Atom Transfer Radical Addition Catalyzed by Ruthenium–Arene Complexes Bearing a Hybrid Phosphine–Diene Ligand

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Supporting Information

ABSTRACT: The synthesis and characterization of a series of arene ruthenium complexes bearing either (3,5-cycloheptadienyl)diphenylphosphine or (cycloheptyl)diphenylphosphine are reported. Upon irradiation or heating, all these complexes lose their arene ligand but then exhibit a different behavior depending on the nature of the phosphine ligand. (Cycloheptadienyl)phosphine complexes **1** and **3** give a cationic dinuclear Ru complex **5** for which the two Ru atoms are bridged by three chlorido ligands and flanked by two tridendate (cycloheptadienyl)phosphines. (Cycloheptyl)diphenylphosphine complexes **2** and **4** undergo arene exchange when toluene is used as solvent or degrade in dichloromethane. ATRA catalytic trials conducted in parallel with these complexes using CCl_4 and styrene as standard substrates, highlighted the deep impact of the dienyl moiety on the results. In smooth conditions (UV irradiation or moderate heating), only (cycloheptyl)phosphine derivatives give Karasch adduct in satisfactory yields. Their performance was considerably improved by combining irradiation and heating. At higher temperature, the cationic dinuclear complex **5** revealed as active and robust, giving turnover numbers as high as 9700 when tetradecene and CCl_4 were used as substrates.

INTRODUCTION

$[RuCl_2(arene)(PR_3)]$ complexes are known for promoting a great variety of catalytic transformations,[1] among which Atom Transfer Radical Addition (ATRA).[2] This reaction, also called Kharasch addition, allows the addition of a polyhalogenated substrate to an olefin in a controlled manner.[3,4] $(Arene)RuCl_2(PR_3)$ complexes are readily available and air-stable.[5] They can be activated by irradiation or simple heating which results in the loss of the arene ligand.[6,7] These precatalysts are thus particularly attractive from a practical point of view. Main drawbacks are their relatively moderate activity in ATRA with respect to the best Ru systems described to date,[8,9] and their propensity to degrade upon prolonged reaction time, thus limiting the turnover number (TON). The recurrent problem of stability met with these catalysts may be explained by the highly coordinatively unsatured nature of the active species formed once the 6π-electrons-arene ligand is released. Chelated Ru complexes with phosphine-arene ligands have been designed to address this issue. Unfortunately, they were found inefficient for promoting mechanistically related Atom Transfer Radical Polymerisation (ATRP) reactions due to their too high intertness.[10] We hypothesized that the use of hybrid phosphine-diene ligand instead might be a good compromise: it should give stable but still active catalyst for ATRA reaction. First set of catalytic trials were done using a (*p*-cymene)Ru complex containing a phosphine with a pendant 1,3-butadiene moiety.[11,12] Some interesting results were obtained for the ATRA reaction. However, all our efforts, at that time, to isolate, characterize or even detect a chelated phosphine-diene complex failed. Thus, we were unable to prove our concept. We therefore decided to use (3,5-cycloheptadienyl)diphenylphosphine in Ru-promoted ATRA reaction since we previously clearly established the chelating abilities of this hybrid phosphine diene ligand with rhodium.[13] Herein, we present the synthesis of (*p*-cymene)Ru complex **1** with cycloheptadienylphosphine ligand (Figure 1). For the sake of comparison, we describe the synthesis of Ru complex **2** with (cycloheptyl)diphenylphosphine ligand. This provides an exact analogue of complex **1** which allows to estimate the contribution of the dienyl moiety while avoiding other electronic and steric features of the ligand. Since the catalytic activity results from the arene release, we also targeted Ru complexes **3**, **4** with more labile electron poor ethyl benzoate ligand. Efforts toward the identification of the species formed upon arene disengagement are described as well as assessment of the catalytic performance of these complexes in ATRA.

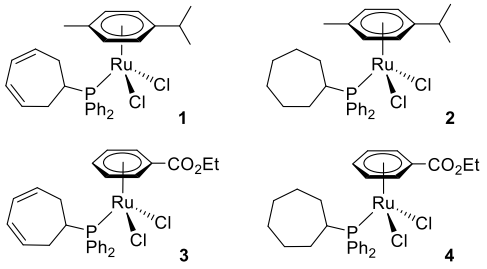


Figure 1: Ruthenium complexes with cycloheptadienyl- or cycloheptylphosphine ligands

RESULTS AND DISCUSSION

(3,5-Cycloheptadienyl)diphenylphosphine has been obtained *via* the catalytic hydrophosphination of 1,3,5-cycloheptatriene with diphenylphosphine in the presence of *n*-BuLi according to our previously described procedure.[14] Its saturated analogue was synthesized by reaction of bromocycloheptane with lithium diphenylphosphide in diethyl ether at room temperature. The (cycloheptyl)phosphine was obtained as a white powder in 94% yield. The synthesis of the Ru complexes **1-4** was then accomplished by reacting the cycloheptadienyl- or cycloheptylphosphine with 0.5 equiv. of the respective dimer $[Ru(\eta^6\text{-arene})Cl_2]_2$ (yields range between 90 and 95%). The complexes **1-4** were fully characterized by 1D NMR (^1H, ^{13}C, ^{31}P), 2D NMR (COSY, HSQC, HMBC), Elemental Analysis, HRMS and IR spectroscopy. The ^{31}P NMR spectra of complexes **1-4** show one singlet at 21.3, 23.7, 25.4 and 27.7 ppm, respectively, downfield shifted of either 25 or 30 ppm relatively to free phosphine depending on the arene ligand. The ^1H NMR spectra of **1** and **3** display only one multiplet between 5.68 and 5.80 ppm for the four protons of the dienyl part, with the same shape and in the same chemical shift range as the free ligand. These results are indicative of the coordination of the phosphorus atoms to the ruthenium metal and of the non-coordinated state of the dienyl part of the (cycloheptadienyl)phosphine. Suitable crystals for X-Ray diffraction studies of complexes **1-4** were obtained by vapour diffusion techniques. ORTEP views of complexes **1-4** are presented in Figure 2.

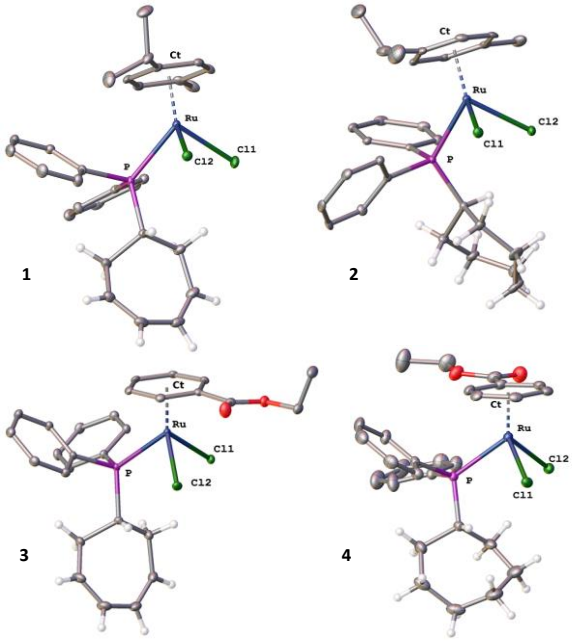


Figure 2: ORTEP views of complexes **1-4** (hydrogen atoms are omitted for clarity). Selected distances (Å) and angles (deg) in **1-4** order: **Ru–Ct** 1.6906(10), 1.7114(15), 1.6949(8), 1.6964(14); **Ru–P** 2.3885(6), 2.3757(9), 2.3650(5), 2.3787(8); **Ru–Cl1** 2.4089(6), 2.4091(8), 2.4037(5), 2.3987(7); **Ru–Cl2** 2.3890(6), 2.4178(8), 2.3959(4), 2.4042(7). **Cl1-Ru-Cl2** 88.86(2), 86.50(3), 89.391(16), 88.31(3); **Cl1-Ru-Ct** 123.29(4), 126.59(6), 125.05(3), 124.35(6); **Cl1-Ru-P** 93.28(2), 90.50(3), 89.727(15); 85.29(3); **Cl2-Ru-Ct** 126.54(4), 124.82(6), 125.76(3), 124.96(6); **Cl2-Ru-P** 84.16(2), 87.71(3), 86.553(16), 93.66(3); **Ct-Ru-P** 128.47(4), 127.89(5), 128.02(3), 128.01(5).

In the four complexes, the arene ruthenium moieties present a three-legged piano stool structure with structural parameters similar to each other and within the range of those observed for related $(\eta^6\text{-arene})RuCl_2(PR_3)$ structures.[15] The cycloheptadienyl and cycloheptyl rings adopt a half-chair-like conformation and chair-like conformation, respectively, and are oriented in an antiperiplanar conformation with respect to the centroid of the arene ring. In complexes **1** and **3**, the diphenylphosphino group is in pseudo equatorial position on the cycloheptadienyl ring leaving the dienyl moiety away from the Ru centre.

With the aim to check to what extent the dienyl part of the (cycloheptadienyl)phosphine can interact with the Ru centre once the arene ligand is released, we have first studied the behaviour of **1** and **3** upon heating. Complex **3** with the more labile benzoate ligand was first heated at 50 °C in $CDCl_3$ in Young NMR tube protected from light. ^1H NMR spectrum registered after 16 h showed only 5% of free benzoate and no change on ^{31}P NMR spectrum. Prolonged heating for 8 h at 50 °C under sunlight led to 60% of benzoate decoordination and the appearance of a new signal at 100 ppm on ^{31}P NMR spectrum. This difference in kinetics of arene decoordination between darkness and daylight prompt us to study the behaviour of complex **3** under photoirradiation. $CDCl_3$ solution of complex **3** was irradiated by 150W mercury lamp (Heraeus TQ150W) at room temperature and reaction progress was monitored by NMR. 15 minutes under irradiation were sufficient to see complete decoordination of the benzoate ligand in ^1H NMR and the presence of only one peak at 100 ppm on ^{31}P NMR spectrum. Similar evolution was observed with complex **1** but it required 2.5 h irradiation time (Figure 3).

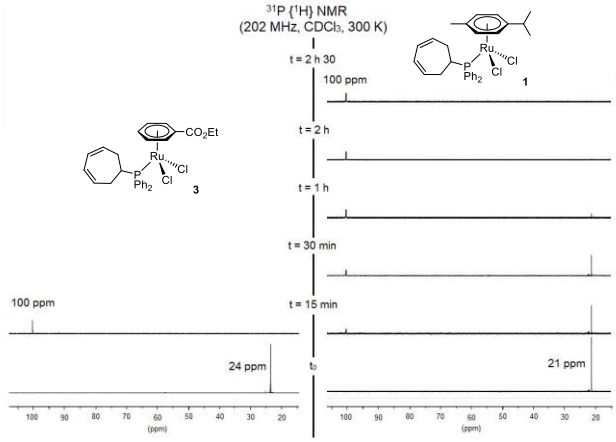
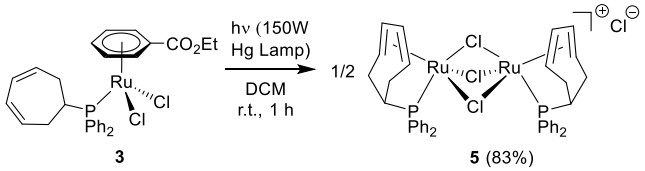


Figure 3: Time course $^{31}P\{^1H\}$ NMR spectra (300 K) of a $CDCl_3$ solution of **1** (right) and **3** (left) under irradiation (150W Hg Lamp).

The reaction was next carried out from complex **3** at preparative scale in Schlenk tube in CH_2Cl_2. One hour under irradiation was necessary to reach completion (Scheme 1). The compound was isolated as brick-red powder after evaporation of CH_2Cl_2 and washing with diethyl ether. It was identified as a cationic dinuclear complex **5** based on HRMS, elemental analysis, X-Ray diffraction study and NMR spectroscopies.



Scheme 1

Expectedly, ^{31}P NMR spectrum of complex **5** displayed a single resonance at 100 ppm. ^1H NMR spectrum registered at 253K

showed disappearance of the signals of the benzoate ligand and a split of the signals of the olefinic protons into two multiplets at δ = 4.89 and 5.61 ppm of equal intensities, which provides evidence of η^4-coordination of the cycloheptadienyl moiety in solution (similar behaviour was observed in Rh complexes).[13] Vapour diffusion of pentane into $CDCl_3$ solution of complex (NMR sample) gave suitable crystals for X-Ray diffraction study (Figure 4). The X-Ray analysis confirmed the complete loss of the benzoate ligand and the tridentate coordination of the cycloheptadienyl phosphine. It showed a dinuclear cation in which the two Ru centres are connected by three bridging chlorido ligands. The structure exhibits a two-fold axis passing through the midpoint of Cl2-Cl3 line and Cl1, the two (cycloheptadienyl)phosphine ligands being oriented in a *cis*-configuration. The two cycloheptadienyl rings adopt a chair-like conformation with the diphenylphosphino group in pseudo axial position, allowing the formation of the Ru-chelates. The bond lengths C3-C4 (1.407(3)), C4-C5 (1.434(3)) and C6-C7 (1.400(3)) range between single and double bound, and clearly indicate the π-back-bonding character of Ru-diene bonds. The Ru-Cl distances are in the expected range with Ru-Cl1 bond longer than Ru-Cl2 and Ru-Cl3 bonds denoting stronger *trans*-effect of the phosphine relative to olefins.

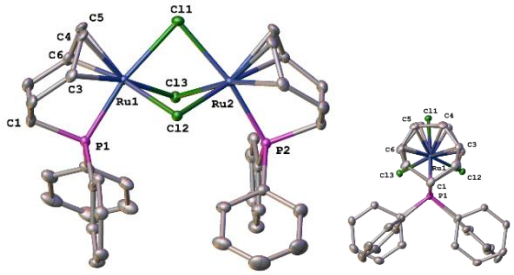


Figure 4: ORTEP views of complex **5** (hydrogen atoms and chloride anion are omitted for clarity). Selected distances (Å) and angles (deg): Ru1–Cl1 2.5280(5), Ru1–Cl2 2.4355(5), Ru1–Cl3 2.4285(5), Ru1–P1 2.3001(6), Ru1–C3 2.266(2), Ru1–C4 2.145(2), Ru1–C5 2.137(2), Ru1–C6 2.263(2), Ru1–Ct1 2.0910(19), Ru1–Ct2 2.0865(16), P1–C1 1.829(2), C3–C4 1.407(3), C4–C5 1.434(3), C5–C6 1.400(3), Cl1-Ru1-P1 168.802(19), Cl2-Ru1-P1 93.878(19), Cl3-Ru1-P1 92.748(19), Cl1-Ru1-Cl2 79.183(17), Cl1-Ru1-Cl3 77.525(17), Cl2-Ru1-Cl3 80.474(17), C3-Ru1-P1 78.04(6), C3-Ru1-Cl1 111.40(6), C3-Ru1-Cl2 97.70(6), C3-Ru1-Cl3 170.51(6), C3-Ru1-C4 37.06(9), C4-Ru1-P1 107.66(7), C4-Ru1-Cl1 83.40(7), C4-Ru1-Cl2 116.71(7), C4-Ru1-Cl3 151.45(7).

As mentioned above, photoirradiation of both complexes **1** and **3** using Heraeus TQ 150W lamp with a broad emission spectrum (230 to 580 nm) led to complex **5**. With the aim to get more insights into the photochemical behaviors of these complexes, we measured their UV-visible spectra. Complexes **1** and **3** show absorption maxima at 369 nm and 362 nm, respectively, while complex **5** gives band at 411 nm. Consistently, UV-visible monitoring of CH_2Cl_2 solution of complexes **1** and **3** irradiated at 360 nm showed that both complexes evolved toward **5** within a few minutes (see SI). We next calculated electronic transitions for these systems using a Time-Dependent DFT method (see the Experimental Section). The data nicely reproduce the fact that complexes **1** and **3** absorb at similar energies while the dimer **5** absorbs at lower energy (Table 1). Moreover, while not being quantitative, our estimation of the molar extinction coefficient (computed as 10^5 times the oscillator strength) correspond to a slightly allowed transition: ε ~ 1000-2000 mol^{-1} L cm^{-1}. This is in agreement with the fact that all transitions have only a partial metal to ligand charge transfer character (MLCT). In complexes **1** and **3**, the vacant orbitals involve the Ru-arene and Ru-phosphine bonds while the occupied ones exhibit mainly a metal d block character (Figure 5 and SI). Remarkably, for both complexes, the vacant transition orbital is anti-bonding between the arene and the ruthenium atom, while the occupied one indicates a bonding interaction. This is in line with the fact that irradiating these complexes around 360 nm will weaken the Ru-Arene bond and eventually lead to dissociation. In complex **5**, because of the resonance that takes place between the two metallic centers, the electronic absorption cannot be described by a single pair of natural transition orbitals but rather by a combination of them.This is at the origin of the transition occurring at lower energy. Combining the natural transition orbital localizes the transition on the left ruthenium atom, as shown on figure 5 (bottom) or on the right one (see SI).

Table 1: Theoretical electronic absorption data obtained for the studied systems.

	Calculated		*Experimental*
	λ_{calc} (nm)	10^5xf^a	λ_{exp} (nm) / ε (mol^{-1} L cm^{-1})
1	399	2340	369 / 1544
3	392	6730	362 / 2432
5	421	1030	411 / 1652

[a] f is the oscillator strength of the transition.

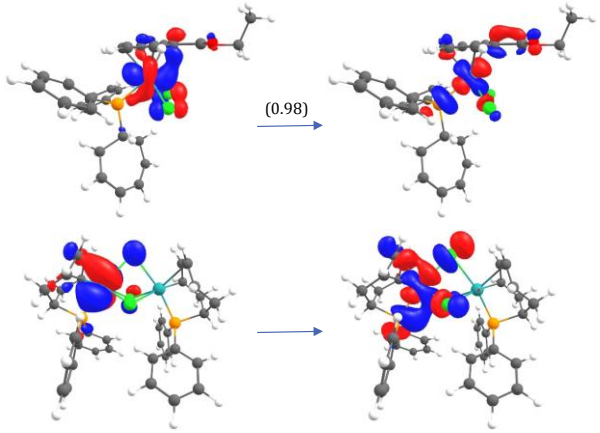


Figure 5: Natural Transition Orbitals of complex **3** (top) and Localized Transition Orbitals of complex **5** (bottom, see also SI). A contour threshold of 0.045 a.u. has been considered. Color code: C in grey, P in orange, Cl in green, O in red, Ru in light blue.

Complex **5** shows similarities with the cationic dinuclear [LRu(μ-Cl)$_3$RuL] complexes reported by Gusev (L= POP pincer ligand),[16] and those reported by Baker and Brown (L= bis(NHC) ligands) (Figure 6).[17] The bimetallic complexes [(*p*-cymene)Ru(μ-Cl_3)Ru(PR_3)(η^2-C_2H_4)] reported by Severin are also particularly relevant to this study.[9f,9j] Beside the similarity of structures, Severin's complexes can be formed by heating a solution of (*p*-cymene)$RuCl_2PR_3$ with half equivalent of the dimer [Ru(η^6-arene)Cl_2]$_2$ under ethylene pressure. These compounds revealed among the best precatalysts in ATRA reaction described so far.[9f,9j] A plausible mechanism of formation of these complexes starts with the arene decoordination to generate a coordinatively unsaturated [$RuCl_2PR_3$] species which next reacts with the Ru dimer and ethylene. In case of complex **3**, we presume that after decoordination of the arene ligand, (cycloheptadienyl)phosphine flips and forms a 16e-chelate [{(η^4-

$C_7H_9)PPh_2$-κP}$RuCl_2$], which subsequently dimerizes to give the dinuclear cation **5**.

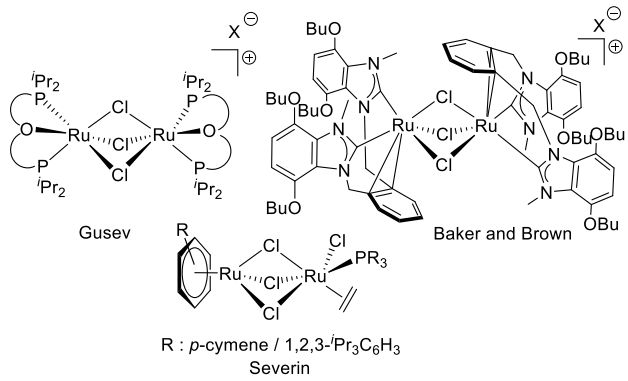
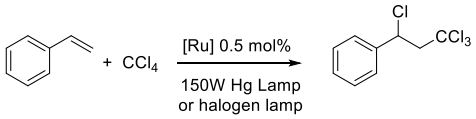


Figure 6: Examples of μ-Cl_3 dinuclear Ru complexes reported in the literature.

We next investigated the ability of complexes **1**-**5** to catalyse Kharasch addition of CCl_4 to styrene. Considering the ease of arene-Ru bond cleaving under light irradiation, we first studied the impact of light on (arene)Ru-catalysed ATRA reaction. The reactions were conducted in toluene at room temperature using 0.5 mol% of ruthenium equiv. (0.5 mol% of complexes **3, 4** or 0.25 mol% of complex **5**). After 24 h in the dark, none of the three complexes tested (**3**-**5**) showed conversion in the Kharasch adduct. When the reaction mixture was allowed to evolve under natural light for 72 h, (cycloheptadienyl)phosphine complexes **3** and **5** showed no improvement. Conversely, (cycloheptyl)phosphine complex **4** gave 89% yield in Kharasch addition. A similar trend was observed using 12V/55W halogen lamp as irradiation source. Among complexes **3**-**5**, only **4** was active and gave 96% yield of the addition product after 96 h (Table 2, entries 1-3).

Table 2: Kharasch addition of carbon tetrachloride to styrene under irradiation[a]



Entry	Cat.	Solvent	Time	Styrene conv. (%)[b]	Kharasch add. (%)[b]
1[c]	3	Toluene	96 h	10	1
2[c]	4	Toluene	96 h	96	96
3[c]	5	Toluene	96 h	13	2
4[d]	1	Toluene	4 h	10	2
5[d]	2	Toluene	4 h	52	44
6[d]	3	Toluene	4 h	2	2
7[d]	4	Toluene	4 h	29	29
8[d]	5	Toluene	4 h	14	1
9[d]	1	DCM	4 h	16	2
10[d]	2	DCM	4 h	36	21
11[d]	3	DCM	4 h	5	2
12[d]	4	DCM	4 h	27	9
13[d]	5	DCM	4 h	15	1

[a][styrene]$_0$/[CCl_4]$_0$/[catalyst]$_0$ = 200:800:1. [b]Determined by GC with dodecane as internal standard. [c]23°C, irradiation: halogen 12V/55W. [d]31°C, irradiation: Heraeus TQ 150W.

The reactions were next conducted under irradiation with the 150W mercury lamp and stopped after 4 h for comparative purposes (Table 2, entries 4-8). In these conditions, (cycloheptadienyl)phosphine ruthenium derivatives **1**, **3** and **5** showed very low styrene conversions (max 14% with **5**) and only traces of the Kharasch adduct. In the same conditions, (cycloheptyl)phosphine derivatives **2** and **4** were more active and allowed higher styrene conversions (52% and 29%, respectively) and higher yields in the addition product (44% and 29%, respectively). The use of dichloromethane instead of toluene (Table 2, entries 9-13) did not improve the catalytic activity of **1**, **3** and **5** and slightly decreased that of **2** and **4**.

This first set of experiments showed that all three complexes with (cyclopheptadienyl)phosphine **1**, **3** and **5** are unable to promote the Kharasch addition contrary to (cycloheptyl)phosphine Ru complexes. We assume that complex **5** is unreactive because it is coordinatively saturated and irradiation is not sufficient to open coordination site on Ru for CCl_4 activation due to chelate effect. We presume that, under catalytic conditions, both (cycloheptadienyl)complexes **1** and **3** are converted in the cationic dinuclear complex **5** which *de facto* put at the same level the three complexes. To verify this hypothesis, we registered NMR spectra of toluene and dichloromethane solutions of complex **3** (0.01 mmol), CCl_4 (30 eq.) and styrene (20 eq.) after 4 h under 150W mercury lamp irradiation at room temperature (Figure 7). In CD_2Cl_2, ^{31}P NMR spectrum displayed the signal of complex **5** at 100 ppm. In toluene, we observed the formation of a precipitate which was also further identified as **5.** In both cases, ^1H NMR spectra showed that only traces of Kharasch addition products are formed in these conditions. These results confirm our hypothesis and also demonstrate that CCl_4 does not react with the butadiene moiety of the hybrid phosphine.[18]

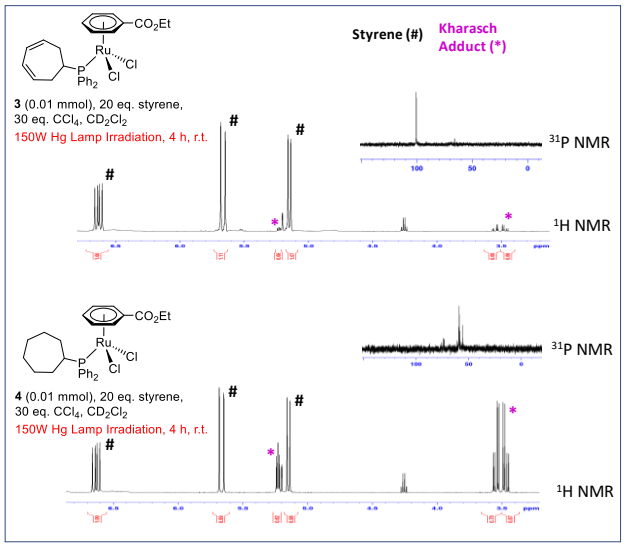


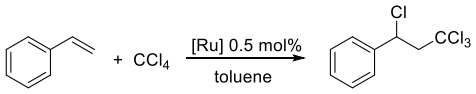
Figure 7: ^{31}P NMR and ^1H NMR of complexes **3** (top) and **4** (bottom) in CD_2Cl_2 in presence of styrene and CCl_4 under irradiation with 150W Hg Lamp, 4 h, r.t.

For comparative purposes, we performed similar experiments with complex **4** under irradiation. In absence of the substrate, ^{31}P NMR spectrum of CD_2Cl_2 solution of complex **4** displayed no peak at all and only non-coordinated ethyl benzoate signals were visible by ^1H NMR. In presence of ATRA substrates (**4**: 0.01 mmol, CCl_4: 30 eq. and styrene: 20 eq.), ^{31}P NMR spectrum displayed several peaks ranging from 50 to 80 ppm and ^1H NMR analysis showed 65% Kharasch addition product (Figure 7). UV exposure of toluene solution of **4** gave a different result.

In absence of substrates, the ^{31}P-NMR spectrum showed complete transformation of **4** (26.2 ppm) in [(η^6-toluene)$RuCl_2${(cycloheptyl)PPh_2}] **6** which presents a signal at 27.8 ppm. This product was isolated and the XRD analysis of crystals confirmed the ethyl benzoate replacement by toluene (see SI). In presence of ATRA substrates (**4**: 0.01mmol, CCl_4: 30 eq. and styrene: 20 eq.), similar transformation of **4** in **6** was observed, giving also Kharasch addition products in 80% conversion. This result might appear surprising at first sight because complex **6** is capped by a toluene ligand. Nevertheless, as the irradiation is maintained throughout the reaction, active species can be restored continuously.

We studied the performances in Kharasch addition of complexes **1**-**5** under heating in the absence of light (Table 3, entries 1-5). The results under irradiation conditions and by heating followed the same trend, but differences emerged between complexes of the same series. After 3 days at 60 °C in toluene, only (cycloheptyl)phosphine benzoate ruthenium complex **4** allowed total conversion of styrene with very good selectivity toward Kharasch adduct (96% yield, Table 3 entry 4). The other ruthenium complexes **1**-**3** and **5** gave very low styrene conversion (16-26%) with a maximum of 13% yield in Kharasch product with complex **2**. In toluene at 85 °C, both (cycloheptyl)phosphine Ru complexes **2** and **4** gave Kharasch adduct in good yields (88% and 98% yield, respectively). At 85 °C the (cycloheptadienyl)phosphine ruthenium derivatives **1** and **3** remained inactive while complex **5** showed a significant improvement in performance (Table 3, entry 10). These differences within cycloheptyl- and cycloheptadienyl Ru complexes series can be explained by the fact that under heating the dissociation of the arene ligand is much slower than under irradiation and becomes a limiting factor.

Table 3: Kharasch addition of carbon tetrachloride to styrene in absence of light at different temperatures[a]



Entry	Cat.	Temperature (°C)	Styrene conv. (%)[b]	Kharasch add. (%)[b]
1	**1**	60	22	1
2	**2**	60	26	13
3	**3**	60	16	1
4	**4**	60	100	96
5	**5**	60	24	7
6	**1**	85	35	2
7	**2**	85	100	88
8	**3**	85	22	1
9	**4**	85	100[c]	98[c]
10	**5**	85	48	26

[a][styrene]$_0$/[CCl_4]$_0$/[catalyst]$_0$ = 200:800:1. [b]Determined by GC with dodecane as internal standard after 3 days heating in absence of light. [c]Reaction already completed after 1 day.

Aware of this limitation, we next tried to improve the catalytic performances of complexes **2** and **4** using simultaneous heating and irradiation (Hg Lamp). Time course of ATRA between styrene and CCl_4 catalyzed by complexes **2** and **4** under irradiation at 25°, 60° and 85°C are presented in Figure 8. For comparative purpose, conversions obtained at 60°C in the absence of light are also reported. Sampling after 1 h, 2 h and 4 h showed that simultaneous irradiation and heating boost the performances of both complexes. After only 1 h under irradiation at 85°C, the yield in Kharasch addition product using complex **4** reached 91% whereas the same complex gave 9% yield at 25°C and 2% at 60°C in the dark.

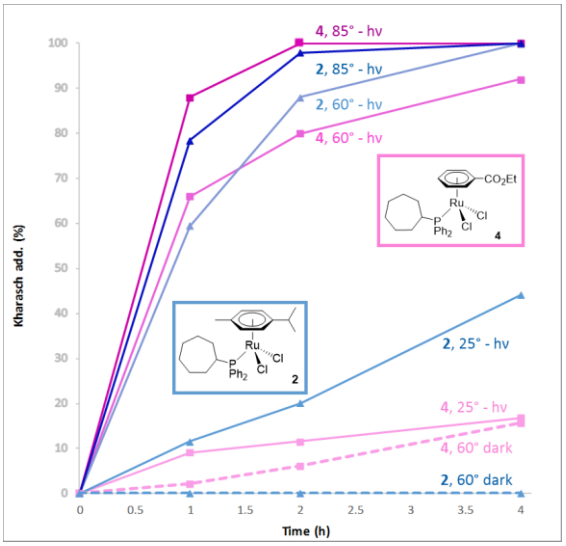


Figure 8: Time course of of Kharasch addition of CCl_4 to styrene with ruthenium complexes **2** (▲) and **4** (■) at different temperatures under 150W Hg Lamp irradiation (continuous lines), or in absence of light (dotted lines) at 60°C. Conditions: [styrene]$_0$/[CCl_4]$_0$/[catalyst]$_0$ = 200:800:1, solvent: toluene.

Concerning (cycloheptadienyl)phosphine Ru complexes **1** and **3**, it was clear that light irradiation was not sufficient to generate active species and/or to maintain them alive. On the other hand, we have shown that complex **5** can promote ATRA between styrene and CCl_4 at 85 °C but only with moderate activity. NMR experiments conducted with **5** showed that it was stable in C_6D_5Br solution even after prolonged time at 147 °C. We therefore thought that this robustness may allow to improve the TON of the catalyst by authorizing ATRA reactions at elevated temperatures. To test this hypothesis, we carried out addition of CCl_4 to styrene in bromobenzene at 147 °C with only 0.1 mol% ruthenium complexes **3**-**5** (1:1000 ratio [Ru]/styrene) without any light source (Figure 9).

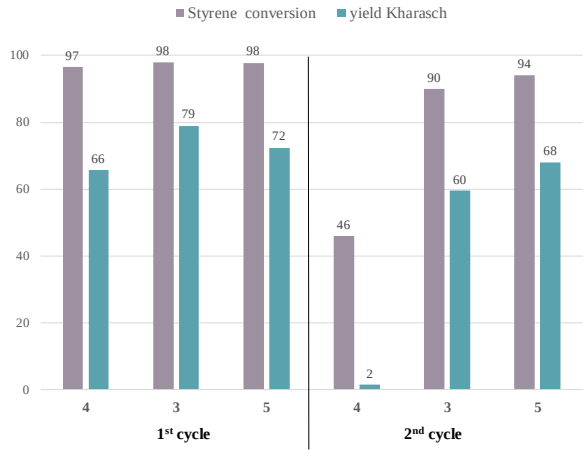


Figure 9: Kharasch addition with complexes **3**-**5** in bromobenzene at 147°C (dark); 1st cycle: [styrene]$_0$/[CCl_4]$_0$/[catalyst]$_0$ = 1000:4000:1 (18 h); 2nd cycle by adding [styrene]/[CCl_4]/[catalyst] = 1000:4000:0 (22h)

After 18 h all three complexes gave almost total conversions of styrene and good yields in Kharasch adduct. To test further the stability of the catalysts, a second cycle was run by adding the same amount of substrates to the reaction mixture. After another 22 h at 147 °C, complex **4** showed reduced activity giving only small amount of Kharasch adduct. In contrary, complexes **3** and **5** were still active, the latter showing almost the same performances than during the first cycle. Lower catalyst loading of **5** has been also tested (Table 4). The reaction with **5** using a styrene/[Ru] ratio of 5000 gave 74 % yield in Kharasch addition product (TON= 3700). We next investigated ATRA reaction of alternative substrates like 1-octene and tetradecene with CCl_4 using complex **5** at an olefin/[Ru] ratio of 10 000. This gave Kharasch adduct in 95% and 98% yields, respectively, after 48 h at 147 °C (TON = 9500 and 9700, respectively). With analogous substrates, monometallic $[RuCl_2(arene)(PR_3)]$ complexes described by Demonceau gave TON ranging from 150 to 280.[2b, 11] The bimetallic complexes $[(p\text{-cymene})Ru(\mu\text{-}Cl_3)Ru(PR_3)(\eta^2\text{-}C_2H_4)]$ reported by Severin reached TON of 1500 but needs Mg as a cocatalyst for regenerating Ru^{II} from the Ru^{III} active species.[9j] The best complex $[Cp^*RuCl_2(PPh_3)]$ reported so far reach TON of 13.200 for styrene and 44.500 for 1-hexene but requires the use of AIBN as cocatalyst.[9g] These last values are clearly superior to those obtained in this study but with complex **5**, no cocatalyst is needed.

Table 4: Kharasch addition of carbon tetrachloride to olefins at low catalyst loading of **5**[a]

Entry	Olefin	S/[Ru] ratio	Styrene conv.(%)[d]	Kharasch add.(%)[d]	TON
1[b]	styrene	5000	96	74	3700
2[c]	1-octene	10000	96	95	9500
3[c]	1-tetradecene	10000	98	97	9700

[a]conditions : reaction in bromobenzene (4mL) at 147°C for 48 h in the absence of light, [b]styrene (10 mmol), CCl_4 (40 mmol), **5** (0.001 mmol); [c]styrene (20 mmol), CCl_4 (80 mmol), **5** (0.001 mmol: 0.002 mmol [Ru]); [d]Determined by GC with dodecane as internal standard.

CONCLUSION

In summary, we have described the synthesis of a series of $(arene)RuCl_2PR_3$ complexes with (cycloheptadienyl)- and (cycloheptyl)diphenylphosphine. Upon irradiation or heating in toluene, all these complexes lose arene ligand but then behave differently depending on the nature of the phosphine ligand. (Cycloheptadienyl)phosphine complexes **1** and **3** give a cationic dinuclear Ru complex **5** bridged by three chlorido ligands and flanked by two tridendate (cycloheptadienyl)phosphine, whose structure has been confirmed by X-Ray diffraction study. Complexes **2** and **4** undergo arene exchange with toluene. ATRA catalytic trials conducted in parallel with these complexes using CCl_4 and styrene as standard substrates, highlighted the deep impact of the dienyl moiety on the results. In smooth conditions (UV irradiation or moderate heating), only (cycloheptyl)phosphine derivatives give Karasch adduct in satisfactory yields. Their performance were further considerably improved by combining irradiation and heating conditions. At higher temperature, the cationic dinuclear complex **5** revealed active and robust, giving turnover numbers close to 10^4 when octene (or tetradecene) and CCl_4 were used as substrates.

EXPERIMENTAL SECTION

General considerations. All reactions, except when indicated, were carried out under an atmosphere of purified argon using conventional Schlenk techniques. DCM, diethyl ether, THF, toluene, and pentane were dried using a MBRAUN SPS 800. $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$,[19] $[(\eta^6\text{-ethyl benzoate})RuCl_2]_2$[20] and (3,5-cycloheptadienyl)diphenylphosphine[14] have been synthesized according to literature procedure. Other reagents were commercially available and used as received from suppliers unless otherwise specified. Analyses were performed at the "Plateforme d'Analyses Chimiques de Synthèse Moléculaire de l'Université de Bourgogne". The identity and purity (≥95%) of the compounds were unambiguously established using elemental analyses, multinuclear NMR spectroscopy, X-ray diffraction analysis, high-resolution mass spectrometry, and Infrared. Elemental analyses were obtained on a Flash EA 1112 CHNS-O Thermo Electron Flash instrument. NMR spectra (^1H, ^{13}C, ^{31}P) were recorded on Bruker 300 Avance III or Bruker 500 Avance III spectrometers. All acquisitions, except when indicated, were performed at 300 K. Chemical shifts are quoted in parts per million (δ) relative to TMS (for ^1H and ^{13}C) or 85% H_3PO_4 (for ^{31}P). For ^1H and ^{13}C spectra, values were determined by using solvent residual signals (e.g. $CHCl_3$ in $CDCl_3$) as internal standards. For ^{31}P, 85% H_3PO_4 was used as an external standard. The coupling constants (*J*) are reported in Hertz (Hz). Multiplicity abbreviations: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets. Assignment of ^1H and ^{13}C signals (when possible) was done through the use of DEPT and 2D experiences (COSY, HSQC). High resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL ESI-MS (ElectroSpray Ionization Mass Spectrometry). Infrared spectra were recorded on a Bruker Vertex 70v spectrophotometer fitted with a Globar MIR source, a Ge/KBr (MIR) or silicon (FIR) beam splitter, a DLaTGS detector and a diamond ATR module. UV-Visible absorption spectra were recorded on a JASCO V630BIO spectrometer. The irradiation experiments were performed by using a JASCO FP8500 spectrofluorometer instrument.

X-Ray experimental procedure: suitable crystals for X-ray analysis were selected and mounted on a mylar loop with oil on a 'Bruker APEX-II CCD' diffractometer. Crystals were kept at 115 K during data collections. Using Olex2[21], the structures were solved with the ShelXT[22] structure solution program using Direct Methods and refined with the XL[23] refinement package using Least Squares minimization against |F|. In **2**, the cycloheptyl group was found disordered and two conformations were refined with occupation factors converged to 0.55/0.45. For **5**, one of the four chloroform solvate molecules present in the asymmetric unit was found disordered over two positions and both components were refined with occupation factors converged to 0.54/0.46.

Computational Details: All DFT and TD-DFT calculations were carried out with the Gaussian09 code,[24] tightening self-consistent field convergence thresholds (10^{-10} a.u.). Geometry optimizations without symmetry constraints and the corresponding frequency calculations were conducted with a LANL2TZ(f)[25] basis set and a pseudo-potential for the Ruthenium atom, and a 6 31+G(d) basis set for all other atoms.[26,27,28] The hybrid functional PBE0[29] was selected given its good performance in previous DFT studies involving ruthenium-containing systems.[30] Vertical excitations were computed with TD-DFT using a larger basis set, i.e. the 6-311++G(d,p) for H, C, N, O, and Cl and the LANL2TZ(f) basis sets and pseudo-potential for the metal. TD-DFT calculations were performed with the PBE0 functional. For each complex, 24 states were considered. The solvent effects of dichloromethane were included according to the Polarizable Continuum Model.[31,32] This procedure allows to reproduce the UV absorption spectrum of our complexes, as shown in the Supporting Information. All orbital isosurfaces have been plotted with the Chemcraft code[33] considering a contour threshold of 0.045 a.u. The orbital transitions of selected excited states were characterized using the natural transition orbital (NTO) method.[34] The LANL2TZ (f) basis set and pseudopotentials were taken from the EMSL Basis Set Exchange Web site.[35]

Cycloheptyldiphenylphosphine. Diphenylphosphine (1 eq., 2.10 g, 11.3 mmol) was diluted in diethyl ether (10 mL). *N*-butyllithium (1 eq.,

11.3 mmol, 2.5 M in hexanes, 4.52 mL) was slowly added, and the resulting mixture was stirred 1 h; a yellow color was observed. Bromocycloheptane (1 eq., 11.3 mmol, 2.00 g) was slowly added, and the reaction mixture was stirred 16 h. The volatiles were evaporated. The residue was extracted with pentane (3 x 20 mL). The filtrate was concentrated to give **I-5** as a white solid (2.99 g, 94 %).Elemental Analysis: calcd for $C_{19}H_{23}P$: C, 80.82; H, 8.21. Found: C, 80.96; H, 8.35. HR-MS (ESI-pos): calcd for $[C_{19}H_{24}P]^+$ [M + H]$^+$: 283.16101. Found: 283.16061 (-1.4 ppm). ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.53–7.47 (m, 4H, *o*-Ph), 7.35–7.27 (m, 4H + 2H, *m*-Ph, *p*-Ph), 2.46–2.38 (m, 1H, PC<u>H</u>), 1.76–1.66 (m, 4H, cycloheptyl), 1.65–1.59 (m, 2H, cycloheptyl), 1.58–1.45 (m, 4H, cycloheptyl), 1.44–1.33 (m, 2H, cycloheptyl). ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2): δ (ppm) = 138.8 (d, $^1J_{CP}$ = 15.5 Hz, *i*-Ph), 134.0 (d, $^2J_{CP}$ = 19.1 Hz, *o*-Ph), 129.0 (s, *p*-Ph), 128.7 (d, $^3J_{CP}$ = 6.9 Hz, *m*-Ph), 35.8 (d, $^1J_{CP}$ = 9.6 Hz, P<u>C</u>H), 31.4 (d, $^2J_{CP}$ = 18.4 Hz, PCH<u>C</u>H$_2$), 29.0 (s, PCHCH$_2$CH$_2$<u>C</u>H$_2$), 28.6 (d, $^3J_{CP}$ = 12.4 Hz, PCHCH$_2$<u>C</u>H$_2$). ^{31}P{^{1}H} NMR (202.4 MHz, CD_2Cl_2): δ (ppm) = -2.8 (s).

RuCl$_2$(*η*^{6}-*p*-cymene)[(3,5-cycloheptadienyl)diphenylphosphine-*κ*P] (1). [RuCl$_2$(*η*^{6}-*p*-cymene)]$_2$ (1 eq., 524 mg, 0.856 mmol) and cycloheptadienyldiphenylphosphine (2.2 eq., 524 mg, 1.88 mmol) in toluene (15 mL) were stirred at room temperature for 16 h in the dark. The solvent was evaporated. The residue was triturated and washed with pentane, and dried to give **1** as an orange solid (940 mg, 94%). Elemental Analysis: calcd for $C_{29}H_{33}Cl_2PRu$: C, 59.59; H, 5.69. Found: C, 59.59; H, 5.81. HR-MS (ESI-pos): calcd for $[C_{30}H_{36}OPRu]^+$ [M - 2Cl + OMe]$^+$: 545.15418. Found: 545.15414 (-0.1 ppm). ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.94–7.87 (m, 4H, *o*-Ph), 7.56–7.43 (m, 4H + 2H, *m*-Ph, *p*-Ph), 5.80–5.68 (m, 4H, diene), 5.03–4.96 (m, 2H, MeC$_q$C<u>H</u>), 4.89 (d, $^3J_{HH}$ = 6.1 Hz, 2H, ^{i}PrC$_q$C<u>H</u>), 3.42–3.32 (m, 1H, PC<u>H</u>), 3.03–2.95 (m, 2H, PCHC<u>H$_a$</u>H$_b$), 2.57 (hept, $^3J_{HH}$ = 6.9 Hz, 1H, C<u>H</u> ^{i}Pr), 1.81 (s, 3H, Me), 1.72–1.63 (m, 2H, PCHCH$_a$<u>H$_b$</u>), 1.02 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH$_3$ ^{i}Pr).^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ (ppm) = 134.1 (d, $^2J_{CP}$ = 8.3 Hz, *o*-Ph), 133.1 (d, $^1J_{CP}$ = 39.1 Hz, *i*-Ph, overlapping with PCHCH$_2$<u>C</u>H=CH), 133.0 (d, $^3J_{CP}$ = 14.5 Hz, PCHCH$_2$<u>C</u>H=CH, overlapping with *i*-Ph), 130.9 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ph), 128.5 (d, $^3J_{CP}$ = 9.1 Hz, *m*-Ph), 125.7 (s, PCHCH$_2$CH=<u>C</u>H), 109.7 (s, ^{i}Pr<u>C$_q$</u>), 95.3 (s, Me<u>C$_q$</u>), 91.2 (d, $^2J_{CP}$ = 4.0 Hz, MeC$_q$<u>C</u>H), 85.7 (d, $^2J_{CP}$ = 5.6 Hz, ^{i}PrC$_q$<u>C</u>H), 35.1 (d, $^1J_{CP}$ = 19.1 Hz, P<u>C</u>H), 33.7 (s, PCH<u>C</u>H$_2$), 30.6 (s, CH ^{i}Pr), 22.1 (s, CH$_3$ ^{i}Pr), 17.8 (s, Me).^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ (ppm) = 21.3 (s). Selected IR Bands (ATR): wavenumber (cm^{-1}) = 290 (ν$_{Ru–Cl}$).

RuCl$_2$(*η*^{6}-*p*-cymene)(cycloheptyldiphenylphosphine-*κ*P) (2). [RuCl$_2$(*η*^{6}-*p*-cymene)]$_2$ (1 eq., 520 mg, 0.849 mmol) and cycloheptyldiphenylphosphine (2.2 eq., 528 mg, 1.87 mmol) in toluene (15 mL) were stirred at room temperature for 16 h in the dark. The solvent was evaporated. The residue was triturated and washed with pentane, and dried to give **2** as an orange powder (902 mg, 90%). Elemental Analysis: calcd for $C_{29}H_{37}Cl_2PRu$: C, 59.18; H, 6.34. Found: C, 59.02; H, 6.32. HR-MS (ESI-pos): calcd for $[C_{29}H_{37}ClPRu]^+$ [M - Cl]$^+$: 553.13594. Found: 553.13416 (-3.2 ppm). ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.95–7.87 (m, 4H, *o*-Ph), 7.52–7.43 (m, 4H + 2H, *m*-Ph, *p*-Ph), 4.97–4.94 (m, 2H, MeC$_q$C<u>H</u>), 4.86 (d, $^3J_{HH}$ = 6.1 Hz, 2H, ^{i}PrC$_q$<u>C</u>H), 3.18–3.07 (m, 1H, PC<u>H</u>), 2.58 (hept, $^3J_{HH}$ = 7.0 Hz, 1H, CH ^{i}Pr), 2.30–2.19 (m, 2H, PCHC<u>H$_a$</u>H$_b$), 1.80 (s, 3H, Me), 1.53–1.45 (m, 4H, cycloheptyl), 1.44–1.37 (m, 2H, cycloheptyl), 1.37–1.27 (m, 2H, cycloheptyl), 1.04 (d, $^3J_{HH}$ = 7.0 Hz, 6H, CH$_3$ ^{i}Pr), 0.80–0.94 (m, 2H, PCHCH$_a$<u>H$_b$</u>). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ (ppm) = 134.2 (d, $^2J_{CP}$ = 8.1 Hz, *o*-Ph), 133.9 (d, $^1J_{CP}$ = 38.4 Hz, *i*-Ph), 130.6 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ph), 128.3 (d, $^3J_{CP}$ = 9.1 Hz, *m*-Ph), 109.4 (s, <u>C$_q$</u>^{i}Pr), 95.1 (s, <u>C$_q$</u>Me), 91.0 (d, $^2J_{CP}$ = 3.9 Hz, MeC$_q$<u>C</u>H), 85.7 (d, $^2J_{CP}$ = 5.7 Hz, ^{i}PrC$_q$<u>C</u>H) 35.8 (d, $^1J_{CP}$ = 20.6 Hz; PCH), 30.6 (s, CH ^{i}Pr), 30.2 (d, $^3J_{CP}$ = 1.8 Hz, PCHCH$_2$<u>C</u>H$_2$), 28.6 (d, $^2J_{CP}$ = 13.4 Hz, PCH<u>C</u>H$_2$), 28.0 (s, PCHCH$_2$CH$_2$<u>C</u>H$_2$), 22.1 (s, CH$_3$ ^{i}Pr), 17.8 (s, Me). **^{31}P{^{1}H} NMR** (202 MHz, CD_2Cl_2): δ (ppm) = 23.7 (s). Selected IR Bands (ATR): wavenumber (cm^{-1}) = 293 (ν$_{Ru–Cl}$).

RuCl$_2$(*η*^{6}-BzOEt)[(3,5-cycloheptadienyl)diphenylphosphine-*κ*P] (3). [RuCl$_2$(*η*^{6}-BzOEt)]$_2$ (1 eq., 536 mg, 0.833 mmol) and cycloheptadyenyldiphenylphosphine (2.2 eq., 510 mg, 1.83 mmol) in toluene (15 mL) were stirred at room temperature for 16 h in the dark. The solvent was evaporated. The residue was triturated and washed with pentane, and dried to give **3** as an orange solid (930 mg, 90%). Elemental Analysis: calcd for $C_{28}H_{29}Cl_2O_2PRu$: C, 56.01; H, 4.87. Found: C, 56.04; H, 5.13. HR-MS (ESI-pos): calcd for $[C_{28}H_{29}Cl_2O_2PRuNa]^+$ [M + Na]$^+$: 623.02179. Found: 623.02230 (0.8 ppm). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 7.93–7.81 (m, 4H, *o*-Ph), 7.59–7.53 (m, 2H, *p*-Ph), 7.48–7.55 (m, 4H, *m*-Ph), 6.23 (d, $^3J_{HH}$ = 6.5 Hz, 2H, *o*-BzOEt), 5.80–5.68 (m, 4H, diene), 5.44–5.36 (m, 1H, *p*-BzOEt), 4.85 (t, $^3J_{HH}$ = 5.6 Hz, 2H, *m*-BzOEt), 4.32 (q, $^3J_{HH}$ = 7.1 Hz, 2H, OC<u>H$_2$</u>CH$_3$), 3.49–3.38 (m, 1H, PCH), 2.97–2.86 (m, 2H, PCHC<u>H$_a$</u>H$_b$), 1.79–1.68 (m, 2H, PCHCH$_a$<u>H$_b$</u>), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH$_2$C<u>H$_3$</u>). ^{13}C{^{1}H} NMR (125.8 MHz, CD_3CN): δ (ppm) = 165.0 (s, C=O), 134.6 (d, $^2J_{CP}$ = 8.3 Hz, *o*-Ph), 133.5 (d, $^3J_{CP}$ = 14.7 Hz, PCHCH$_2$<u>C</u>H=CH), 133.0 (d, $^1J_{CP}$ = 42.5 Hz, *i*-Ph), 131.9 (d, $^4J_{CP}$ = 2.6 Hz, *p*-Ph), 129.3 (d, $^3J_{CP}$ = 9.6 Hz, *m*-Ph), 126.3 (s,PCHCH$_2$CH=<u>C</u>H), 96.6 (d, $^2J_{CP}$ = 3.3 Hz, *o*-BzOEt), 91.2 (s, *p*-BzOEt), 87.3 (d, $^2J_{CP}$ = 7.8 Hz, *p*-BzOEt), 85.4 (d, $^2J_{CP}$ = 2.7 Hz, *m*-BzOEt), 63.1(s, O<u>C</u>H$_2$CH$_3$), 36.3 (d, $^1J_{CP}$ = 20.1 Hz, P<u>C</u>H), 34.3 (d, $^2J_{CP}$ = 1.4 Hz, PCH<u>C</u>H$_2$), 14.9 (s, OCH$_2$<u>C</u>H$_3$). ^{31}P{^{1}H} NMR (202.4 MHz, CD_3CN): δ (ppm) = 25.4 (s). Selected IR Bands (ATR): wavenumber (cm^{-1}) = 300 (ν$_{Ru–Cl}$), 1111 (ν$_{O–C–C}$), 1272 (ν$_{C–C(=O)–O}$), 1708 (ν$_{C=O}$).

RuCl$_2$(*η*^{6}-BzOEt)(cycloheptyldiphenylphosphine-*κ*P) (4). [*η*^{6}-(ethyl benzoate)RuCl$_2$]$_2$ (1 eq., 533 mg, 0.827 mmol) and cycloheptyldiphenylphosphine (2.2 eq., 514 mg, 1.82 mmol) in toluene (15 mL) were stirred at room temperature for 16 h in the dark. The solvent was evaporated. The residue was triturated and washed with pentane, and dried to give **4** as an orange solid (950 mg, 95%). Elemental Analysis: calcd for $C_{28}H_{33}Cl_2O_2PRu$: C, 55.63; H, 5.50. Found: C, 56.13; H, 5.52. HR-MS (ESI-pos): calcd for $[C_{28}H_{33}Cl_2O_2PRuNa]^+$ [M + Na]$^+$: 627.05309. Found: 627.05280. (-0.5 ppm). ^{1}H NMR (500 MHz, CD_2Cl_2): δ (ppm) = 7.91–7.84 (m, 4H, *o*-Ph), 7.54–7.46 (m, 4H + 2H, *m*-Ph, *p*-Ph), 6.28 (d, $^3J_{HH}$ = 6.6 Hz, 2H, *o*-BzOEt), 5.30–5.31 (m, 1H, *p*-BzOEt, overlapping with CD_2Cl_2 residual signal), 4.71 (t, $^3J_{HH}$ = 5.8 Hz, 2H, *m*-BzOEt), 4.36 (q, $^3J_{HH}$ = 7.1 Hz, 2H, O<u>C</u>H$_2$CH$_3$), 3.26–3.17 (m, 1H, PCH), 2.22–2.13 (m, 2H, PCHC<u>H$_a$</u>H$_b$), 1.56–1.45 (m, 4H, cycloheptyl overlapping with H_2O signal), 1.45–1.30 (m, 4H, cycloheptyl overlapping with OCH$_2$<u>C</u>H$_3$ signal), 1.38 (t, $^3J_{HH}$ = 7.1 Hz, 3H, OCH$_2$<u>C</u>H$_3$ overlapping with cycloheptyl signal), 1.06–0.95 (m, 2H, PCHCH$_a$<u>H$_b$</u>). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ (ppm) = 164.4 (s, C=O), 134.0 (d, $^2J_{CP}$ = 8.0 Hz, *o*-Ph), 133.1 (d, $^1J_{CP}$ = 41.5 Hz, *i*-Ph), 131.0 (d, $^4J_{CP}$ = 2.4 Hz, *p*-Ph), 128.5 (d, $^3J_{CP}$ = 9.4 Hz, *m*-Ph), 96.3 (d, $^2J_{CP}$ = 3.1 Hz, *o*-BzOEt), 91.0 (s, *p*-BzOEt), 86.1 (d, $^2J_{CP}$ = 7.4 Hz, *i*-BzOEt), 84.3 (d, $^2J_{CP}$ = 2.8 Hz, *m*-BzOEt), 62.8 (s, O<u>C</u>H$_2$CH$_3$), 36.1 (d, $^1J_{CP}$ = 21.9 Hz), 30.4 (d, $^2J_{CP}$ = 2.2 Hz, PCH<u>C</u>H$_2$), 28.6 (d, $^3J_{CP}$ = 13.9 Hz, PCHCH$_2$<u>C</u>H$_2$), 27.9 (s, PCHCH$_2$CH$_2$<u>C</u>H$_2$), 14.7 (s, OCH$_2$<u>C</u>H$_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2): δ (ppm) = 27.7 (s). Selected IR Bands (ATR): wavenumber (cm^{-1}) = 294 (ν$_{Ru–Cl}$), 1098 (ν$_{O–C–C}$), 1263 (ν$_{C–C(=O)–O}$), 1729 (ν$_{C=O}$).

[Ru$_2$(*μ*-Cl)$_3$((*η*^{4}-3,5-cycloheptadienyl)diphenylphosphine-*κ*P)$_2$][Cl] (5). Complex **3** (240 mg, 0.400 mmol) was dissolved in DCM (8 mL), and exposed to light (mercury lamp Heraeus TQ150W) for 1 h under stirring. Solvent was evaporated. The residue was washed with diethyl ether and dried to give **5** as a brick red powder (150 mg, 83%). Elemental Analysis: calcd for $C_{38}H_{38}Cl_4P_2Ru_2$: C, 50.68; H, 4.25. Found: C, 50.36; H, 4.33. HR-MS (ESI-pos) calcd for $[C_{38}H_{38}Cl_3P_2Ru_2]^+$ [M - Cl]$^+$: 864.96014. Found: 864.95562. (-3.4 ppm). ^{1}H NMR (500 MHz, $CDCl_3$, 253 K): δ (ppm) = 7.59–7.49 (m, 8H + 4H, *o*/*m*-Ph, *p*-Ph), 7.35–7.29 (m, 8H, *o*/*m*-Ph), 5.61–5.55 (m, 4H, CH$_2$CH=C<u>H</u>), 4.88–4.81 (m, 4H, CH$_2$C<u>H</u>=CH), 2.99–2.94 (m, 2H, PCH), 1.97–1.88 (m, 4H, PCHC<u>H$_a$</u>H$_b$), 0.90 (dd, $^3J_{CP}$ = 46.3 Hz, $^2J_{HH}$ = 14.3 Hz, 4H, PCHCH$_a$<u>H$_b$</u>). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$, 253 K): δ (ppm) = 134.0 (d, J_{CP} = 8.5 Hz, *o*/*m*Ph), 132.1 (d, $^4J_{CP}$ = 2.4 Hz, *p*-Ph), 128.9 (d, J_{CP} = 10.3 Hz, *o*/*m*Ph), 128.0 (d, $^1J_{CP}$ = 48.3 Hz, *i*-Ph), 87.6 (s, CH$_2$CH=<u>C</u>H), 77.6 (s, overlapping with $CDCl_3$, CH$_2$<u>C</u>H=CH), 51.8 (d, $^1J_{CP}$ = 36.0 Hz, P<u>C</u>H), 27.6 (d, $^2J_{CP}$ = 6.8 Hz, PCH<u>C</u>H$_2$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 253K): δ (ppm) = 100.0 (bs).

RuCl$_2$(*η*^{6}-toluene)(cycloheptyldiphenylphosphine-*κ*P) (6). In a NMR tube 20 mg (0.033 mmol) of complex **4** were dissolved in toluene and irradiated at room temperature with 150W mercury lamp to give after 3h complete conversion in complex **6** which was further isolated as red crystals. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.94–7.86 (m, 4H, Ph), 7.51–7.43 (m, 6H, Ph), 5.08–5.03 (m, 2H, CH Tol), 4.95 (bd, $^3J_{HH}$ = 5.8 Hz, 2H, CH Tol), 4.40 (bt, $^3J_{HH}$ = 5.2Hz, 1H,

CH Tol), 3.34-3.26 (m, 1H, PCH), 2.26–2.15 (m, 2H, cycloheptyl), 2.13 (s, 3H, CH_3-Tol), 1.57–1.37 (m, 6H, cycloheptyl), 1.36–1.26 (m, 2H, cycloheptyl), 1.04–0.94 (m, 2H, cycloheptyl). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ (ppm) = 133.8 (d, $^1J_{CP}$ = 39.6 Hz, C_q *i*-Ph), 133.5 (d, J_{CP} = 8.0 Hz, CH Ph), 130.33 (d, J_{CP} = 1.9 Hz, CH Ph), 128.2 (d, J_{CP} = 9.9 Hz, CH Ph), 107.3 (d, J_{CP} = 4.6 Hz, C_q Tol), 89.1 (s, CH Tol), 88.3 (d, J_{CP} = 5.4 Hz, CH Tol), 80.8 (s, CH Tol), 34.9 (d, $^1J_{CP}$ = 20.8 Hz, PCH), 29.9 (d, J_{CP} = 2.0 Hz, CH_2-cycloheptyl), 28.3 (d, J_{CP} = 13.4 Hz, CH_2-cycloheptyl), 27.5 (s, CH_2-cycloheptyl), 18.6 (s, $\underline{C}H_3$-Tol). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): δ (ppm) = 28.4 (s).

Kharasch addition : In a typical experiment styrene (2 mmol), CCl_4 (8 mmol), dodecane (internal standard, 0.44 mmol), Ru complex (0.01 mmol of **1**-**4** or 0.005 mmol **5**; 0.5 mol% to styrene) and 2 mL of the appropriate solvent were introduced in a Schlenk tube in the glove box and then irradiated with 150W mercury lamp (Heraeus TQ 150W) or heated to the desired temperature under light protection. The styrene conversion and the yield of the Kharasch adduct were determined by GC after calibration with respect to the internal standard. All solvents and reagents were dried and kept under argon prior to use. The sampling of the reaction mixture was made in the glove box under argon.

GC method : 100°C, 10°/min, 220°C (10min), column flow: 1 $mL.mn^{-1}$, split ratio:100, column : QUADREX 60329B, length 30.0m, Inner diameter 0.25mm, Film Thickness 0.25µm.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^1H, ^{13}C, ^{31}P NMR spectra of complexes **1**-**6**, UV visible spectra of complexes 1-**5**, evolution of UV-Visible spectra of compounds **1** and **3** under irradiation at 360 nm, tables of crystal data for complexes **1**-**6** and calculated transition orbitals of complexes **1**, **3** and **5**.

Accession Codes

CCDC 1578509-1578514 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or 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.

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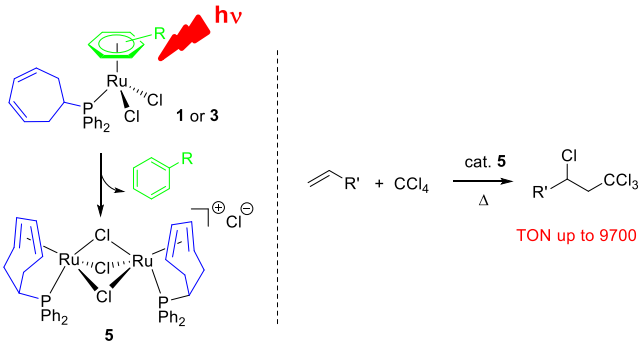

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