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Influence of arene dissociation and phosphine coordination on the catalytic activity of [RuCl(κ^2-triphos)(*p*-cymene)]PF_6

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ABSTRACT

The catalytic activity of a ruthenium(II)-*p*-cymene complex containing a partially coordinated triphosphine ligand, [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 **1**, has been investigated in the hydrogenation of styrene to ethylbenzene. The influence of arene dissociation and coordination of the free phosphine donor group on the catalytic activity have been probed directly and indirectly by comparison to structural analogues. Analogues of **1** containing in a diphosphine ligand, [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 **2**, or a labile arene ligand, [RuCl(κ^2-triphos)(η^6-$PhCO_2Et$)]PF_6 **3**, show significantly enhanced catalytic activity – demonstrating the importance of ligand coordination/dissociation dynamics in ruthenium(II)-arene compounds during catalysis. These observations are supported by thermolysis reactions of **1** in DMSO. In addition, improved syntheses of **1** and **2** are reported together with the solid-state structures of *syn*-**1**, *syn*-**3** and [Ru(η^3-C_8H_{13})(κ^3-triphos)]PF_6.

1. Introduction

Tripodal triphosphine ligands continue to find widespread application in coordination chemistry and catalysis [1,2]. Among these ligands, the C_3 symmetric phosphine 1,1,1-tris(diphenylphosphinomethyl)-ethane (triphos) and it's derivatives are the most extensively investigated, forming a large variety of transition metal complexes, many of which have been evaluated as catalysts [1–3]. While predominately forming complexes adopting a κ^3-coordinaton mode [2], triphos is also known to partially bind to metal centres in a κ^2-manner [4]. The interconversion between these two coordination modes, by 'arm-off, arm-on' dissociation/association of one of the phosphine centres, has significant consequences for the reactivity of the complex [5]. Examples of dynamic coordination include reversible arm-off triphos dissociation and concomitant addition of CO to [Rh(CO)H(κ^3-triphos)], under hydroformylation conditions [6], and equilibration between κ^3 and μ:κ^2,κ^1- coordination modes in [Rh(COD)(κ^3-triphos)]PF_6 on addition of $[RuCl_2(p\text{-cymene})]_2$ [7].

Ruthenium(II)-arene complexes have been used extensively as catalyst precursors in many different reactions. Complexes of this type bearing chiral amino-amido ligands are especially notable as catalysts for the asymmetric transfer hydrogenation of carbonyl compounds [8]. Other transformations mediated by ruthenium(II)-arene pre-catalysts include alkyne oxidation [9], C–C bond formation [10], olefin metathesis [11], Diels–Alder reactions [12], and free-radical polymerization [13]. As part of our on-going investigations on the catalytic activity of ruthenium(II)-arene complexes [14,15], we report here further on a complex containing a κ^2-coordinated triphos ligand, [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 **1**. Isolation and characterisation of two isomers of this complex together with a study of their catalytic activity is described. The role of arene and phosphine coordination on the catalytic activity has been probed by comparison to structural analogues and thermolysis reactions.

2. Results and discussion

The κ^2-triphos complex [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 **1** is readily prepared by reaction of triphos with the activated ruthenium arene precursor, $[Ru_2(\mu\text{-}Cl)_3(p\text{-cymene})_2]PF_6$ and $[NH_4]PF_6$ in refluxing methanol [16]. Two isomers of **1**, differing by the orientation of the pendant arm of the triphos ligand with respect to the metallocyclic ring, are formed in a 1:1 ratio. Separation was achieved by selective precipitation of the less soluble *anti*-**1** from methanol and subsequent recrystallisation, allowing the definitive characterisation of both isomers – absent in the initial communication [16]. The κ^2-coordination of the triphos ligand is readily apparent from the ^1H and $^{31}P\{^1H\}$ NMR spectra of **1**, the later showing two ^{31}P environments (integral 2:1 ratio) for each of the isomers. The resonances of the two phosphorous centres are observed at 26.9 and 25.2 ppm for the *syn*- and *anti*-isomers,

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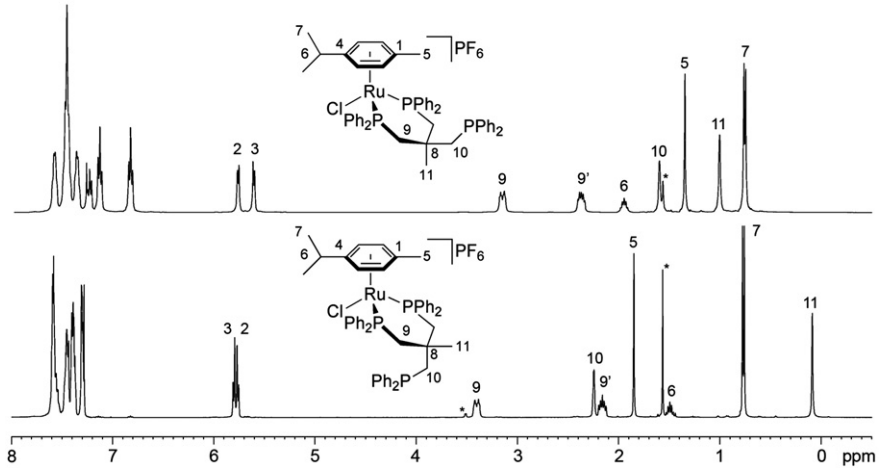


Fig. 1. ^{1}H NMR spectra of *syn*-**1** (top) and *anti*-**1** (bottom) ($CDCl_3$, 293 K).

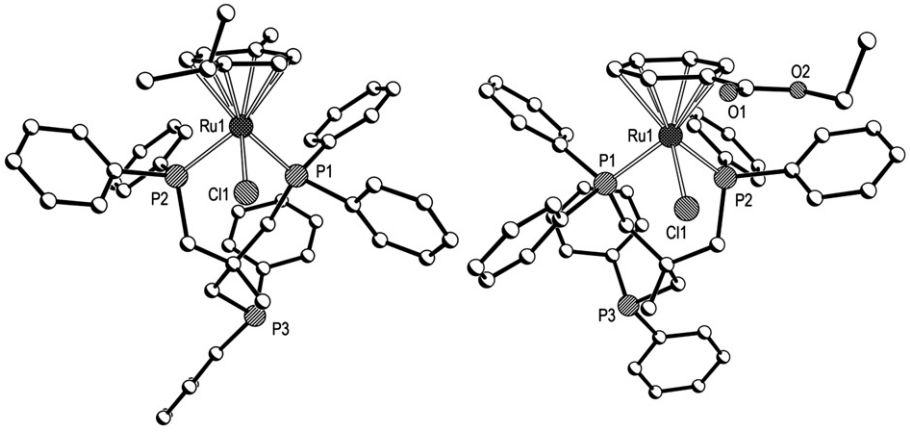
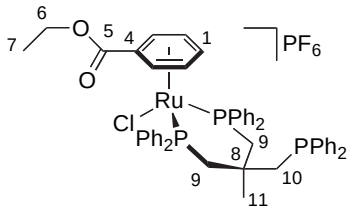


Fig. 2. Ball and stick representations of *syn*-**1** (left) and *syn*-**3** (right). Counter anions, solvent molecules and hydrogen atoms are omitted for clarity. Selected bond lengths (Å): *syn*-**1**: Ru1-P1, 2.3278(14); Ru1-P2, 2.3295(14); Ru1-Cl1, 2.4038(12), Ru1-C, 2.223(5) – 2.324(5). *syn*-**3**: Ru1-P1, 2.328(2); Ru1-P2, 2.330(2); Ru1-Cl1, 2.401(2); Ru1-C, 2.216(6) – 2.276(6).

respectively. Both are similar to that observed for [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 **2** (25.5 ppm) [17]. The chemical shifts of the uncoordinated phosphorus centres (*syn*-**1**, −29.1; *anti*-**1**, −27.6 ppm) are similar to that of free triphos (−25.8 ppm). Inequivalent hydrogen environments on C^9 and large differences in the chemical shift values of H^{10} and H^{11} between the isomers ($\Delta\delta$ = 0.65 and 0.93 ppm, respectively) are observed by ^{1}H NMR spectroscopy (Fig. 1). Both structural assignments are supported by solid-state structures determined by X-ray diffraction; that of *syn*-**1** is depicted Fig. 2 and that of *anti*-**1** was reported earlier [16]. Both structures exhibit comparable structural metrics to related ruthenium(II)-arene phosphine complexes [15,17,18]. The triphos configuration assignments are consistent with those observed in *fac*-[ReX(CO)$_3$(κ^2-triphos)] (X = Cl, Br) [4c]. No interconversion between the isomers was observed on prolonged heating in MeOH.

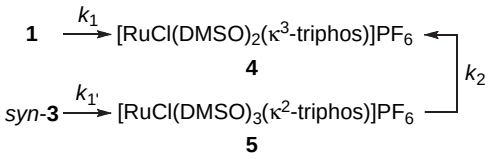
Structural analogues of **1** containing a diphosphine ligand, [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 **2**, or a labile arene ligand, [RuCl(κ^2-triphos)(η^6-$PhCO_2Et$)]PF_6 **3**, where chosen to investigate the role of the free phosphine donor and arene dissociation in the catalytic activity of **1**, respectively. Complex **2** was prepared via a new procedure from [RuCl(PPh_3)(κ^1-dppp)(*p*-cymene)]PF_6 by intramolecular substitution of PPh_3 in almost quantitative yield [18b]. Complex **3** is new and was isolated as the *syn*-isomer in modest yield from the reaction between [$RuCl_2$(η^6-$PhCO_2Et$)]$_2$, triphos and $TlPF_6$ in CH_2Cl_2 at room temperature (Chart 1) [19]. The solid-state structure of *syn*-**3** is depicted in Fig. 2. The structure demonstrates the η^6-coordination of the arene ligand [Ru1-C = 2.216(6)–2.276(6) Å] and the adoption of a "piano-stool" geometry about the ruthenium centre. In solution the structure observed in the solid-state is retained; notably the ^{1}H NMR spectrum of *syn*-**3** exhibits chemical shifts for H^9, H^{10} and H^{11} that are similar to those in *syn*-**1**. The ^{31}P resonances for the triphos ligand are observed at 25.5 and −30.7 in a 2:1 ratio, comparable to **1**.

To establish the relative binding strength of the arene ligands, thermolysis reactions were carried by heating solutions of **1**–**3** in DMSO (Scheme 1). These reactions were monitored in situ using ^{31}P



syn-**3**

Chart 1.



Scheme 1. Thermally induced arene displacement from **1** and *syn*-**3** in DMSO.

{^{1}H} NMR spectroscopy. At elevated temperatures, **1** and *syn*-**3** react with DMSO ultimately resulting in the formation of [RuCl(DMSO)$_2$(κ^3-triphos)]PF$_6$ **4**, by arene displacement and κ^3-coordination of the triphos ligand [20]. The identity of this new complex was confirmed by independent synthesis, as the BF_4^- salt, from [RuCl(κ^3-triphos)]$_2$(BF_4)$_2$. The formation of **4** from **1** at 90 and 100 °C proceeds without the observation of any intermediates and the rate is approximately two times faster for *syn*-**1** than *anti*-**1** (Table 1). Substitution of ethyl benzoate by DMSO in *syn*-**3** occurs at much lower temperatures (≥50 °C) and proceeds via an intermediate species, identified by the presence of an additional pair of resonances at 29.1 and −27.3 ppm, in 2:1 ratio, in the ^{31}P{^{1}H} NMR spectrum. This intermediate species is tentatively assigned as [Ru(DMSO)$_3$Cl(κ^2-triphos)]PF$_6$ **5** on the basis of the aforementioned ^{31}P{^{1}H} NMR data and because the appearance of uncoordinated ethyl benzoate, shown by ^{1}H NMR spectroscopy, parallels its formation by ^{31}P{^{1}H} NMR spectroscopy [21]. The relative ease in which ethyl benzoate is substituted, in comparison to *p*-cymene, is in line with the more electron deficient nature of the arene, a feature that previous synthetic strategies have exploited [22]. In comparison to **1** and *syn*-**3**, no arene displacement was observed for **2** on heating at 90 °C in DMSO for 12 h.

The activation parameters for arene displacement in *syn*-**3** have been determined by ^{31}P{^{1}H} NMR spectroscopy; values for **1** were *estimated* from the measured rates at 90 and 100 °C (Table 1). The significantly negative values of $\Delta S^{\ddagger}$ for the arene displacement steps are indicative of a large degree of associative character. To account for these observations, mechanisms involving $\eta^6 \rightarrow \eta^4$ ring slippage of the arene ligand and coordination of the pendant phosphine arm in **1**, and DMSO in *syn*-**3**, seem probable. Similar mechanisms have been proposed for arene exchange in chromium(0)-arene compounds [Cr(CO)$_2$L(η^6-arene)], where L is a κ^1-coordinated bidentate ligand that facilitates this process by κ^2-coordination [23]. The lower magnitude of $\Delta S^{\ddagger}$ for the reaction of *syn*-**3** implies a somewhat more concerted process in comparison to **1**, which are characterised by $\Delta S^{\ddagger}$ values of much higher magnitude. This difference could be reflective of the more labile nature of the ethyl benzoate ligand in *syn*-**3** in comparison to the *p*-cymene ligand in **1**, which appears to require the associated coordination of the pendant triphos arm to effect ring slippage (*cf.* reactivity of **2**). The enhanced rate of *p*-cymene substitution in *syn*-**1**, in comparison to *anti*-**1**, is in agreement with the mechanistic proposal for these complexes, as the conformation of the triphos ligand in *syn*-**1** enables the pendant phosphine to access the metal centre more readily. The positive $\Delta S^{\ddagger}$ value for the formation of **4** from **5** suggests a mechanism with significant dissociative character.

Table 1
Kinetic data for arene displacement from **1** and *syn*-**3** in DMSO.[a]

	rxn	Rate ($t_{1/2}$)		Activation parameters	
		90 °C	100 °C	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ Jmol^{-1}K^{-1}
syn-**1**	1	9 ± 2 h	4.4 ± 0.3 h	~80[b]	~ −120[b]
anti-**1**	1	20 ± 7 h	9.7 ± 1.1 h	~70[b]	~ −140[b]
syn-**3**	1′	<3 min[c]	<3 min[c]	91 ± 3	−38 ± 9
	2	<3 min[c]	<3 min[c]	112 ± 4	+29 ± 11

[a] Determined by ^{31}P{^{1}H} NMR spectroscopy, [Ru] = 10 mM. 1, 1′ or 2 refers to the corresponding process indicated in Scheme 1.
[b] Approximate values – estimated from rate at two different temperatures.
[c] Extrapolated from lower temperature data.

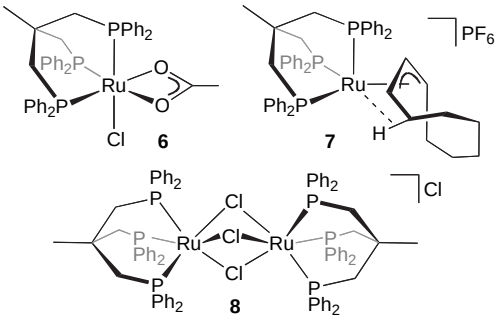


Chart 2.

The catalytic activity of **1** and the structural analogues **2** and *syn*-**3** were evaluated for the hydrogenation of styrene to ethyl benzene in THF (S:C = 2000:1, 50 bar H_2, 90 °C, 2 h). A range of κ^3-triphos complexes; [RuCl(OAc)(κ^3-triphos)] **6** [24], [Ru(η^3-C_8H_{13})(κ^3-triphos)]PF$_6$ **7** (see Supporting information for solid-state structure) [25], and [Ru$_2$(μ-Cl)$_3$(κ^3-triphos)$_2$]Cl **8** [26], were also evaluated under the same conditions for comparison purposes (Chart 2, Table 2).

The catalytic activity of each isomer of **1** was similar and low (<5% conversion), even under these relatively forcing conditions. Addition of mercury, as a selective poison for heterogeneous catalysts [27], did not inhibit catalytic activity suggesting that, while low, the observed activity is the result of homogenous catalysis. In contrast to **1**, good conversion was observed with the related diphosphine complex (**2**, 79% conversion). The active species in [RuCl(κ^2-diphosphine)(η^6-arene)]$^+$ systems are believed to be formed following chloride dissociation (rate limiting) and coordination of dihydrogen [15b]. With this in mind, and in view of the slow rate of arene loss observed under similar conditions, the most reasonable explanation for the low activity for **1** is that the triphos ligand suppresses activity by undergoing κ^2–κ^3 coordination following chloride dissociation, preventing subsequent coordination of dihydrogen. Complex *syn*-**3** was found to be a highly active catalyst precursor under the conditions; the activity in this case is may be attributed to facile arene loss as demonstrated during the thermolysis reactions described above. The κ^3-triphos complexes **6**–**8** also showed good catalytic activity. Moreover, the acetate complex **5** was found to be an exceptional catalyst, even when

Table 2
Hydrogenation of styrene to ethylbenzene catalysed by **1**–**3** and **6**–**8** (0.05 mol% Ru).[a]

Precatalyst	Temp/°C	Conversion
syn-**1**	90	3%
syn-**1**[b]	90	4%
anti-**1**	90	4%
anti-**1**[b]	90	5%
2	90	79%
syn-**3**	90	100%
syn-**3**	50	<1%
6	90	100%
6	50	100%
7	90	53%
8[c]	90	93%

[a] Conditions: 5.0 × 10^{-6} mol pre-catalyst, S:C = 2000:1, 2 ml THF, 100 mg octane (internal standard), 50 bar H_2, 2 h. Conversion determined by GC; Ethyl benzene was the only product observed. Values averaged over duplicate runs.
[b] 0.1 ml Hg added.
[c] 5.0 × 10^{-6} mol/ruthenium.

catalytic runs were preformed at 50 °C (for comparison *syn*-**4** was inactive) [24]. The high activity of the κ^3-triphos complexes, particularly those containing chloride ligands, and the trends established from thermolysis reactions together suggest that the active species for **1** and *syn*-**3** are mostly likely based on the [RuCl(κ^3-triphos)]$^+$ moiety.

Hydrogenation of the aromatic ring was not observed during the hydrogenation of styrene with all complexes studied. Complex **1** (mixture of isomers) has been previously reported to be a catalyst precursor for the homogeneous hydrogenation of arenes [16]. Related ruthenium(II)-arene diphosphine complexes have also been suggested to be catalyst precursors for both heterogeneous and homogenous catalysed hydrogenation of benzene, depending on the diphosphine, anion and reaction conditions [28]. However, under similar conditions to those reported previously (except using a glass-lined autoclave and Teflon coated magnetic stirrer bar in place of an autoclave with stainless steel fittings) no benzene or toluene hydrogenation was observed with *syn*-**1** or *anti*-**1**. This lack of activity is consistent with the strong arene coordination in these complexes, demonstrated by the thermolysis reactions. It seems plausible that the reported activity for the hydrogenation of arenes with **1** may be due to the formation (or presence) of catalytic active nanoparticles [27a,29]. Notably, closely related homogeneous complexes immobilized on surfaces containing metal particles have been shown to hydrogenate arenes under pseudo-homogeneous conditions [30]. It is also noteworthy that nanoparticle catalysts tend to give significantly higher reaction rates in hydrogenation reactions and are also capable of hydrogenating aromatic systems [31].

In summary, under controlled conditions complex **1** shows low activity as a pre-catalyst for the hydrogenation of styrene to ethylbenzene. This low activity may be attributed to κ^2–κ^3 coordination of the triphos ligand and to the stability of the Ru-*p*-cymene bond. These assertions are supported by the high catalytic activity of structural analogues, containing instead a diphosphine ligand (**2**) or a labile arene ligand (*syn*-**3**), and thermolysis reactions in DMSO. The identification of these factors are relevant to the future development of catalytically active ruthenium(II)-arene compounds and complexes containing the triphos ligand.

3. Experimental section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. CH_2Cl_2, diethyl ether, benzene, toluene and pentane, were dried under nitrogen using a solvent purification system (Innovative Technology Inc). Octane and CH_2ClCH_2Cl were distilled from CaH_2 and P_2O_5, respectively, and stored over molecular sieves under nitrogen. All other solvents were p.a. quality and saturated with nitrogen prior to use, with the exception of DMSO which was purchased extra dry (<50 ppm H_2O) over molecular sieves under N_2 from ACROS. Styrene was saturated with nitrogen and stored over molecular sieves. [$Ru_2(\mu$-Cl)$_3$(*p*-cymene)$_2$]PF_6 [32], [RuCl(PPh_3)(κ^1-dppp)(*p*-cymene)]PF_6 [18b], [$RuCl_2(\eta^6$-$PhCO_2Et)]_2$ [22d], [RuCl(OAc)(κ^3-triphos)] [24], [RuCl(κ^3-triphos)]$_2(BF_4)_2$ [24], [Ru(η^3-C_8H_{13})(κ^3-triphos)]PF_6 [25], and [$Ru_2(\mu$-Cl)$_3(\kappa^3$-triphos)$_2$]Cl [26] were prepared as described elsewhere. All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at room temperature unless otherwise stated. Chemical shirts are given in ppm and coupling constants (*J*) in Hz. NMR labelling schemes for **1** and *syn*-**3** are detailed in Fig. 1 and Chart 1, respectively. ESI-MS were recorded on a Thermo Finnigan LCQ DecaXP Plus quadrupole ion trap instrument using a literature protocol [33]. Microanalyses were performed at the EPFL.

3.1. Preparation of [RuCl(κ^2-triphos)(*p*-cymene)]PF_6 *1*

A suspension of [$Ru_2(\mu$-Cl)$_3$(*p*-cymene)$_2$]PF_6, (0.58 g, 0.80 mmol), [NH_4]PF_6 (0.13, 0.80 mmol) and (PPh_2CH_2)$_3$CMe (1.00 g, 1.60 mmol) in MeOH (200 ml) was heated at reflux for 3 h. After cooling, the solution was slowly concentrated in vacuo at RT. Following the onset of precipitation, the composition of the solution phase was monitored by $^{31}P\{^1H\}$ NMR spectroscopy until precipitation of *anti*-isomer was nearly complete (ca. 143 ml). The solid was filtered, washed with diethyl ether (ca. 25 ml) and dried in vacuo to yield 0.67 g (40% by ruthenium) of the *anti*-isomer as a yellow powder. The filtrate was reduced to dryness and the residue extracted with CH_2Cl_2 through celite. The resulting crude product was recrystallised from hot MeOH to yield 0.49 g (29% by ruthenium) of the *syn*-isomer as a yellow crystalline solid. Yellow crystals of the *syn*-isomer suitable for X-ray diffraction were obtained by recrystallisation from CH_2Cl_2-pentane at RT. Isolated yields of the *anti*-isomer (30–40% by ruthenium) and *syn*-isomer (10–40% ruthenium) varied between different preparations. NMR data are in agreement with the literature data [16], with data for each isomer presented here.

syn-**1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.08–7.66 (m, 26H), 6.77–6.88 (m, 4H), 5.79 (d, $^3J_{HH}$ = 6.2, 2H, H^2), 5.64 (d, $^3J_{HH}$ = 6.3, 2H, H^3), 3.18 (dt, $^2J_{HH}$ = 14.6, J_{PH} = 4.3, 2H, H^9), 2.41 (dt, $^2J_{HH}$ = 14.6, J_{PH} = 6.4, 2H, $H^{9'}$), 1.93 (sept, $^3J_{HH}$ = 6.9, 1H, H^6), 1.58–1.62 (m, 2H, H^{10}), 1.41 (s, 3H, H^5), 1.02 (s, 3H, H^{11}), 0.79 (d, $^3J_{HH}$ = 6.9, 6H, H^7). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 128–139 (m), 123.7 (br, C^4), 105.2 (br, C^1), 95.5 (t, $^2J_{PC}$ = 3, C^3), 92.5 (br, C^2), 45.0–45.4 (m, C^{10}), 38.2 (d, $^2J_{PC}$ = 16, C^8), 33.0–34.0 (m, C^{11} + C^9), 30.0 (s, C^6), 21.4 (s, C^7), 16.7 (s, C^5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 26.9 (s, 2P, Ru–$\underline{P}Ph_2$), −29.1 (s, 1P, *pend*-$\underline{P}Ph_2$), −144.1 (sept, $^1J_{PF}$ = 714, 1P, $\underline{P}F_6$,). ESI-MS (CH_2Cl_2, 60 °C, 5.0 kV) positive ion: *m*/*z*, 895 $[M]^+$; negative ion: *m*/*z*, 145 $[PF_6]^-$. Anal. Calcd for $C_{51}H_{53}ClF_6P_4Ru$ (1040.30 gmol^{-1}): C, 58.88; H, 5.13. Found: C, 58.84; H, 5.11. *anti*-**1**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.26–7.64 (m, 30H), 5.80 (d, $^3J_{HH}$ = 6.4, 2H, H^3), 5.76 (d, $^3J_{HH}$ = 6.4, 2H, H^2), 3.40 (dt, $^2J_{HH}$ = 14.2, J_{PH} = 4.1, 2H, H^9), 2.21–2.27 (m, 2H, H^{10}), 2.16 (dt, $^2J_{HH}$ = 14.1, J_{PH} = 7.4, 2H, $H^{9'}$), 1.85 (s, 3H, H^5), 1.49 (sept, $^3J_{HH}$ = 6.8, 1H, H^6), 0.77 (d, $^3J_{HH}$ = 6.9, 6H, H^7), 0.09 (s, 3H, H^{11}). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 128–139 (m), 118.9 (br, C^4), 110.4 (br, C^1), 97.7 (br, C^3), 90.0 (br, C^2), 50.0–50.5 (m, C^{10}), 39.0 (d, $^2J_{PC}$ = 14, C^8), 34.2–34.8 (m, C^9), 30.7 (br d, $^3J_{PC}$ = 9, C^{11}), 29.6 (s, C^6), 22.0 (s, C^7), 18.4 (s, C^5). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 162 MHz): δ 25.2 (s, 2P, Ru–$\underline{P}Ph_2$), −27.6 (s, 1P, *pend*-$\underline{P}Ph_2$), −144.1 (sept, $^1J_{PF}$ = 714, 1P, $\underline{P}F_6$). ESI-MS (CH_2Cl_2, 60 °C, 5.0 kV) positive ion: *m*/*z*, 895 $[M]^+$; negative ion: *m*/*z*, 145 $[PF_6]^-$. Anal. Calcd for $C_{51}H_{53}ClF_6P_4Ru$ (1040.30 gmol^{-1}): C, 58.88; H, 5.13. Found: C, 58.86; H, 5.35.

3.2. Preparation of [RuCl(κ^2-dppp)(*p*-cymene)]PF_6 *2*

A solution of [RuCl(PPh_3)(κ^1-dppp)(*p*-cymene)]PF_6 (0.15 g, 0.14 mmol) in CH_2ClCH_2Cl (20 ml) was heated at reflux for 60 min. The solution was concentrated to ca. 2 ml and the product precipitated, as a yellow powder, by addition of diethyl ether (30 ml). The precipitate was filtered, washed with diethyl ether (3 × 10 ml) and pentane (2 × 10 mL) and dried in vacuo. Yield: 0.11 g (96%). NMR data are in agreement with the literature data [17].

3.3. Preparation of [RuCl(κ^2-triphos)(η^6-$PhCO_2Et$)]PF_6 *3*

A suspension of [$RuCl_2(\eta^6$-$PhCO_2Et)]_2$ (0.20 g, 0.31 mmol), (PPh_2CH_2)$_3$CMe (0.39 g, 0.62 mmol) and $TlPF_6$ (0.22 g, 0.63 mmol, *highly toxic!*) in CH_2Cl_2 (25 ml) was stirred at RT for 14 h. The suspension was then filtered through celite and the solvent removed in vacuo. Recrystallisation of the resulting residue by slow evaporation of a CH_2Cl_2–pentane solution gave *syn*-**3** as a yellow

powder. Yield: 0.069 g (11%/ruthenium). Yellow crystals of *syn*-**3** suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution layered with toluene and pentane at RT. *anti*-**3** could not be obtained in pure form.

syn-**3:** ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.40–7.65 (m, 20H, P$\underline{Ph}_2$C^9), 6.79–7.31 (m, 10H, P$\underline{Ph}_2$C^{10}), 6.51 (d, $^3J_{HH}$ = 6.1, 2H, H^3), 6.05 (t, $^3J_{HH}$ = 5.6, 1H, H^1), 5.55–5.70 (m, 2H, H^2), 4.05 (q, $^3J_{HH}$ = 7.0, 2H, H^6), 3.22 (dt, $^2J_{HH}$ = 14.5, $^2J_{PH}$ = 5, 2H, H^9), 2.51 (dt, $^2J_{HH}$ = 14.5, $^2J_{PH}$ = 7, 2H, H$^{9'}$), 1.52–1.57 (m, 2H, H^{10}), 1.24 (t, $^3J_{HH}$ = 7.0, 3H, H^7), 0.99 (s, 3H, H^{11}). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100 MHz): δ 161.4 (s, C^5), 128–139 (m), 102.8 (t, $^2J_{PC}$ = 3, C^3), 96.3 (br, C^4), 91.5 (br, C^1), 90.4 (t, $^2J_{PC}$ = 2, C^2), 63.0 (s, C^6), 43.3–43.7 (m, C^{10}), 38.6 (d, $^2J_{PC}$ = 17, C^8), 33.9 (q, $^3J_{PC}$ = 11, C^{11}), 33.2 (td, $^1J_{PC}$ = 19, $^3J_{PC}$ = 7, C^9), 13.9 (s, C^7). ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ 25.5 (s, 2P, Ru–$\underline{P}Ph_2$), −30.7 (s, 1P, *pend*-$\underline{P}Ph_2$), −144.3 (sept, $^1J_{PF}$ = 711, 1P, $\underline{P}F_6$). ^{31}P{^{1}H} NMR (d_6-DMSO, 162 MHz): δ 26.5 (s, 2P, Ru–$\underline{P}Ph_2$), −30.8 (s, 1P, *pend*-$\underline{P}Ph_2$), −144.1 (sept, $^1J_{PF}$ = 713, 1P, $\underline{P}F_6$). ESI-MS (CH_2Cl_2, 60 °C, 5.0 kV) positive ion: *m*/*z*, 911 $[M]^+$; negative ion: *m*/*z*, 145 $[PF_6]^-$. Anal. Calcd for $C_{50}H_{49}ClF_6O_2P_4Ru$ (1056.35 gmol^{-1}): C, 56.85; H, 4.68. Found: C, 56.93; H, 4.72. *anti*-**3**: ^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz, complex only): δ 24.6 (s, 2P, Ru–$\underline{P}Ph_2$), −28.1 (s, 1P, *pend*-$\underline{P}Ph_2$).

3.4. Preparation of [RuCl(DMSO)$_2$(κ^3-triphos)]BF$_4$ (**4.BF$_4$**)

This complex is prepared quantitatively by dissolving [RuCl(κ^3-triphos)]$_2$(BF_4)$_2$ in d_6-DMSO and was characterised in situ by NMR spectroscopy. **4.BF$_4$** is unstable in the absence of DMSO.

^{1}H NMR (d_6-DMSO, 400 MHz, N_2, 293 K): δ 7.53–6.99 (m, 30H), 2.33 (br, 6H, CH_2), 1.48 (br, 3H, CH_3). OS$\underline{Me}_2$ were not unambiguously located. ^{31}P{^{1}H} NMR (d_6-DMSO, 162 MHz, N_2, 293 K): δ 35.1 (br (fwhm ~ 23 Hz), 3P).

For low temperature characterisation: A screw cap NMR tube was charged with [RuCl(κ^3-triphos)]$_2$(BF_4)$_2$ (7 mg) and placed under a nitrogen atmosphere. Dry DMSO (0.05 ml) followed by CD_2Cl_2 (0.45 ml) were then added and the tube sealed. Yield: 93% of **4.BF$_4$** by ^{31}P{^{1}H} NMR spectroscopy. Consistent with the structural assignment, cooling to 183 K resolves the broad ^{31}P resonance observed at RT into resonances at 40.4 and 20.0 ppm in a 2:1 ratio (see Supporting information).

^{1}H NMR (CD_2Cl_2 + 10% *v*/*v* DMSO, 400 MHz, N_2, 293 K): δ 7.03–7.45 (m, 30H), 2.30–2.36 (m, 6H, $C\underline{H}_2$), 1.49–1.55 (m, 3H, $C\underline{H}_3$). OS$\underline{Me}_2$ were not unambiguously located. ^{13}C{^{1}H} NMR (CD_2Cl_2 + 10% *v*/*v* DMSO, 100 MHz, N_2, 293 K): δ 127–136 (m), 37.7–37.9 (m, $\underline{C}(CH_2)$), 37.1 (q, $^3J_{PC}$ = 11, $\underline{C}H_3$), 33.2–33.8 (m, CH_2). OS$\underline{Me}_2$ were not unambiguously located. ^{31}P{^{1}H} NMR (CD_2Cl_2 + 10% *v*/*v* DMSO, 162 MHz, 293 K, N_2): δ 37.5 (br, 3P). ^{31}P{^{1}H} NMR (CD_2Cl_2 + 10% *v*/*v* DMSO, 162 MHz, 183 K, N_2): δ 40.4 (d, $^2J_{PP}$ = 46, 2P, Ru–$\underline{P}Ph_2$), 20.0 (t, $^2J_{PP}$ = 46, 1P, Ru–$\underline{P}Ph_2$).

3.5. Catalytic studies

All catalytic experiments were conducted using a home-built multi-cell autoclave containing an internal temperature probe. Each glass reaction vessel was charged with the pre-catalyst, substrate, internal standard (100 mg octane) and solvent and then placed inside the autoclave and sealed. This procedure was carried out in air. Following flushing with H_2 (3 × 10 bar), the autoclave was heated to the desired temperature under H_2 (10 bar) and then maintained at the desired pressure for the duration of the catalytic run. The autoclave was then cooled to ambient temperature (typically ≤5 min when run at 50 °C, ≤10 min when run at 90 °C) using an external water-cooling jacket and the pressure released. Conversions were determined by GC analysis of the samples using a Varian chrompack CP-3380 gas chromatograph, with species verified by comparison to authentic samples.

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Appendix. Supplementary information

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2011.02.022.

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[19] Although low yielding (ca. 66% by $^{31}P\{^{1}H\}$ NMR spectroscopy), the *syn*-isomer was formed selectively using this procedure (*syn*:*anti* ~ 3:1) allowing pure *syn*-**3** to be isolated readily by recrystallisation (11% yield/Ru). The synthetic procedures available for the synthesis of **3** were limited by the low thermal stability of this complex.
[20] Small quantities of $[Ru_2(\mu\text{-}Cl)_3(\kappa^3\text{-triphos})_2]^+$ can also be detected during the thermolysis of both **1** and *syn*-**3** in DMSO.
[21] A solution of *syn*-**3** in d_6-DMSO was heated at 50 °C for 20 min and then cooled to RT [data for **5**: $^{31}P\{^{1}H\}$ NMR (d_6-DMSO, 162 MHz, 293 K): δ 29.1 (br, 2P, Ru–$\underline{P}Ph_2$), −27.3 (s, 1P, *pend*-$\underline{P}Ph_2$), −144.1 (sept, $^{1}J_{PF} = 713$, 1P, PF_6)]. The *syn*-**3**:**5** ratio was 1:0.18 (only trace quantity of **4**) by integration of $^{31}P\{^{1}H\}$ NMR data. The ratio of coordinated {δ 3.93 (q, $^{3}J_{HH} = 7$ Hz, $\underline{CH}_2$)} to uncoordinated {δ 4.32 (q, $^{3}J_{HH} = 7$ Hz, $\underline{CH}_2$)} ethyl benzoate was 1:0.20 by integration of ^{1}H NMR data.
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