^{-1}, respectively, indicative of sulfur rather than oxygen coordination. Treatment of **6** with dimethylsulfide, *tert*-butylisonitrile, *p*-toluenesulfonylmethylisonitrile, or quinoline gave the requisite cationic compounds **20** to **23**, respectively, (*see* Scheme 4). The partial ^{1}H NMR chemical shift data for compounds **18** to **23** showing the cymene ring and isopropyl ligand methyl group resonances are collected in Table 3. The assignment of the ring protons is given such that H_A and H_B are mutually coupled and H_C and H_D form the other coupled pair. It seems reasonable to conclude that H_A and H_C are the $H_{2,6}$ pair while H_B and H_D are the $H_{3,5}$ ring protons. The appearance of "AB-roofing"

Table 3
^{1}H NMR chemical shifts for [(η^6-cymene)Ru(L)(L')Cl]PF_6 (**18**)–(**23**)

L	L′		H_A	H_B	H_C	H_D	Me	Me′
$P(OPh)_3$	$S(O)Me_2$	**18**	6.23	6.23	5.78	5.01	1.25	1.12
$P(OMe)_3$	$S(O)Me_2$	**19**[a]	6.53	6.45	6.51	6.27	1.31	1.30
PPh_3	SMe_2	**20**	5.93	5.89	5.45	4.96	1.29	1.28
PPh_3	CN^{t}Bu	**21**	6.09	4.95	5.78	5.59	1.30	1.24
PPh_3	CNTos	**22**[b]	6.13	4.77	6.08	5.95	1.27	1.22
PPh_3	quinoline	**23**[b]	6.01	5.97	5.52	5.33	1.06	1.03

Other compounds are recorded in deuterodichloromethane.
[a] Recorded in deuteroacetone.
[b] Recorded in deuterochloroform.

Table 4
Selected bond lengths (Å) and bond angles (°) for **4**

Ru(1)–C(1)	2.199(3)	Ru(1)–C(2)	2.241(3)
Ru(1)–C(3)	2.246(3)	Ru(1)–C(4)	2.222(3)
Ru(1)–C(5)	2.202(3)	Ru(1)–C(6)	2.177(3)
Ru(1)–Cl(1)	2.4022(8)	Ru(1)–Cl(2)	2.3992(8)
Ru(1)–P(1)	2.2642(8)	P(1)–O(1)	1.596(2)
P(1)–O(2)	1.607(2)	P(1)–O(3)	1.584(2)
Cl(1)–Ru(1)–Cl(2)	87.45(3)	O (1)–P(1)–O(2)	104.74(11)
Cl(1)–Ru(1)–P(1)	87.91(2)	O (1)–P(1)–O(3)	98.70(10)
Cl(2)–Ru(1)–P(1)	85.01(3)	O (2)–P(1)–O(3)	102.06(11)

in the 300 MHz ^{1}H NMR spectra of these compounds has been used to aid this assignment.

These compounds all show inequivalence of the diastereotopic methyl groups of the isopropyl fragment and of the four ring protons. The relative shieldings for some particular complexes, such as **21** and **22**, indicate some preferred conformations leading to differential proximity shielding arising from the π-system of the isonitrile group. The dimethylsulfide group of compound **20** exhibited a broad singlet resonance (δ 2.40) at 294 K which changed into the expected pair of singlets on cooling (δ 2.49, 2.22); the barrier (ΔG_{245}) to this rotation-inversion process was 49.1 kJ mol^{-1} at coalescence (see Scheme 5).

In compounds **18** and **19** where this exchange process is not possible the methyl groups of the dimethylsulfoxide ligands were anisochronous (δ 3.55, 3.37) and (δ 3.55, 3.27), respectively, as required by the lack of molecular mirror planes.

The reaction of the dimer **1** with bis-1,2-(diphenylphosphino)ethane (dppe) and ammonium hexafluorophosphate in 1,2-dichloroethane under reflux produced the symmetrical cation [(η^6-cymene)Ru(dppe)(Cl)]PF_6 (**24**). The conductivity of a dilute nitromethane solution (ca. 5 mM) of this salt was 57.3 Ω^{-1} cm^2 mol^{-1} while that of the very weakly ionized **8** and **9** was 2.0 and 1.3 Ω^{-1} cm^2 mol^{-1}, respectively.

The X-ray single crystal structure of **4** was determined at 203K in order to confirm the disposition of the three metal σ-bound ligands relative to the cymene ligand. The ruthenium–phosphorus bond Ru(1)–P(1) bisects one edge of the cymene ligand, C(5)–C(6), the arrangement expected for minimization of intramolecular repulsions. Selected bond lengths and angles are given in Table 4. The general structure is similar to that

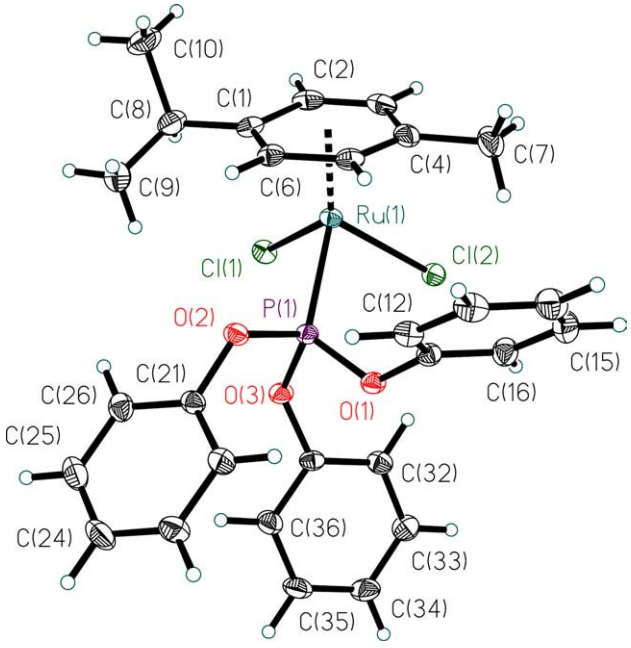


Fig. 2. Structure of the ruthenium containing fragment in **4** showing 25% probability ellipsoids.

found for other [(η^6-cymene)Ru(L)($Cl)_2$] compounds, for example L = PCy_3 [10], L = P(*m*-tolyl)$_3$ [10] and L = $PPh_2{}^tBu$ [11].

Fig. 2 shows the structure obtained of the ruthenium containing fragment and omits the dichloromethane solvent molecule which is also present in the unit cell. The solution structure of **4**, as evidenced by the ^{1}H NMR spectrum, shows that there is free rotation of the cymene ligand about the ruthenium centre and this is consistent with the general disposition of the phenyl rings in the triphenylphosphite ligand.

3. Conclusions

The methine protons of the cymene ligand in these complexes are a sensitive reporter of the auxiliary ligand environment in ^{1}H NMR spectroscopy. Even the presence of a very remote chiral centre in the complex **17** differentiates these ring protons. There does not appear to be a straightforward predictive method of absolutely assigning $\delta(C_{2,6})$ and $\delta(C_{3,5})$ in the ^{13}C NMR spectra of these complexes, the relative ordering being variable unlike the ordering in their ^{1}H NMR spectra. We will report subsequently our results with related compounds possessing planar chiral arene ligands where the asymmetry of the arene ligand facilitates absolute assignment, and also our results concerning the absence of a barrier to rotation of the cymene ring in the compounds [(η^6-cymene)Ru(L)Cl_2] in the range 170–350 K [12].

4. Experimental

All reactions and preparations were carried out on a vacuum/nitrogen line using standard Schlenk-tube techniques. Diethylether was dried over sodium wire. Dichloromethane, hexane, heptane, petroleum ether (40–60 °C) and Analar grade acetone were used as supplied. All solvents were degassed prior to use. All products isolated were dried under reduced pressure, in a hot water bath for at least one hour. Infrared spectra were recorded on a Perkin–Elmer 1710 FTIR instrument, calibrated against polystyrene film; only significant absorption bands are reported. Nuclear magnetic resonance spectra were recorded on Bruker AC300 (300.13 MHz, ^{1}H; 75.47 MHz, ^{13}C; 121.49 MHz ^{31}P) and Bruker Avance 400 (400.13 MHz, ^{1}H; 100.62 MHz, ^{13}C; 161.98 MHz ^{31}P) spectrometers. All ^{1}H and ^{13}C NMR chemical shifts are expressed in ppm relative to $SiMe_4$ (0.00 ppm) and ^{31}P NMR chemical shifts relative to $P(OPh)_3$ (126.5 ppm). All NMR and infrared spectra were measured at room temperature. Standard Bruker microprograms were used for the acquisition of HETCORR, NOESY and COSY-45 spectra. Elemental analyses were obtained at Butterworth Laboratories, London and Manchester University laboratories. Fast Atom Bombardment (FAB) mass spectra were obtained on a Kratos Concept S1 spectrometer. *R*(−)-α-Phellandrene (technical grade) was used as received from Fluka. *Tert*-butylisonitrile and *S*(−)-α-methylbenzylisonitrile were prepared from the respective amines by the phase-transfer Hofmann carbylamine reaction. Compounds **2** and **3** were prepared from **1** by a literature procedure [13].

4.1. Preparation of {[(η^6-cymene)RuCl]$_2$(μ-Cl)$_2$} (*1*)

Hydrated ruthenium trichloride (0.74g, 2.83 mmol) in ethanol (40 ml) was heated under reflux overnight with α-phellandrene (2 ml, 16.4 mmol). The orange precipitate was filtered off, washed with methanol and dried under reduced pressure, yield 0.55 g, 63.5%. ^{1}H NMR [$CDCl_3$]: δa 5.44, δb 5.30 (dd, *J*(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 2.90 (sept, *J*(HH) ~ 7 Hz, H, *CH*(Me)$_2$), 2.12 (s, 3H, CH_3{ring}), 1.24 (d, *J*(HH) ~ 7.0 Hz, 6H, CH(*Me*)$_2$); ^{13}C{^{1}H} NMR [$CDCl_3$]: δ 101.1 (s, $C1_{(quat)}$), 96.7 (s, $C4_{(quat)}$), 81.2 (s, C2,6-H{ring}), 80.5 (s, C3,5-H{ring}), 30.6 (s, *CH*(Me)$_2$), 22.1 (s, CH(*Me*)$_2$), 18.9 (s, Me{ring}).

4.2. Preparation of [(η^6-cymene)Ru(P{OPh}$_3$)Cl_2] (*4*)

A mixture of **1** (0.30 g, 0.49 mmol) and triphenylphosphite (1 ml) in hexane (30 ml) was heated under reflux for 8 h. The reaction mixture yielded a red microcrystalline solid which was filtered warm. The product was washed with light petroleum ether (2 × 10 ml). The crude product was crystallised from dichloromethane and light petroleum ether to give bright red crystals, yield 0.38 g, 62%. ^{1}H NMR [$CDCl_3$]: δ 7.22 (m, 15H, Ph_3), δa 5.39, δb 5.07 (dd, *J*(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 2.70 (sept, *J*(HH) ~ 7.0 Hz, H, *CH*(Me)$_2$), 1.8 (s, 3H, CH_3{ring}), 1.16 (d, *J*(HH) ~ 7.0 Hz, 6H, CH(*Me*)$_2$)); ^{13}C{^{1}H}NMR [$CDCl_3$]: δ 151.44 (d, *J*(PC) ~ 11.0 Hz, C_{ipso}, P{OPh}$_3$), 129.42 (s, C_{ortho}, P{OPh}$_3$), 125.06 (s, C_{para}, P{OPh}$_3$), 121.74 (d, *J*(PC) ~ 4.0 Hz, C_{meta}, P{OPh}$_3$) 109.37 (s, $C1_{(quat)}$), 103.07 (s, $C4_{(quat)}$), 88.92 (d, *J*(PC) ~ 7.0 Hz, C3,5-H{ring}), 88.60 (d, *J*(PC) ~ 6.0 Hz, C2,6-H{ring}), 30.55 (s, *CH*(Me)$_2$), 22.11 (s, CH(*Me*)$_2$), 17.96 (s, Me{ring}); ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 104.2 (s, P{OPh}$_3$).

4.3. Preparation of [(η^6-cymene)Ru(P{OMe}$_3$)Cl_2] (*5*)

A suspension of **1** (0.1 g, 0.16 mmol) and trimethylphosphite (0.1 ml) in hexane (30 ml) was heated under reflux for 4 h. After solvent removal under reduced pres-

sure, fine orange crystals were obtained by crystallising the orange residue at −30 °C from dichloromethane and light petroleum ether overnight, yield 0.14 g, 99.6%. Calc. for $C_{13}H_{23}Cl_2O_3PRu$: C, 36.27; H, 5.34. Found: C, 36.24; H, 5.19%. IR (nujol): ν_{max} 1042 s, 839 w cm^{-1} (PO). ^1H NMR [$CDCl_3$]: δa 5.52, δb 5.38 (dd, J(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 3.77 (d, J(PH) ~ 10.8 Hz, 9H, P{OMe}$_3$), 2.90 (sept, J(HH) ~ 7.0 Hz, H, CH(Me)$_2$), 2.15 (s, 3H, CH_3{ring}), 1.22 (d, J(HH) ~ 7.0 Hz, 6H, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 109.9 (s, $C1_{(quat)}$), 101.9 (s, $C4_{(quat)}$), 89.1 (d, J(PC) ~ 6.0 Hz, C2,6-H{ring}), 88.8 (d, J(PC) ~ 6.0 Hz, C3,5-H{ring}), 54.3 (d, J(PC) ~ 6.0 Hz, P(OMe)$_3$), 30.4 (s, CH(Me)$_2$), 22.0 (s, CH(Me)$_2$) 18.3 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 115.9 (s, P{OMe}$_3$). M.S.[FAB]: m/z 432 {M^+}.

4.4. Preparation of [(η^6-cymene)Ru(PPh_3)Cl_2] (6)

A suspension of **1** (0.4 g, 0.32 mmol) and triphenylphosphine (0.4 g, 1.52 mmol) in hexane (30 ml) was heated under reflux for 5 h. After solvent removal under reduced pressure, bright red crystals were obtained by crystallising the red residue at −30 °C from dichloromethane and light petroleum ether overnight, yield 0.59 g, 80%. ^1H NMR [$CDCl_3$]: δ 7.84−7.24 (m, 15H, PPh_3), δa 5.17, δb 4.97 (2d, 4H, J(HH) ~ 6.0 Hz, C-H{ring}), 2.83 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 1.84 (s, 3H, CH_3{ring}), 1.07 (d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 134.3 (d, J(PC) ~ 10.0 Hz, C_{ortho}, PPh_3), 128.0 (s, C_{para}, PPh_3), 128.0 (d, J(PC) ~ 10.0 Hz, C_{meta}, PPh_3), 111.2 (s, $C1_{(quat)}$), 96.0 (s, $C4_{(quat)}$), 89.0 (s, C2,6-H{ring}), 87.2 (s, C3,5-H{ring}), 30.2 (s, CH(Me)$_2$), 21.9 (s, CH(Me)$_2$), 17.7 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 23.1 (s, PPh_3). M.S.[FAB]: m/z 568 {M^+}.

4.5. Preparation of [(η^6-cymene)Ru(PMe_3)Cl_2] (7)

A suspension of **1** (0.2 g, 0.32 mmol) and trimethylphosphine (0.15 ml) in hexane (30 ml) was heated under reflux for 4 h. After solvent removal under reduced pressure, fine orange crystals were obtained by crystallising the orange residue at −30 °C from dichloromethane and light petroleum ether overnight, yield 0.22 g, 88%. ^1H NMR [$CDCl_3$]: δ 5.39 (d, 4H, J(HH) ~ 6.0 Hz, C-H{ring}), 2.81 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 2.02 (s, 3H, CH_3{ring}), 1.57 (d, 9H, J(PH) ~ 11.0 Hz, PMe_3), 1.18 (d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 106.8 (s, $C1_{(quat)}$), 93.4 (s, $C4_{(quat)}$), 89.2 (d, J(PC) ~ 3.5 Hz, C-H{ring}), 84.7 (d, J(PC) ~ 5.5 Hz, C-H{ring}), 30.5 (s, CH(Me)$_2$), 21.9 (s, CH(Me)$_2$), 18.2 (s, Me{ring}), 16.3 (d, J(PC) ~ 33.5 Hz, PMe_3); $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 3.08 (s, PMe_3). M.S.[FAB]: m/z 382 {M^+}.

4.6. Preparation of [(η^6-cymene)Ru(CO)Cl_2] (8)

A suspension of **1** (0.18 g, 0.29 mmol) in hexane (30ml) was pressurised with carbon monoxide (150 psig.) in a Fischer–Porter bottle and stirred at 50 °C for 2 h. Evaporation of the solvent under reduced pressure produced a salmon pink solid, which upon crystallisation from dichloromethane and petroleum ether afforded bright red microcrystals, yield 0.12 g, 56.0%. Calc. for $C_{11}H_{14}Cl_2ORu$: C, 39.51; H, 4.19. Found: C, 38.34; H, 4.06%. IR (nujol): ν_{max} 2042 s, cm^{-1} (CO); ^1H NMR [$CDCl_3$]: δa 5.94, δb 5.79 (dd, J(HH) ~ 6.5 Hz, 4H, C2,3,5,6-H{ring}), 2.87 (sept, J(HH) ~ 7.0 Hz, H, CH(Me)$_2$), 2.35 (s, 3H, CH_3{ring}), 1.30 (d, J(HH) ~ 7.0 Hz, 6H, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 189.7 (s, CO), 114.8 (s, $C1_{(quat)}$), 113.5 (s, $C4_{(quat)}$), 93.4 (s, C2,6-H{ring}), 93.0 (s, C3,5-H{ring}), 31.4 (s, CH(Me)$_2$), 22.5 (s, CH(Me)$_2$) 19.1 (s, Me{ring}).

4.7. Preparation of [(η^6-cymene)Ru(SMe_2)Cl_2] (9)

A suspension of **1** (0.2 g, 0.33 mmol) and dimethylsulfide (0.3 ml) in hexane (30 ml) was heated under reflux in an oil bath overnight. The solvent was removed under reduced pressure. Dissolution in dichloromethane (30 ml), and slow addition of light petroleum ether yielded bright red crystals on storage at −30 °C overnight, yield 0.18 g, 74.8%. Calc. for $C_{12}H_{20}Cl_2SRu$: C, 39.12; H, 5.43. Found: C, 39.09; H, 5.45%. ^1H NMR [$(CD_3)_2$ CO]: δa 5.61, δb 5.43 (dd, J(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 2.92 (sept, J(HH) ~ 7.0 Hz, H, CH(Me)$_2$), 2.29 (s, 6H, SMe_2), 2.18 (s, 3H, CH_3{ring}), 1.31 (d, J(HH) ~ 7.0 Hz, 6H, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [$(CD_3)_2$ CO]: δ 104.6 (s, $C1_{(quat)}$), 99.4 (s, $C4_{(quat)}$), 84.2 (s, C2,6-H{ring}), 83.8 (s, C3,5-H{ring}), 31.4 (s, CH(Me)$_2$), 22.6 (s, SMe_2), 22.3 (s, CH(Me)$_2$), 18.3 (s, Me{ring}). M.S.[FAB]: m/z 577 {$C_{20}H_{28}Cl_3Ru_2^+$}, 368 {M^+}.

4.8. Preparation of [(η^6-cymene)Ru(CN^tBu)Cl_2] (10)

Tert-butylisonitrile (0.2 ml) was added to a suspension of **1** (0.15 g, 0.25 mmol) in hexane (30 ml) and heated under reflux in an oil bath overnight. Filtration and evaporation under reduced pressure produced an orange residue. Dissolution in dichloromethane and slow addition of light petroleum ether afforded a bright orange microcrystalline solid **10**, yield 0.12 g, 61.5%. Calc. for $C_{15}H_{23}Cl_2NRu$: C, 46.26; H, 5.91. Found: C, 45.95; H, 5.91%. IR (nujol): ν_{max} 2194 s, cm^{-1} (CN). ^1H NMR [$CDCl_3$]: δa 5.53, δb 5.37 (dd, J(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 2.80 (sept, J(HH) ~ 7.0 Hz, H, CH(Me)$_2$), 2.26 (s, 3H, CH_3{ring}), 1.58 (s, CNC(CH_3)$_3$), 1.27 (d, J(HH) ~ 7.0 Hz, 6H, CH(Me)$_2$); *$^{13}C\{^1H\}$ NMR [$CDCl_3$]:* δ 137.0 (s, $CNC(CH_3)_3$), 107.6 (s, $C1_{(quat)}$), 106.3 (s, $C4_{(quat)}$), 87.4 (s, C2,6-H{ring}),

87.2 (s, C3,5-H{ring}), 58.5 (s, CN*C*(CH_3)$_3$), 31.3 (s, *CH*(Me)$_2$), 30.6 (s, CNC(CH_3)$_3$), 22.5 (s, CH(*Me*)$_2$), 18.7 (s, Me{ring}).

4.9. Preparation of [(η^6-cymene)Ru($CNCH_2SO_2C_6H_4Me$)Cl_2] (**11**)

A mixture of **1** (0.15 g, 0.25 mmol) and *p*-toluenesulfonylmethylisocyanide (0.18 g, 0.92 mmol) was suspended in hexane and heated under reflux for 12 h. The product was filtered, washed with petroleum ether and dried under reduced pressure. Dissolution in dichloromethane followed by slow addition of light petroleum ether afforded an orange microcrystalline solid, characterised as **11**, yield 0.15 g, 61.1%. Calc. for $C_{19}H_{23}O_2Cl_2NSRu$: C, 45.50; H, 4.59. Found: C, 43.84; H, 4.61%. IR (nujol): ν_{max} 2162 s, cm^{-1} (CN). ^{1}H NMR [$CDCl_3$]: δa 7.87, δb 7.41 (dd, J(HH) ~ 8.0 Hz, 4H, Me(*C_6H_4*)SO_2CH_2CN), δa 5.72, δb 5.40 (dd, J(HH) ~ 5.5 Hz, 4H, C2,3,5,6-H{ring}), 4.96 (s, 2H, Me(C_6H_4)SO_2CH_2CN), 2.92 (sept, J(HH) ~ 7.0 Hz, H, *CH*(Me)$_2$), 2.43 (s, 3H, Me(C_6H_4)SO_2CH_2CN), 2.30 (s, 3H, Me{ring}), 1.29 (d, J(HH) ~ 7.0 Hz, 6H, CH(*Me*)$_2$)). ^{13}C{^{1}H} NMR [$CDCl_3$]: δ 147.1 (s, $C_{(quat)}$, Me(*C_6H_4*)SO_2CH_2CN), 132.5 (s, $C_{(quat)}$, Me(*C_6H_4*)SO_2CH_2CN), 130.8 (s, Me(*C_6H_4*)SO_2CH_2CN), 129.1 (s, Me(*C_6H_4*)SO_2CH_2CN), 109.9 (s, $C1_{(quat)}$), 108.5 (s, $C4_{(quat)}$), 89.5 (s, C2,6-H{ring}), 89.4 (s, C3,5-H{ring}), 63.6 (s, Me(C_6H_4)SO_2*CH_2*CN), 31.2 (s, *CH*(Me)$_2$), 22.4 (s, CH(*Me*)$_2$) 21.8 (s, *Me*(C_6H_4)SO_2CH_2CN) 18.9 (s, Me{ring}). M.S.[FAB]: *m*/*z* 501 {M^+}.

4.10. Preparation of [(η^6-cymene)Ru(P{*OPh*}$_3$)I_2] (**12**)

A mixture of **3** (0.30 g, 0.49 mmol) and triphenylphosphite (1 ml) in heptane (30 ml) was heated under reflux for 6 h. The reaction mixture yielded a purple microcrystalline solid which was filtered warm. The product was washed with light petroleum ether (2 × 10 ml). The crude product was crystallised from dichloromethane and light petroleum ether to give light purple crystals, yield 0.6 g, 85%. Calc. for $C_{28}H_{29}O_3PI_2Ru$: C, 42.00; H, 3.63. Found: C, 41.88; H, 3.85%. ^{1}H NMR [$CDCl_3$]: δ 7.41 (m, 15H, Ph_3), δa 5.32, δb 5.17 (dd, J(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 3.07 (sept, J(HH) ~ 7.0 Hz, H, *CH*(Me)$_2$), 2.11 (s, 3H, CH_3){ring}), 1.13 (d, J(HH) ~ 7.0 Hz, 6H, CH(*Me*)$_2$)); ^{13}C{^{1}H} NMR [$CDCl_3$]: δ 152.03 (d, J(PC) ~ 12.0 Hz, C_{ipso}, P{OPh}$_3$), 129.48 (s, C_{ortho}, P{OPh}$_3$), 125.00 (s, C_{para}, P{OPh}$_3$), 121.86 (d, J(PC) ~ 4.0 Hz, C_{meta}, P{OPh}$_3$) 114.17 (s, $C1_{(quat)}$), 102.84 (s, $C4_{(quat)}$), 87.85 (d, J(PC) ~ 7.0 Hz, C2,6-H{ring}), 90.33 (d, J(PC) ~ 6.0 Hz, C3,5-H{ring}), 31.69 (s, *CH*(Me)$_2$), 22.49 (s, CH(*Me*)$_2$), 19.93 (s, Me{ring}); ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 105.7 (s, P{OPh}$_3$).

4.11. Preparation of [(η^6-cymene)Ru(P{*OMe*}$_3$)I_2] (**13**)

A suspension of **3** (0.2 g, 0.32 mmol) and trimethylphosphite (0.2 ml) in heptane (30 ml) was heated under reflux for 5 h. Dissolution into dichloromethane, filtration, concentration and slow addition of light petroleum ether yielded deep red/purple crystals on storage at −30 °C, overnight, yield 0.21 g, 80%. Calc. for $C_{13}H_{23}O_3PI_2Ru$: C, 25.41; H, 3.75. Found: C, 25.24; H, 3.69%). ^{1}H NMR [$CDCl_3$]: δa 5.56 δb 5.38 (2d, 2H, J(HH) ~ 6.0 Hz, C-H{ring}), 3.73 (d, 9H, J(PH) ~ 11.0 Hz, P{OMe}$_3$), 3.22 (sept, H, J(HH) ~ 7.0 Hz, *CH*(Me)$_2$), 2.39, (s, 3H, CH_3){ring}), 1.23 (d, 6H, J(HH) ~ 7.0 Hz, CH(*Me*)$_2$); ^{13}C{^{1}H} NMR [$CDCl_3$]: δ 113.31 (d, J(PC) ~ 5.0 Hz, $C1_{(quat)}$), 103.38 (d, J(PC) ~ 3.0 Hz, $C4_{(quat)}$), 89.31 (d, J(PC) ~ 4.0 Hz, C2,6-H{ring}), 89.31 (d, J(PC) ~ 4.0 Hz, C3,5-H{ring}), 55.30 (d, J(PC) ~ 7.0 Hz, P(OMe)$_3$), 31.55 (s, *CH*(Me)$_2$), 22.56 (s, CH(*Me*)$_2$) 20.06 (s, Me{ring}); ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 118.7 (s, P{OMe}$_3$). M.S.[FAB]: *m*/*z* 613 {M^+}.

4.12. Preparation of [(η^6-cymene)Ru(PPh_3)I_2] (**14**)

An acetone solution of **6** (0.22 g) and a large excess of NaI (0.5 g, 3.34 mmol) was heated to 50 °C for 4 h. The solvent was removed under reduced pressure. Dissolution into dichloromethane, filtration, concentration and slow addition of light petroleum ether yielded deep red/purple crystals on storage at −30 °C, overnight, yield 0.20 g, 80%. Calc. for $C_{28}H_{29}PI_2Ru$: C, 44.68; H, 3.89. Found: C, 44.78; H, 4.09%. ^{1}H NMR [$CDCl_3$]: δ 7.77−7.34 (m, 15H, PPh_3), δa 5.42, δb 4.90 (2d, 4H, J(HH) ~ 6.0 Hz, C-H{ring}), 3.42 (sept, H, J(HH) ~ 7.0 Hz, *CH*(Me)$_2$), 1.94 (s, 3H, CH_3){ring}), 1.06 (d, 3H, J(HH) ~ 7.0 Hz, CH(*Me*)$_2$); ^{13}C{^{1}H} NMR [$CDCl_3$]: δ 135.6 (d, J(PC) ~ 47.0 Hz, C_{ipso}, PPh_3), 135.0 (d, J(PC) ~ 8.5 Hz, C_{ortho}, PPh_3), 130.2 (s, C_{para}, PPh_3), 127.6 (d, J(PC) ~ 9.5 Hz, C_{meta}, PPh_3), 112.71 (br.s, $C1_{(quat)}$), 99.5 (s, $C4_{(quat)}$), 88.7, 88.6 (2s, C-H{ring}), 32.0 (s, *CH*(Me)$_2$), 18.9 (s, CH(*Me*)$_2$), 18.1 (s, Me{ring}); ^{31}P{^{1}H} NMR [$CDCl_3$]: δ 21.4 (s, PPh_3).

4.13. Preparation of [(η^6-cymene)Ru(P{*OMe*}$_3$)($SnCl_3$)$_2$] (**15**)

Prior to use $SnCl_2 \cdot 2H_2O$ was dehydrated by stirring vigorously in acetic anhydride (120 g salt for 100 g anhydride) for 1 h. The salt was filtered, washed with dry ether (2 × 50 ml) and dried under reduced pressure. Dehydrated stannous chloride (0.07 g, 0.39 mmol) was then added to a solution of **5** (0.1 g, 0.23 mmol) in THF and heated under refluxing conditions for 4 h. A yellow precipitate formed, concentration and filtration

gave **12** as a yellow solid. Evaporation of the filtrate gave a small amount of a crystalline yellow-orange solid identified as **15** by ^{1}H NMR spectroscopy. Yield 0.12 g, 65%. Calc. for $C_{13}H_{23}PO_3Cl_6Sn_2Ru$: C, 19.27; H, 2.84. Found: C, 20.08; H, 3.20%. ^{1}H NMR [CD_2Cl_2]: δa 6.18 δb 6.02 (2d, 4H, J(HH) ~ 6.5 Hz, C-H{ring}), 3.83 (d, 9H, J(PH) ~ 12.0 Hz, P{OMe}$_3$), 2.99 (sept, H, J(HH) ~ 7.0 Hz, *CH*(Me)$_2$), 2.47 (d, 3H, J(PH) ~ 1.5 Hz, CH_3{ring}), 1.30 (d, 6H, J(HH) ~ 7.0 Hz, CH(*Me*)$_2$); ^{13}C{^{1}H} NMR [CD_2Cl_2]: δ 121.0 (s, C1$_{(quat)}$), 113.8 (br.s, C4$_{(quat)}$), 92.0, 91.8, (2s, C-H{ring}), 56.0 (d, J(PC) ~ 9.5 Hz, P{OMe}$_3$), 31.6 (s, *CH*(Me)$_2$), 23.2 (s, CH(*Me*)$_2$), 20.0 (s, Me{ring}); ^{31}P{^{1}H} NMR [CD_2Cl_2]: δ 127.8 (s, PMe_3). M.S.[FAB]: *m*/*z* 773 {M^+}.

4.14. Preparation of [(η^6-cymene)Ru(PPh$_3$)Cl(SnCl$_3$)] (**16**)

Freshly dehydrated stannous chloride (0.03 g, 0.16 mmol) was added to a solution of **6** (0.1 g, 0.12 mmol) in dry THF (30 ml) and heated under refluxing conditions for 4 h. The solution changed from red to orange. Removal of the solvent under reduced pressure produced an orange solid, which was crystallised from dichloromethane and diethylether. Yield 0.10 g, 71%. Calc. for $C_{28}H_{29}PCl_4SnRu$: C, 44.34; H, 3.83. Found: C, 44.38; H, 3.74%). ^{1}H NMR [CD_2Cl_2]: δ 7.71−7.32 (m, 15H, Ph), δa 6.11 δb 6.01 (2d, 2H, J(HH) ~ 6.0 Hz, C-H{ring}), 5.29 (d, H, J(HH) ~ 6.0 Hz, C-H{ring}), 4.95 (d, H, J(HH) ~ 6.0 Hz, C-H{ring}), 2.45 (sept, H, J(HH) ~ 7.0 Hz, *CH*(Me)$_2$), 1.84 (s, 3H, CH_3{ring}), 1.21, 1.14 (2d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); ^{13}C{^{1}H} NMR [CD_2Cl_2]: δ 134.9 (s, C$_{ipso}$, PPh_3), 134.2 (d, J(PC) ~ 9.5 Hz, C$_{ortho}$, PPh_3), 131.3 (s, C$_{para}$, PPh_3), 129.0 (d, J(PC) ~ 10.0 Hz, C$_{meta}$, PPh_3), 116.5 (s, C1$_{(quat)}$), 102.8 (s, C4$_{(quat)}$), 92.3, 90.9, 89.3 (3s, C-H{ring}), 89.0 (d, J(PC) ~ 5.0 Hz, C-H{ring}), 30.5 (s, *CH*(Me)$_2$), 22.6, 22.4 (2s, CH(*Me*)(Me′)), 18.1 (s, Me{ring}); ^{31}P{^{1}H} NMR [CD_2Cl_2]: δ 27.7 (s, Sn satellites, ^2J(^{119}Sn–^{31}P) ~ 704 Hz, ^2J(^{117}Sn–^{31}P) ~ 671 Hz, PPh_3). M.S.[FAB]: *m*/*z* 534 {M^+}.

4.15. Preparation of [(η^6-cymene)Ru(CN-(*S*)-CH(Me)(Ph))Cl$_2$] (**17**)

S(−)-α-Methylbenzylisonitrile (0.2 ml) was added to a suspension of **1** (0.15 g, 0.49 mmol) in hexane and heated at 70 °C for 12 h. Filtration and evaporation under reduced pressure produced a red residue. Crystallisation from dichloromethane and petroleum ether (40–60 °C) afforded microcystalline **17**. Yield 0.19 g, 89%. Calc. for $C_{19}H_{23}NCl_2Ru$: C, 52.17; H, 5.26; N, 3.20. Found: C, 52.36; H, 5.46; N, 3.05%. IR (nujol): ν_{max} 2186 (CN) cm^{-1}. ^{1}H NMR [CD_2Cl_2]: δ 7.40–7.24 (m, 5H, Ph), δa 5.56, δb 5.54 (dd, 2H, J(HH) ~ 6.0 Hz, C-H{ring}), δa 5.40, δb 5.38 (2d, 2H, J(HH) ~ 6.0 Hz, C-H{ring}), 5.18 (q, H, J(HH) ~ 7.0 Hz, CHMeNC), 2.72 (sept, J(HH) ~ 7.0 Hz, H, CH(Me)$_2$), 2.22 (s, 3H, CH_3{ring}), 1.72 (d, 3H, J(HH) ~ 7.0 Hz, CHMeNC), 1.19, 1.18 (2d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); ^{13}C{^{1}H} NMR [CD_2Cl_2]: δ 140.9 ('t', J(NC) ~ 15.0 Hz, CHMeNC), 137.9 (s, C$_{ipso}$, Ph), 129.0 (s, C$_{ortho}$, Ph), 128.5 (s, C$_{para}$, Ph), 125.5 (s, C$_{meta}$, Ph), 107.4 (s, C1$_{(quat)}$), 106.9 (s, C4$_{(quat)}$), 87.9, 87.6, 87.5, 87.4 (4s, C-H{ring}), 53.8 (s, CHMeNC), 31.1 (s, CH(Me)2), 24.8 (s, CHMeNC), 22.3, 22.2 (2s, CH(Me)$_2$), 18.7 (s, Me{ring}). M.S.[FAB]: *m*/*z* 437 {M^+}.

4.16. Preparation of [(η^6-cymene)Ru(P{OPh}$_3$)(SOMe$_2$)Cl]PF$_6$ (**18**)

Dimethylsulfoxide (1 ml) was added to a solution of **4** (0.15 g, 0.24 mmol) and ammonium hexafluorophosphate (0.2 g, 1.22 mmol) in methanol (30 ml) and stirred at 50 °C for 6 h. The solution turned progressively paler. The solvent was removed under reduced pressure to give a bright orange oil. A mixture of dichloromethane (20 ml) and water (5 ml) was added and shaken, the dichloromethane layer was separated and dried with calcium chloride. Filtration and addition of diethylether afforded bright yellow microcrystals, identified as **18**. Yield 0.10 g, 50%. Calc. for $C_{30}H_{35}ClF_6O_4P_2SRu$: C, 41.59; H, 4.04. Found: C, 41.90; H, 4.12%. IR (nujol): ν_{max} 1124, 1054 br, 845 s (PF_6^-) cm^{-1}. ^{1}H NMR [CD_2Cl_2]: δ 7.40−6.89 (m, 15H, Ph), 6.23 (d, 2H, J(HH) ~ 6.5 Hz, C-H{ring}), 5.78, 5.01 (2d, H$_c$, H$_d$, J(HH) ~ 6.5 Hz, C-H{ring}), 3.55, 3.37 (2s, 6H, SO*Me*$_2$), 2.65 (sept, J(HH) ~ 7.0 Hz, H, *CH*(Me)$_2$), 2.07 (s, 3H, CH_3{ring}), 1.25, 1.12 (2d, 6H, J(HH) ~ 7.0 Hz, CH(*Me*)$_2$); ^{13}C{^{1}H} NMR [CD_2Cl_2]: δ 151.0 (d, J(PC) ~ 14.0 Hz, C$_{ipso}$, P{OPh}$_3$), 130.7 (s, C$_{ortho}$, P{OPh}$_3$), 126.9 (s, C$_{para}$, P{OPh}$_3$), 121.4 (d, J(PC) ~ 3.0 Hz, C$_{meta}$, P{OPh}$_3$), 126.1 (s, C1$_{(quat)}$), 108.7 (s, C4$_{(quat)}$), 98.9 (s, C-H{ring}), 97.6 (d, J(PC) ~ 5.0 Hz, C-H{ring}), 93.8 (d, J(PC) ~ 10.0 Hz, C-H{ring}), 89.8 (s, C-H{ring}), 51.6, 51.2 (2s, SO*Me*$_2$) 31.7 (s, *CH*(Me)$_2$), 21.7, 21.6 (2s, CH(*Me*)$_2$), 18.4 (s, Me{ring}); ^{31}P{^{1}H} NMR [CD_2Cl_2]: δ 109.0 (s, P{OPh}$_3$). M.S.[FAB]: *m*/*z* 721 {M^+}.

4.17. Preparation of [(η^6-cymene)Ru(P{OMe}$_3$)(SOMe$_2$)Cl]PF$_6$ (**19**)

NH_4PF_6 (80 mg, 0.49 mmol) was added to a solution of complex **5** (0.15 g, 0.35 mmol) and dimethylsulfoxide (0.2 ml) in methanol (30 ml) and stirred at room temperature for 48 h. The solvent was removed under reduced pressure and the orange residue extracted with dichloromethane. Concentration and slow addition of diethylether afforded bright yellow crystals

on storage in a refrigerator (−30 °C, overnight), yield 0.14 g, 64%. Calc. for $C_{15}H_{29}ClF_6O_4P_2SRu$: C, 29.15; H, 4.70. Found: C, 28.71; H, 4.80%). IR (nujol): ν_{max} 1129, 1064 br (SO), 839 s (PF_6^-) cm^{-1}. ^1H NMR [acetone-d_6]: δa 6.53, δb 6.45, δa 6.51, δb 6.27 (4d, 4H, C-H{ring}), 4.02 (d, 9H, J(PC) ~ 11.0 Hz, P{OMe}$_3$), 3.56, 3.27 (2s, 6H, SOMe_2), 2.89 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 2.26 (s, 3H, CH_3{ring}), 1.31, 1.30 (2d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [acetone-d_6]: δ 123.2 (s, C1$_{(quat)}$), 109.2 (s, C4$_{(quat)}$), 98.2, 97.0, 96.9, 91.9 (4s, C-H{ring}), 55.8 (d, J(PC) ~ 8.5 Hz, P{OMe}$_3$), 31.8 (s, CH(Me)$_2$), 21.9, 21.6 (2s, CH(Me)$_2$), 18.4 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [acetone-d_6]: δ 119.8 (s, P{OMe}$_3$). M.S.[FAB]: m/z 473 {M^+}.

4.18. Preparation of [(η^6-cymene)Ru(PPh_3)(SMe_2)Cl] (**20**)

Dimethylsulfide (1 ml) was added to a solution of **6** (0.3 g, 0.53 mmol) and ammonium hexafluorophosphate (0.2 g, 1.22 mmol) in methanol (30 ml) and stirred at 50 °C for 6 h. The solvent was removed under reduced pressure to give a yellow oily solid. Crystallisation from dichloromethane and diethylether gave yellow/orange fluffy microcrystals of **20** yield 0.29 g, 74%. Calc. for $C_{30}H_{35}ClF_6P_2SRu$: C, 48.68; H, 4.47. Found: C, 49.01; H, 4.84%. IR (nujol): ν_{max} 841 s (PF_6) cm^{-1}. ^1H NMR [CD_2Cl_2]: δ 7.58−7.44 (m, 15H, Ph), δa 5.93, δb 5.89 (2d, 2H, J(HH) ~ 7.0 Hz, C-H{ring}), 5.45 (d, H, J(HH) ~ 6.5 Hz, C-H{ring}), 4.96 (dd, H, J(HH) ~ 6.5 Hz, J(PH) ~ 3.0 Hz, C-H{ring}), 2.82 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 2.40 (s, 6H, SMe_2) 1.67 (s, 3H, CH_3{ring}), 1.29, 1.28 (2d 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [CD_2Cl_2]: δ 134.6 (d, J(PC) ~ 9.5 Hz, C_{ortho}, PPh_3), 131.8 (s, C_{para}, PPh_3), 131.3 (d, J(PC) ~ 49.0 Hz, C_{ipso}, PPh_3), 129.0 (d, J(PC) ~ 10.5 Hz, C_{meta}, PPh_3), 122.1 (br.s, C1$_{(quat)}$), 101.5 (s, C4$_{(quat)}$), 93.0 (s, C-H{ring}), 91.0 (s, C-H{ring}), 89.5 (d, J(PC) ~ 7.5 Hz, C-H{ring}), 87.4 (s, C-H{ring}), 31.3 (s, CH(Me)$_2$), 26.3 (s, SMe_2), 22.1, 21.6 (2s, CH(Me)$_2$), 17.9 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [CD_2Cl_2]: δ 29.7 (s, PPh_3). M.S.[FAB]: m/z 595 {M^+}.

4.19. Preparation of [(η^6-cymene)Ru(PPh_3)(CN^tBu)Cl]PF_6 (**21**)

Tert-butylisonitrile (0.5 ml), NH_4PF_6 (0.1 g, 0.61 mmol) and **6** (0.1 g, 0.18 mmol) were dissolved in methanol (30 ml) and stirred at room temperature for 3 h. The solution turned pale yellow after 10 min. Evaporation of the solvent and crystallisation from dichloromethane and diethylether afforded yellow microcrystalline **21**, yield 0.12 g, 75%. Calc. for $C_{33}H_{38}ClF_6NP_2Ru$: C, 52.07; H, 5.00; N, 1.84. Found: C, 52.74; H, 4.91; N, 1.78%. IR (nujol): ν_{max} 2180 (CN), 840 s (PF_6) cm^{-1}. ^1H NMR [CD_2Cl_2]: δ 7.59−7.46 (m, 15H, Ph), δa 6.09, δb 5.78 (2d, 2H, J(HH) ~ 6.5 Hz, C-H{ring}), 5.59, 4.95 (2d, H_c, H_d, J(HH) ~ 6.5 Hz, C-H{ring}), 2.78 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 1.96 (s, 3H, CH_3{ring}), 1.33, 1.24 (2d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 1.23 (s, 9H, CNC(Me)$_3$); $^{13}C\{^1H\}$ NMR [CD_2Cl_2]: δ 156.6 (s, CNC(Me)$_3$), 134.2 (d, J(PC) ~ 10.0 Hz, C_{ortho}, PPh_3), 132.0 (s, C_{para}, PPh_3), 131.6 (d, J(PC) ~ 51.5 Hz, C_{ipso}, PPh_3), 129.3 (d, J(PC) ~ 10.5 Hz, C_{meta}, PPh_3), 118.7 (d, J(PC) ~ 5.5 Hz, C1$_{(quat)}$), 113.6 (s, C4$_{(quat)}$), 99.3 (d, J(PC) ~ 5.0 Hz, C-H{ring}), 98.2, 94.5, 91.9 (3s, C-H{ring}), 60.1 (s, CNC(Me)$_3$), 32.2 (s, CH(Me)$_2$), 29.9 (s, CNC(Me)$_3$), 23.7, 21.6 (2s, CH(Me)$_2$), 18.9 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [CD_2Cl_2]: δ 36.1 (s, PPh_3). M.S.[FAB]: m/z 616 {M^+}.

4.20. Preparation of [(η^6-cymene)Ru(PPh_3)(p-$CNCH_2SO_2C_6H_4Me$)Cl]PF_6 (**22**)

p-Toluenesulfonylmethylisocyanide, NH_4PF_6 (0.1 g, 0.61 mmol) and **6** (0.1 g, 0.18 mmol) were dissolved in methanol (30 ml) and stirred at room temperature for 3 h. The solution turned bright yellow after 10 min. Evaporation of the solvent and crystallisation from dichloromethane and diethylether afforded yellow microcrystalline **22**. Yield 0.11 g, 73%. Calc. for $C_{37}H_{38}ClF_6NO_2P_2SRu$: C, 52.07; H, 5.00; N, 1.84. Found: C, 50.91; H, 4.39; N, 1.59%. IR (nujol): ν_{max} 2185 (CN), 842 s (PF_6) cm^{-1}. ^1H NMR [$CDCl_3$]: δa 7.77 (d, J(AB) ~ 8.0 Hz, 4H, Me(C_6H_4)SO_2CH_2CN), 7.48−7.31 (m, 17H, Me(C_6H_4)SO_2CH_2CN + PPh_3), 6.13 (dd, H, J(HH) ~ 6.5 Hz, J(PH) ~ 1.0 Hz, C-H{ring}), δa 6.08, δb 5.95 (2d, 2H, J(AB) ~ 6.5 Hz, C-H{ring}), 5.09 (d, H, J(HH) ~ 15.5 Hz, Me(C_6H_4)-SO_2CH_2CN), 4.77 (d, H, J(HH) ~ 6.5 Hz, C-H{ring}), 4.03 (dd, H, J(HH) ~ 15.5 Hz, J(PH) ~ 2.0 Hz, Me(C_6H_4)SO_2CH_2CN), 2.93 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 2.44 (s, 3H, Me(C_6H_4)SO_2CH_2CN), 1.80 (d, 3H, J(PH) ~ 1.0 Hz, CH_3{ring}), 1.27 (d, 3H, J(HH) ~ 7.0 Hz, CH(Me)(Me′)), 1.22 (d, 3H, J(HH) ~ 7.0 Hz, CH(Me)(Me')); $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 150.0 (d, J(PC) ~ 29.0 Hz, Me(C_6H_4)-SO_2CH_2CN), 146.5, 132.7 (2s, C$_{(quat)}$, Me(C_6H_4)-SO_2CH_2CN), 133.9 (d, J(PC) ~ 10.0 Hz, C_{ortho}, PPh_3), 131.6 (s, C_{para}, PPh_3), 130.4 (s, Me(C_6H_4)SO_2CH_2CN), 130.2 (d, J(PC) ~ 53.0 Hz, C_{ipso}, PPh_3), 129.5 (s, Me(C_6H_4)SO_2CH_2CN), 128.8 (d, J(PC) ~ 10.5 Hz, C_{meta}, PPh_3), 121.3 (d, J(PC) ~ 5.0 Hz, C1$_{(quat)}$), 115.6 (s, C4$_{(quat)}$), 1 01.9 (d, J(PC) ~ 5.0 Hz, C-H{ring}), 98.0, 93.7, 92.2 (3s, C-H{ring}), 63.1 (s, Me(C_6H_4) SO_2CH_2CN), 31.6 (s, CH(Me)$_2$), 23.5 (s, CH(Me) (Me′)), 21.8 (s, Me(C_6H_4)SO_2CH_2CN), 21.4 (s, CH(Me)(Me')), 18.6 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 38.1 (s, PPh_3). M.S.[FAB]: m/z 728 {M^+}.

4.21. Preparation of [(η^6-cymene)Ru(PPh_3)(C_9H_7N)-Cl]PF_6 (**23**)

A red solution of **6** (0.10 g, 0.18 mmol) and KPF_6 in methanol (30 ml) was treated with quinoline (1 ml) and stirred at room temperature for 24 h. A bright yellow solid precipitated out on concentration. The solution was filtered and the yellow solid washed with diethylether. Crystallisation from dichloromethane and diethylether afforded microcrystalline **23**. Yield 0.09 g, 62%. Calc. for $C_{37}H_{36}ClF_6NP_2Ru$: C, 55.05; H, 4.46; N, 1.74; recalc. for 0.5 mol CH_2Cl_2: C, 53.00; H, 4.36; N, 1.65. Found: C, 53.58; H, 4.44; N, 1.63%. IR (nujol): ν_{max} 837 s (PF_6) cm^{-1}. ^1H NMR [$CDCl_3$]: δ 9.41 (s, H, C_9H_7N), 8.67 (d, H, J(HH) ~ 6.5 Hz, C_9H_7N), 7.87–7.47 (m, 22H, Ph, C_9H_7N), 6.01, 5.97, 5.52, 5.33 (4d, 4H, J(HH) ~ 6.0 Hz, C-H{ring}), 2.17 (sept, H, J(HH) ~ 7.0 Hz, CH(Me)$_2$), 1.65 (s, 3H, CH_3{ring}), 1.06, 1.03 (2d, 6H, J(HH) ~ 7.0 Hz, CH(Me)$_2$); $^{13}C\{^1H\}$ NMR [$CDCl_3$]: δ 159.4 (s, C_9H_7N), 147.8 (s, C_9H_7N), 134.0 (s, C_{ortho}, PPh_3), 133.0 (s, C_9H_7N), 131.0 (s, C_{para}, PPh_3), 128.6 (d, J(PC) ~ 8.5 Hz, C_{meta}, PPh_3), 128.6, 128.5 (s, C_9H_7N), 128.2 (s, C_9H_7N), 126.0 (s, C_9H_7N), 123.0 (s, C_9H_7N), 114.1 (d, J(PC) ~ 8.0 Hz, $C1_{(quat)}$), 103.5 (s, $C4_{(quat)}$), 94.7 (d, J(PC) ~ 6.0 Hz, C-H{ring}), 90.2, 88.7, 84.0 (3s, C-H{ring}), 30.8 (s, CH(Me)$_2$), 23.1, 20.9 (2s, CH(Me)$_2$), 18.1 (s, Me{ring}); $^{31}P\{^1H\}$ NMR [$CDCl_3$]: δ 36.6 (s, PPh_3). M.S.[FAB]: m/z 662 {M^+}.

4.22. Preparation of [(η^6-cymene)Ru(dppe)Cl]PF_6 (**24**)

A Schlenk tube was charged with a solution of **1** (0.2 g, 0.33 mmol) in 1,2 dichloroethane (25 ml), NH_4PF_6 (0.3 g, 1.84 mmol), dppe (0.52 g, 1.31 mmol) and a magnetic stirrer bar. The orange solution was stirred under reflux conditions for 16 h. After solvent removal under reduced pressure the yellow residue was extracted in dichloromethane (2 × 15 ml). Concentration followed by addition of light petroleum ether produced yellow microcrystals on storage at −30 °C overnight, yield 0.32 g, 60.2%. H NMR [acetone-d_6]: δ 7.97–7.36 (m, 20H, Ph) δa 6.38, δb 6.24 (dd, J(HH) ~ 6.0 Hz, 4H, C2,3,5,6-H{ring}), 3.12-2.92 (m, 4H, $PPh_2(CH_2)_2PPh_2$) 2.24 (sept, J(HH) ~ 7 Hz, H,$CH(CH_3)_2$), 1.21 (s, 3H, CH_3{ring}), 0.87 (d, J(HH) ~ 7 Hz, 6H, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR [acetone-d_6]: δ 136.3 ('t', J(PC) ~ 46.5 Hz, C_{ipso}), 134.7, 133.1 (2s, C_{ortho}, PPh_3), 132.2, 131.9 (2s, C_{para}, PPh_3), 130.0, 129.2 (2'st', J(PC) ~ 10.0 Hz, C_{meta}, PPh_3), 123.5 (s, $C1_{(quat)}$), 101.3 (s, $C4_{(quat)}$), 96.2 (s, C2,6-H{ring}), 92.3 (s, C3,5-H{ring}), 31.1 (s, CH(Me)$_2$), 26.8 (t, J(PC) ~ 22 Hz, $PPh_2(CH_2)_2PPh_2$) 21.4 (s, CH(Me)$_2$) 15.8 (s, Me{ring}). $^{31}P\{^1H\}$ NMR [acetone-d_6]: δ 72.7 (s, $PPh_2(CH_2)_2PPh_2$), 144.1 (sept, PF_6^-). M.S.[FAB]: m/z 669 {M^+}.

4.23. X-ray structure of (**4**)

Well-shaped red cubes were obtained by crystallisation from a dichloromethane/diethylether mixture on cooling to −30 °C. A suitable crystal specimen was mounted on a glass fibre with epoxy resin and cooled on the goniometer head by means of nitrogen gas to 203 K. Precession photographs and intensity data were collected on a Siemens R3m/V diffractometer using graphite monochromatised Mo Kα X-rays.

Crystal data. $C_{28}H_{29}Cl_2O_3PRu\cdot CH_2Cl_2$, M = 701.4, monoclinic, space group $P2_1/n$, a = 12.936(2), b = 16.809(3), c = 13.979(2) Å, β = 98.06(1)°, U = 3009.6(8) Å^3, D_c = 1.548 g cm^{-3} for Z = 4, F(0 0 0) = 1424, μ(Mo Kα) = 9.59 cm^{-1}, T = -70 °C, crystal size 0.45 × 0.45 × 0.50 mm^3. Cell dimensions were obtained from 50 centred reflections with 2θ values from 22.5° to 32.1°. Intensity data in the range 3.5° < 2θ < 58.0° were collected using a 2θ–θ scan technique. The intensities of three reflections measured periodically showed a decrease of less than 1% over the data collection. An empirical absorption correction was applied using azimuthal scan data for twelve selected reflections. A total of 8285 reflections were collected of which 7966 were independent and 6992, for which $I > 2\sigma(I)$, were used in the refinement. The structure was solved by standard heavy atom routines and refined by full matrix least squares methods. All non-hydrogen atoms were given anisotropic temperature factors. Hydrogen atoms were placed in the model at calculated positions and allowed to ride on their respective carbon atoms. The highest peaks in the final difference map were <1.6 e Å^3, at convergence R_1 = 4.55% and wR_2 = 12.73%, $w = [\sigma^2 (F_o) + 0.0822P^2 + 2.0235P]^{-1}$ where $P = (F_o^2 + 2F_o^2)/3$, S = 1.10 for a data/parameter ratio 20.4:1.

5. Supplementary material

CCDC-236210 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax +44 1223 336033.

Acknowledgements

We thank the S.E.R.C. for a studentship (E.H.), Johnson–Matthey Chemicals Ltd., for a generous loan of $RuCl_3$, and we acknowledge the use of the EPSRC's Chemical Database Service at Daresbury [14].

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