Atom Transfer Radical Additions with the Cationic Half-Sandwich Complex $[Cp^*Ru(PPh_3)_2(CH_3CN)]OTf$

Laurent Quebatte,[a] Rosario Scopelliti,[a][‡] and Kay Severin*[a]

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The cationic ruthenium half-sandwich complex $[Cp^*Ru(PPh_3)_2(CH_3CN)][OTf]$ (**2**) ($Cp^* = \eta^5$-C_5Me_5, OTf = SO_3CF_3) was synthesized by reduction of $[Cp^*RuCl_2]_2$ with zinc in the presence of NaOTf and subsequent reaction with PPh_3. When NaOTf was omitted, the corresponding tetrachlorozincate salts were obtained. Complex **2**, as well as the salts $[Cp^*Ru(CH_3CN)_3]_2[ZnCl_4]$ (**3**) and $[Cp^*Ru(PPh_3)_2(CH_3CN)]_2[ZnCl_4]$ (**4**), were characterized by single-crystal X-ray analysis. Complex **2** proved to be a potent catalyst for the atom transfer radical addition of CCl_4 and $CHCl_3$ to terminal olefins, displaying a performance superior to that of the previously described neutral catalyst $[Cp^*RuCl(PPh_3)_2]$. For the addition of $CHCl_3$ to styrene, a total turnover number of 890 was achieved.

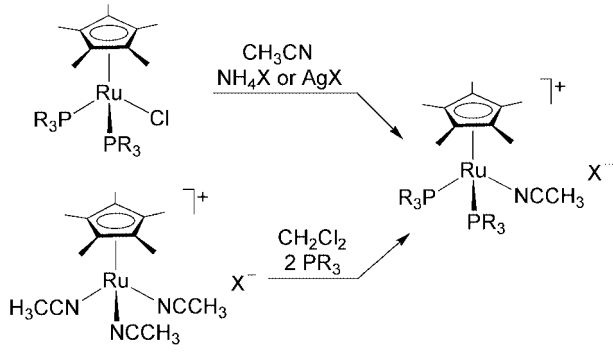
Introduction

The atom transfer radical addition (ATRA) of polyhalogenated compounds to olefins ("Kharasch reaction")[1] is a versatile method for C–C bond formation and has found several applications in organic synthesis.[2] In 1973, it was reported that the complex $[RuCl_2(PPh_3)_3]$ is able to efficiently catalyze this type of reaction and it was subsequently used as the catalyst of choice for more than 20 years.[3] Over the last 6 years, however, several new ruthenium-based catalysts with superior performance have been reported.[4] Among these, the complex $[Cp^*RuCl(PPh_3)_2]$ (**1**) is of special interest since it is one of the few catalysts, which allows to carry out the addition of CCl_4 and $CHCl_3$ to olefins at ambient temperatures.[5,6] Despite its high activity, complex **1** suffers from poor long term stability, a characteristic shared by many other highly active catalysts for the Kharasch reaction.[4]

Nagashima et al. have reported that the ATRA activity of the dinuclear complex $[Cp^*Ru\{\mu_2$-*i*PrN=C(Me)-N*i*Pr$\}RuClCp^*]$ could be increased by transforming it into a cationic species using $NaPF_6$ or $NaBPh_4$.[7] Similarly, the activity of ruthenium chloro catalysts for the closely related atom transfer radical polymerization (ATRP)[8] could be enhanced by chloride abstraction with silver salts.[9] For Ru vinylidene catalysts, on the other hand, it was reported that the abstraction of a chloro ligand lead to a decrease in ATRA activity.[10] In the following we show that the cationic complex $[Cp^*Ru(PPh_3)_2(CH_3CN)][OTf]$ (**2**) is a very potent catalyst for ATRA reactions. Its stability is significantly higher than that of the neutral counterpart **1**. Consequently, good turnover numbers (TONs) were observed, even for "difficult" reactions such as the addition of $CHCl_3$ to styrene.

Results and Discussion

Cationic complexes of the general formula $[Cp^*Ru(PR_3)_2(CH_3CN)]X$ (X^- = weakly coordinating anion) have been obtained by reaction of complex **1** with MX in acetonitrile ($M^+ = Ag^+$, NH_4^+)[11] or by reaction of $[Cp^*Ru(CH_3CN)_3]X$ with PR_3 in CH_2Cl_2 (Scheme 1).[12] For the synthesis of the complex $[Cp^*Ru(PPh_3)_2(CH_3CN)][OTf]$ (**2**), we decided to use the latter pathway since the trisacetonitrile complex $[Cp^*Ru(CH_3CN)_3]X$ is easily accessible by reduction of $[Cp^*RhCl_2]_n$ with zinc in acetonitrile in the presence of MX salts.[12]



Scheme 1. Synthesis of cationic complexes of the general formula $[Cp^*Ru(PR_3)_2(CH_3CN)]X$ (X^- = weakly coordinating anion).

Following this synthetic route it was possible to prepare the cationic complex **2** in 95% yield by reaction of

[a] Institut de Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL)
1015 Lausanne, Switzerland
Fax: +41-21-693-9305
E-mail: kay.severin@epfl.ch
[‡] X-ray structural analysis.

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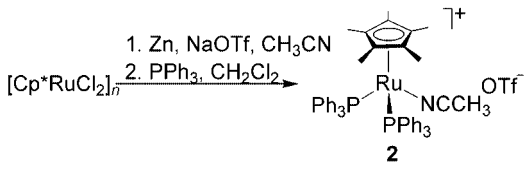
$[Cp^*RuCl_2]_2$ with zinc in acetonitrile in the presence of NaOTf and direct conversion of the product with two equivalents of PPh_3 (Scheme 2). Complex **2** displays a good solubility in polar organic solvents such as THF, dichloromethane and chloroform, and a moderate solubility in toluene. The identity of **2** was confirmed by NMR spectroscopy, elemental analysis and single-crystal X-ray analysis (Figure 1).



Scheme 2. Synthesis of complex **2**.

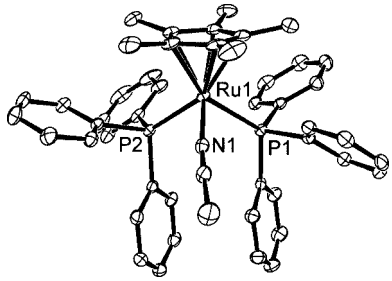
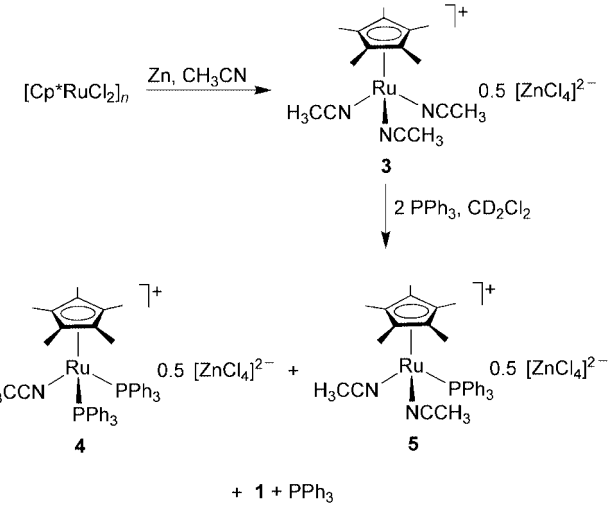


Figure 1. ORTEP[22] drawing of the molecular structure of **2** in the crystal. The OTf^- anion and the hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N1 2.056(2), Ru1–P1 2.3709(6), Ru1–P2 2.3462(7); P2–Ru1–P1 99.41(2), N1–Ru1–P1 87.97(5), N1–Ru1–P2 87.95(6).

The cation of complex **2** displays the expected pianostool geometry. As a consequence of the steric demand of the triphenylphosphane ligands, the P–Ru–P angle [99.41(2)°] is larger than the N–Ru–P angles [N1–Ru1–P1 87.97(5)°; N1–Ru1–P2 87.95(6)°]. The Ru–P bond lengths [Ru1–P1 2.3709(6) Å, Ru1–P2 2.3462(7) Å] are similar to what has been found for the neutral complex **1**.[13]

In order to investigate the influence of the NaOTf salt during the synthesis of complex **2**, we have performed the reduction of $[Cp^*RuCl_2]_2$ with zinc in acetonitrile in the absence of this salt. The formation of a trisacetonitrile complex $[Cp^*Ru(CH_3CN)_3]^+$ (**3**) was observed but as the counterion, the tetrachlorozincate anion was formed as revealed by single-crystal X-ray analysis (Scheme 3, Figure 2). Complex **3** proved to be not suited for a clean synthesis of a bis(triphenylphosphane) adduct: when two equivalents of PPh_3 were added to a solution of **3** in CD_2Cl_2, the desired cationic bisadduct **4** was formed but along with the neutral complex **1**, the monoadduct **5**,[14,15] and free PPh_3 as evidenced by ^1H and ^{31}P NMR spectroscopy. From this mixture, it was possible to obtain single crystals of complex **4** by addition of pentane. A graphic representation of the structure of **4** is depicted in Figure 3.



Scheme 3. Synthesis of the tetrachlorozincate complex **3** and its reaction with PPh_3.

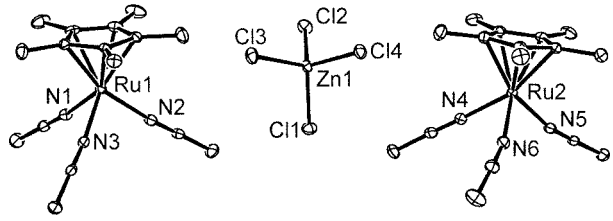


Figure 2. ORTEP[13] drawing of the molecular structure of **3** in the crystal. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–N1 2.095(2), Ru1–N2 2.108(2), Ru1–N3 2.103(2), Ru2–N4 2.110(2), Ru2–N5 2.102(2), Ru2–N6 2.109(2); N1–Ru1–N2 88.19(8), N1–Ru1–N3 84.67(8), N3–Ru1–N2 90.60(7), N5–Ru2–N4 90.84(8), N5–Ru2–N6 91.66(8), N–Ru2–N4 81.76(8).

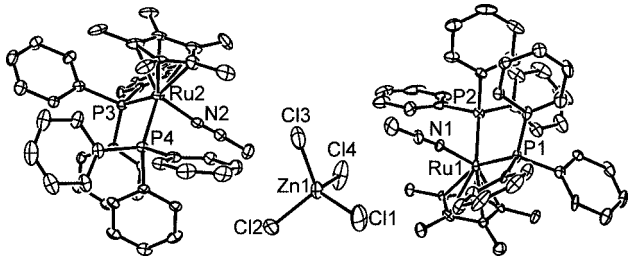


Figure 3. ORTEP[13] drawing of the molecular structure of **4** in the crystal. The hydrogen atoms and the solvent molecules ($3\times CH_2Cl_2$) are omitted for clarity. Selected bond lengths [Å] and angles [°]:Ru1–N1 2.037(6), Ru1–P1 2.3568(19), Ru1–P2 2.343(2), Ru2–N2 2.061(7), Ru2–P3 2.3556(19), Ru2–P4 2.346(2); N1–Ru1–P1 87.44(16), N1–Ru1–P2 88.12(18), P2–Ru1–P1 99.00(7), N2–Ru2–P4 89.28(18), N2–Ru2–P3 90.17(17), P4–Ru2–P3 97.19(7).

The bond lengths and angles found for the two crytallographically independent cations of complex **3** are very similar to those observed for other $[Cp^*Ru(CH_3CN)_3]^+$ complexes.[16] The N–Ru–N angles are close to 90°. The geometry of the cations can thus be described as pseudo-octahe-

dral with the Cp* ligand occupying three facial coordination sites. As it was observed for complex **2**, the P–Ru–P angles of **4** [99.00(7) and 97.19(7)°] are larger than the P–Ru–N angles [P–Ru–N 87.44(16)–90.17(17)°].

To evaluate the ability of the cationic complex **2** to catalyze ATRA reactions, we first investigated the addition of CCl_4 to styrene at 60 °C using a molar ratio of **2**/styrene/CCl_4 = 1:300:432. The complete conversion of the olefin was observed within 2 h. For the neutral complex **1**, a conversion of 97% was reported after 5 h.[5] In order to obtain more information about differences in activity and stability of the catalysts **1** and **2**, we have investigated the time course of the reaction between styrene and CCl_4 at room temperature in chloroform with a molar ratio of Ru/styrene/CCl_4 = 1:300:600 (Figure 4). For reactions with the cationic catalyst **2**, a quantitative reaction was observed after ca. 4 h. For reactions catalyzed by the neutral complex **1**, on the other hand, a very fast product formation was found for the first 20 min, but then the rates dropped dramatically and the conversion reached a plateau at around 40%. When the solvent was changed to toluene and the CCl_4 concentration was reduced, an increased lifetime of the catalyst was observed but still the final conversion (60%) was lower than what was found for **2**. This data suggested that the neutral catalyst **1** shows a higher intrinsic activity than the cationic complex **2** but a significantly lower stability. This is in agreement with the observation of Simal et al. that complex **1** rapidly decomposed in presence of CCl_4: when 10 equivalents of CCl_4 were added to a solution of **1** in toluene at 20 °C, the complete conversion into a paramagnetic Ru^{III} compound occurred within 2 h.[5] When a similar experiment was performed with the cationic complex **2**, only 40% decomposition was observed after 2 h. For complex **1** it was suggested that PPh_3 dissociation is required to activate the catalyst.[5] This step is likely to be faster for the neutral complex **1** as compared to the cationic complex **2**, which may explain the higher initial activity of the former. The higher stability of the cationic complex **2**, on the other hand, may be due to a different activity of the Ru^{III} species formed by atom transfer but further investigations are needed to clarify this point.

The good performance of the cationic catalyst **2** was confirmed in other ATRA reactions (Table 1). As mentioned above, the reaction between styrene and CCl_4 could be completed within 5 h using 0.33 mol% of complex **2** at room temperature (entry 1). Using only 0.02 mol% catalyst, a total TON of 3050 was measured after 5 weeks.[17] A remarkably fast and clean reaction was observed with methyl methacrylate (MMA) and CCl_4 as the substrates (entry 2). After 2 h at room temperature, a yield of 93% was obtained. For the neutral catalyst **1**, for comparison, a yield of only 36% was found after 24 h.[5] The olefins *n*-butyl acrylate (entry 3) and 1-decene (entry 4) gave lower yields of 67 and 77%, respectively. For the former substrate, this was due to competing oligomerization reactions.

In order to perform ATRA reactions with the significantly less active substrate $CHCl_3$, the reaction temperature was increased to 40 °C and a catalyst concentration of 1 mol% was employed (entries 5–9). Under these conditions, catalyst **2** provided the chloroform adducts of the aromatic olefins styrene, *p*-chlorostyrene, and *p*-methoxystyrene with good yields (entries 5–7). A TON of 890 was obtained for the addition of $CHCl_3$ to styrene using 0.1 mol% of complex **2**. This is – to the best of our knowledge – the highest value ever reported for a ruthenium-based catalyst. For acrylate substrates, almost complete conversions were determined after 24 h. The yields of the desired addition products, however, were very modest due to competing polymerization reactions (entries 8 and 9).

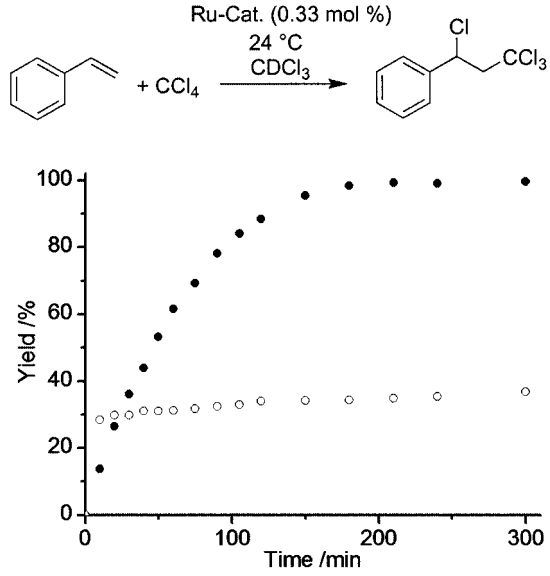


Figure 4. Time course of the reaction between styrene and CCl_4 catalyzed by complexes **1** (○) or **2** (●). Reaction conditions: Ru/styrene/CCl_4 = 1:300:600; solvent = $CDCl_3$; [Ru] = 4.6 mM; 24 °C. The yield is based on the formation of the product as determined by ^1H NMR spectroscopy.

Table 1. ATRA reactions catalyzed by complex **2**.[a]

Entry	Olefin	$CXCl_3$	*T* [°C]	*t* [h]	Conv. [%]	Yield [%]
1	styrene	CCl_4	24	5	100	97
2	methyl methacrylate	CCl_4	24	2	100	93
3	*n*-butyl acrylate	CCl_4	24	10	98	67
4	1-decene	CCl_4	40	24	80	77
5	styrene	$CHCl_3$	40	24	96	88
6	*p*-chlorostyrene	$CHCl_3$	40	48	95	92
7	*p*-methoxystyrene	$CHCl_3$	40	48	96	90
8	methyl methacrylate	$CHCl_3$	40	24	96	33
9	*n*-butyl acrylate	$CHCl_3$	40	24	99	15

[a] Reaction conditions: **2**/olefin/CCl_4 = 1:300:600, [**2**] = 4.6 mM, solvent: $CHCl_3$ or **2**/olefin/$CHCl_3$ = 1:100, [**2**] = 13.8 mM, solvent = $CHCl_3$. The conversion is based on the consumption of the olefin and the yield is based on the formation of the product as determined by GC or ^1H NMR spectroscopy after the time given.

Conclusions

Over the last few years, several highly active ruthenium-based catalysts for ATRA reactions have been described.[4]

These catalysts allow to perform Kharasch reactions under very mild conditions with few side products. But still, there are some important challenges that need to be addressed by future research in this area. First of all, the mechanistic understanding of ruthenium-catalyzed ATRA reactions is rudimentary which hampers a more rational approach towards catalyst discovery (e.g. stereoselective catalysts) and optimization. Furthermore, catalyst stability is a problem for several of the newly developed complexes and apart from optimizing the reaction conditions (temperature, concentrations etc.), solutions to this dilemma are not evident. The results described above demonstrate that a simple modification such as the conversion of a chloro complex into a cationic acetonitrile complex may result in a significantly increased catalyst stability. Although it remains to be seen whether similar effects can be observed for other catalysts, it seems worthwhile to consider modifications of this type in future investigations.

Experimental Section

General: All reactions were performed under a dry dinitrogen atmosphere. The solvents and substrates were distilled from appropriate drying agents and stored under dinitrogen. Zn dust (< 10 micron; 98+%) was obtained from Aldrich, NaOTf (97+%) and PPh_3 (98.5+%) were obtained from Fluka. The complexes $[Cp^*RuCl_2]_2$[18] and $[Cp^*RuCl(PPh_3)_2]$[19] were prepared according to literature procedures. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Advance DPX 400 spectrometer with the solvents as internal standards (^1H, ^{13}C) or a solution of H_3PO_4 in D_2O as external standard (^{31}P). All spectra were recorded at room temperature. GC-MS analyses were performed with a WCOT Fused Silica column (30 m) coupled to a Varian Saturn 2200 mass spectrometer.

Synthesis of Complex 2: Zn (0.2 g, 3.1 mmol) and NaOTf (84 mg, 488 μmol) were added to a solution of $[Cp^*RuCl_2]_2$ (100 mg, 162 μmol) in CH_3CN (5 mL) and the mixture was stirred for 2 h at room temperature. The yellow solution was filtered and the remaining Zn was washed with additional solvent (2 × 3 mL). After evaporation of the solvent, the resulting powder was dissolved in CH_2Cl_2 (5 mL), filtered, and the filtrate was washed with additional CH_2Cl_2 (2 × 3 mL). PPh_3 (256 mg, 976 μmol) was added to the combined solutions whilst stirring. After for 20 min, the mixture was concentrated to 2 mL and poured into a flask containing hexane (15 mL) to precipitate the product as a yellow powder, which was isolated by filtration, washed with hexane (2 × 3 mL), and dried under vacuum. Yield: 294 mg (95%). Single crystals were obtained by diffusion of pentane into a solution of **2** in CH_2Cl_2. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.13 (t, $^4J_{H,P}$ = 1.6 Hz, 15 H, Cp*), 2.65 (t, $^5J_{H,P}$ = 0.6 Hz, 3 H, CH_3CN), 7.13–7.46 (m, 30 H, Ph) ppm. ^{13}C NMR (101 MHz, CD_2Cl_2): δ = 5.9 (CH_3CN), 9.7 (CH_3, Cp*), 93.1 (C, Cp*), 128.2–134.2 (Ph), 129.3 (CH_3CN) ppm. ^{31}P NMR (162 MHz, CD_2Cl_2): δ = 42.20 ppm. Elemental analysis: calcd. (%) for $C_{49}H_{48}F_3NO_3P_2RuS \times H_2O$ (969.0): C 60.73, H 5.20, N 1.45; found C 60.84, H 5.17, N 1.56.

Synthesis of Complex 3: A solution of $[Cp^*RuCl_2]_2$ (736 mg, 1196 μmol) in CH_3CN (35 mL) was added Zn (5.0 g, 76.5 mmol) and stirred for 5 h at room temperature. The initial dark brown color changed to bright yellow. The solution was filtered and the remaining Zn was washed with additional solvent (15 mL). After evaporation of the solvent under vacuum, the resulting powder was suspended in Et_2O (15 mL), isolated by filtration, washed with additional Et_2O (15 mL) and dried under vacuum. Yield: 1030 mg (93%). Single crystals were obtained by slow diffusion of Et_2O into a solution of **3** in CH_3CN. ^1H NMR (400 MHz, CD_3CN): δ = 1.59 (s, 15 H, Cp*) ppm. ^{13}C NMR (101 MHz, CD_3CN): δ = 9.7 (CH_3, Cp*), 80.6 (C, Cp*) ppm. Elemental analysis: calcd. (%) for $C_{32}H_{48}Cl_4N_6Ru_2Zn \times 3/4\ CH_3CN$ (956.9): C 42.05, H 5.29, N 9.88; found: C 42.36, H 5.36, N 9.47.

Reaction of Complex 3 with PPh_3: PPh_3 (5.7 mg, 21.7 μmol) was added to a solution of complex **3** (5.0 mg, 5.4 μmol) in CD_2Cl_2 (500 μL). The resulting bright orange solution was analyzed by ^1H and ^{31}P NMR spectroscopy. Single crystals of **4** were obtained by slow diffusion of pentane into the reaction mixture. NMR [400 (^1H), 162 (^{31}P) MHz, aromatic protons, free CH_3CN and PPh_3 are omitted]: **4:** ^1H: δ = 1.13 (t, $^4J_{H,P}$ = 1.6 Hz, 15 H, Cp*), 2.87 (t, $^5J_{H,P}$ = 1.4 Hz, 3 H, CH_3CN) ppm. ^{31}P: δ = 43.0 ppm. **1:** ^1H: δ = 1.01 (t, $^4J_{H,P}$ = 1.4 Hz, 15 H, Cp*) ppm. ^{31}P: δ = 41.0 ppm. **5:** ^1H: δ = 1.42 (d, $^4J_{H,P}$ = 1.6 Hz, 15 H, Cp*), 2.22 (d, $^5J_{H,P}$ = 1.2 Hz, 6 H, CH_3CN) ppm. ^{31}P: δ = 48.9 ppm.

General Procedure for the ATRA of CCl_4 to Olefins: 1000 μL of a $CDCl_3$ stock solution of the olefin, CCl_4, and the internal standard mesitylene were added to a 1.5 mL vial containing the solid catalyst **2** (final conc.: [**2**] = 4.6 mM, [olefin] = 1.38 M, [CCl_4] = 2.76 M, [mesitylene] = 0.36 M). For 1-decene, the resulting solution was placed in an oil bath tempered at 40 °C. After the given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (550 μL) and analyzed by ^1H NMR spectroscopy or gas chromatography. The kinetic experiments were performed in an analogous fashion by removing several samples at regular time intervals.

General Procedure for the ATRA of $CHCl_3$ to Olefins: 500 μL of a $CDCl_3$ stock solution of the olefin and the internal standard mesitylene were added to a 1.5 mL vial containing the solid catalyst **2** (final conc.: [**2**] = 13.8 mM, [olefin] = 1.38 M, [mesitylene] = 0.36 M). The resulting solution was placed in an oil bath tempered at 40 °C. After the given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (550 μL) and analyzed by ^1H NMR spectroscopy or gas chromatography.

Decomposition Experiment: Complex **2** (2.8 mg, 2.9 μmol) and CCl_4 (2.9 μL, 30.1 μmol) were dissolved in CD_2Cl_2 (500 μL). The reaction followed by ^1H and ^{31}P NMR (400 and 162 MHz, respectively) for 10 h at 21 °C.

X-ray Crystallography: Details about the crystals and their structure refinement are listed in Table 2 and Table 3 whereas some relevant geometrical parameters are included into the picture captions. Data collection were performed at 140(2) K on a 4-circle goniometer having kappa geometry and equipped with an Oxford Diffraction KM4 Sapphire CCD. Data reduction was carried out with CrysAlis RED, release 1.7.0.[20] Absorption correction has been applied to all data sets. Structure solution and refinement were performed with the SHELXTL software package, release 5.1.[21] The structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the "riding model". CCDC-268907–268909 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Crystallographic data for the complexes **2** and **3**.

	2	**3**
Empirical formula	$C_{49}H_{48}F_3NO_3P_2RuS$	$C_{32}H_{48}Cl_4N_6Ru_2Zn$
Molecular weight [g mol^{-1}]	950.95	926.07
Crystal size	0.16 × 0.13 × 0.11	0.18 × 0.13 × 0.09
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a [Å]	10.5409(4)	9.3648(4)
b [Å]	13.3793(7)	12.9800(8)
c [Å]	16.2230(9)	18.3753(10)
α [°]	88.977(4)	72.891(5)
β [°]	86.567(4)	88.514(4)
γ [°]	75.659(4)	72.566(5)
Volume [Å^3]	2212.64(18)	2031.94(18)
Z	2	2
Density [g cm^{-3}]	1.427	1.514
Temperature [K]	140(2)	140(2)
Absorption coefficient [mm^{-1}]	0.529	1.611
Θ range [°]	3.12 to 25.03	3.15 to 25.03
Index ranges	–10 → 10, –15 → 15, –19 → 19	–10 → 11, –15 → 15, –21 → 20
Reflections collected	13077	12149
Independent reflections	6823 (R_{int} = 0.0200)	6273 (R_{int} = 0.0225)
Absorption correction	semi-empirical	empirical
Max. and min. transmission	0.9638 and 0.8015	0.887 and 0.620
Data/restraints/parameters	6823/0/541	6273/0/406
Goodness-of-fit on F^2	1.044	0.985
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0307, wR_2 = 0.0799	R_1 = 0.0219, wR_2 = 0.0567
R indices (all data)	R_1 = 0.0340, wR_2 = 0.0822	R_1 = 0.0265, wR_2 = 0.0581
Largest diff. peak/hole [e·Å^{-3}]	0.653 and –0.810	0.466 and –0.675

Table 3. Crystallographic data for the complex **4**.

	4 × 3CH_2Cl_2
Empirical formula	$C_{99}H_{102}Cl_{10}N_2P_4Ru_2Zn$
Molecular weight [g mol^{-1}]	2065.72
Crystal size	0.22 × 0.20 × 0.11
Crystal system	monoclinic
Space group	$P2_1$
a [Å]	10.6258(4)
b [Å]	21.7283(11)
c [Å]	20.4384(11)
α [°]	90
β [°]	90.815(4)
γ [°]	90
Volume [Å^3]	4718.3(4)
Z	2
Density [g cm^{-3}]	1.454
Temperature [K]	140(2)
Absorption coefficient [mm^{-1}]	0.966
Θ range [°]	2.99 to 25.03
Index ranges	–11 → 10, –25 → 25, –24 → 24
Reflections collected	27665
Independent reflections	15206 (R_{int} = 0.0498)
Absorption correction	empirical
Max. and min. transmission	0.823 and 0.458
Data/restraints/parameters	15206/1/1063
Goodness-of-fit on F^2	0.923
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0517, wR_2 = 0.1063
R indices (all data)	R_1 = 0.0715, wR_2 = 0.1135
Largest diff. peak/hole [e·Å^{-3}]	1.158 and –0.707

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