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Atom transfer radical addition (ATRA) of carbon tetrachloride and chlorinated esters to various olefins catalyzed by Cp'Ru(PPh₃)(PR₃)Cl complexes

Radhika P. Nair¹, Jocelyn A. Pineda-Lanorio, Brian J. Frost*

Department of Chemistry, University of Nevada, Reno, NV 89557-0216, United States

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ABSTRACT

Cp*Ru(PPh₃)(PR₃)Cl complexes, where PR₃ = PMe₃, PPh₃, or PTA (PTA = 1,3,5-triaza-7-phosphaadamantane), were used to catalyze the atom transfer radical addition of chlorinated esters (CCl₃CO₂Et, CH₂ClCO₂Et) to styrene, and that of CCl₄ to a variety of olefins. The monoadducts were obtained in moderate to excellent yields. Moreover, high selectivities were obtained for the addition of CCl₄ to internal olefins. The activity of Cp*Ru(PTA)(PPh₃)Cl and Cp*Ru(PTA)(PMe₃)Cl were comparable to that of the highly efficient ATRA catalyst, Cp*Ru(PPh₃)₂Cl. The addition of CCl₃CO₂Et to styrene catalyzed by Cp'Ru(PPh₃)(PR₃)Cl (Cp' = Dp, Ind, Cp, Tp) are also reported here. Two new compounds, 3-chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one and 1,3,3,3-tetrachloro-1,2-diphenylpropane, resulting from the addition of CCl₄ to chalcone and *cis*-stilbene have been isolated and characterized by NMR spectroscopy and X-ray crystallography.

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1. Introduction

The addition of halogenated compounds to olefins is one of the fundamental reactions in organic synthesis and has gained considerable attention over the years [1–5]. This simple reaction, reported by Kharasch in 1938, is a classic example of anti-Markovnikov addition and is commonly referred to as atom transfer radical addition (ATRA) [1]. The first successful examples of transition-metal-catalyzed ATRA were the additions of CCl_4 and $CHCl_3$ to a variety of olefins in the presence of iron and copper salts. Today, a variety of metal complexes are known to catalyze ATRA reactions [4]. Amongst them, nickel [5,6], copper [7,8], and particularly ruthenium based systems [9–16] have displayed remarkable catalytic performance. Intramolecular ATRA or atom transfer radical cyclization (ATRC) is an effective tool for the synthesis of 5- or 6-membered carbocycles, macrocyclic compounds, lactams and lactones, alkaloids, and other functionalized ring systems [7a,17,18].

The transition-metal-promoted ATRA emerged in the early 1970's with the discovery of RuCl₂(PPh₃)₃ as a highly efficient and versatile catalyst for ATRA [19,20]. The pioneering work of Sawamoto in RuCl₂(PPh₃)₃ catalyzed controlled polymerization (ATRP) provided an impetus to the development of ruthenium-based ATRA catalysts. A variety of ruthenium complexes are known to catalyze ATRA reactions with half-sandwich ruthenium phosphine complexes bearing η^5 -carborane [13] or η^5 -cyclopentadienyl-based

ligands [14–16] among the most superior catalysts reported to date. The use of 2,2'-azobis(isobutyronitrile) (AIBN) in transition-metalcatalyzed ATRA was introduced by Severin and co-workers [15], and has successfully been employed in ruthenium [15,16] and copper [8b,c] catalyzed reactions, drastically increasing catalytic activity.

We have recently reported the efficiency of a series of $Cp'Ru(PR_3)(PPh_3)Cl$ complexes, where $Cp' = (\eta^5 - C_5Me_5^-, Cp^*), (\eta^5 - C_5Me_5^-, Cp^*)$ $C_8H_9^-$, Dp), ($\eta^5-C_9H_7^-$, Ind), ($\eta^5-C_5H_5^-$, Cp) or ($\eta^3-HB(N_2C_3H_3)_3^-$, Tp); PR₃ = 1,3,5-triaza-7-phosphaadamantane (PTA) or PMe₃ to catalyze various ATRA reactions in good to excellent yields [16]. Our previous studies revealed that the electron-donating ability of the ancillary ligand (Cp') and the relative facility of dissociation of the phosphine are crucial for good catalytic activity of the ruthenium complexes. Among the series of complexes investigated, the Cp* complexes Cp*Ru(PTA)(PPh₃)Cl 1 and Cp*Ru(PMe₃)(PPh₃)Cl 2 exhibited high activity, Fig. 1. We now report on the efficiency of catalytic systems 1 and 2 for the addition of chlorinated esters to styrene, and the addition of CCl₄ to more challenging olefins in the presence of AIBN, Scheme 1. For comparison, one of the best ruthenium catalysts reported to date for ATRA [14a], Cp*Ru(PPh₃)₂Cl (**3**), has also been employed under our reactions conditions.

2. Experimental

2.1. Materials and methods

All reactions were performed under a dry nitrogen atmosphere, using conventional Schlenk vacuum-line techniques and





^{*} Corresponding author. Tel.: +1 775 784 1993; fax: +1 775 784 6804. E-mail address: frost@unr.edu (B.I. Frost).

¹ Present address: Physical Science Department, Southern Utah University, Cedar City, UT 84720, United States.



Fig. 1. Ruthenium complexes used as catalyst precursors for ATRA.



Scheme 1. General reaction scheme for the atom transfer radical addition (ATRA) of X–Cl to terminal olefins catalyzed by Cp/Ru(PR₃)(PPh₃)Cl complexes in the presence of AlBN (PR₃ = PPh₃, PMe₃, or PTA).

glove-box. Reagents were purchased from commercial suppliers, and used as received. Solvents were dried with molecular sieves and degassed with N₂, prior to use. Column chromatography was performed using Silicycle silica gel (60-200 mesh). Cp'Ru(P-Me₃)(PPh₃)Cl [16] (Cp' = Cp*, Dp, Cp, Tp), Cp*Ru(PTA)(PPh₃)Cl [16], Cp*Ru(PPh₃)₂Cl [21], IndRu(PMe₃)(PPh₃)Cl [22], Cp'Ru(P-TA)(PPh₃)Cl [23] (Cp' = Dp, Cp, Ind), and TpRu(PTA)(PPh₃)Cl [24] were synthesized according to literature procedures. Kharasch addition reactions were carried out under nitrogen in standard NMR tube or in J-Young tube. Each catalytic run was repeated at least twice to ensure reproducibility. The known Kharasch adducts 12 [12], 13 [11], 14 [8d], 15 [25,26], 16 [13a,14b], 17 [25], and 18 [11] were identified by comparison of their spectral data with those reported in the literature. The new compounds 19 and 20 were isolated and fully characterized. NMR spectra were recorded with a Varian NMR System 400 spectrometer with ¹H and ¹³C NMR spectra referenced to residual solvent relative to tetramethylsilane (TMS). APPI-MS data were recorded on a Waters Micromass 20 mass spectrometer. X-ray crystallographic data was collected at $100(\pm 1)$ K on a Bruker APEX CCD diffractometer with MoK α radiation (λ = 0.71073 Å) and a detector-to-crystal distance of 4.94 cm. Data collection was optimized utilizing the APEX2 software with a 0.5° rotation about ω between frames, and an exposure time of 10 s per frame. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using SAINTPLUS, and corrected for absorption using SADABS. The structures were solved using direct methods followed by successive least squares refinement on F^2 using the SHELXTL 6.10 software package [27]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in calculated positions. Crystallographic data and data collection parameters are listed in Table 1.

2.2. Catalysis

2.2.1. ATRA of CCl₃CO₂Et or CH₂ClCO₂Et to styrene

To a 1.5 mL vial was added 1 mol% catalyst (0.0138 mmol), 5 mol% AIBN (11.3 mg, 0.069 mmol), styrene (158 μ L, 1.38 mmol), CCl₃CO₂Et (230 μ L, 1.66 mmol) or CH₂CICO₂Et (177 μ L, 1.66 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene- d_8 was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and heated at 60 °C in an oilbath. The formation of product was monitored by ¹H NMR spectroscopy at predetermined intervals. The isolated yield for the Cp*Ru(PPh₃)₂Cl catalyzed reaction of ethyl trichloroacetate with

Та	hl	e	1

Crystallographic data and structural refinement for compounds 19 and 20.

	19	20
Formula	C ₁₆ H ₁₂ Cl ₄ O	C15H12Cl4
Formula weight	362.06	334.05
Color	light yellow	colorless
T (K)	100 (2)	100 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	orthorhombic
Space group	P2(1)/c	Pna2(1)
a (Å)	10.83540(10)	11.7247(2)
b (Å)	8.01140(10)	19.7528(3)
<i>c</i> (Å)	18.1558(2)	6.09430(10)
α (°)	90	90
β (°)	97.5090(10)	90
γ (°)	90	90
$V(Å^3)$	1562.53(3)	1411.41(4)
Ζ	4	4
D_{calc} (Mg m ⁻³)	1.539	1.572
Absorption coefficient (mm ⁻¹)	0.752	0.820
F(000)	736	680
Crystal size (mm ³)	$0.56 \times 0.23 \times 0.12$	$0.518 \times 0.065 \times 0.06$
2θ Range (°)	1.90-32.56	2.02-31.01
Index ranges	$-16 \leqslant h \leqslant 16$,	$-17 \leqslant h \leqslant 16$,
	$-12 \leqslant k \leqslant 11$,	$-28 \leqslant k \leqslant 28$,
	$-26 \leqslant l \leqslant 26$	$-8 \leqslant l \leqslant 8$
Number of reflections collected	22693	33086
Number of independent reflections (<i>R</i> _{int})	5613 (0.0247)	4366 (0.0279)
Number of data/ restraints/	5613/0/190	4366/1/220
parameters	1 007	1.004
on F^2	1.097	1.064
Final R indices	$R_1 = 0.0311,$	$R_1 = 0.0195,$
$[I > 2\sigma(I)]$	$wR_2 = 0.0866$	$wR_2 = 0.0530$
R indices (all data)	$R_1 = 0.0345$,	$R_1 = 0.0200$,
	$wR_2 = 0.0895$	$wR_2 = 0.0534$
CCDC no.	830022	830023

styrene was obtained by column chromatography on silica (10% ethyl acetate/hexanes) yielding **12** as a clear colorless liquid in 61% yield.

2.2.2. ATRA of CCl_4 to various olefins

To a 1.5 mL vial was added 1 mol% catalyst (0.0138 mmol), 5 mol% AIBN (11.3 mg, 0.069 mmol), olefin (1.38 mmol), CCl₄ (533 μ L, 5.52 mmol), and hexamethylbenzene as an internal standard (5 mg, 0.031 mmol). Toluene-*d*₈ was added to bring the total volume to 1 mL. The resulting solution was sealed in an NMR tube and heated to 60–85 °C in an oil-bath. The formation of product was monitored by ¹H NMR spectroscopy at predetermined intervals.

2.3. Synthesis

2.3.1. Synthesis of 3-chloro-3-phenyl-2-(trichloromethyl)-1-phenylpropan-1-one (**19**)

To a Schlenk tube with Teflon seal was added Cp*Ru(P-TA)(PPh₃)Cl (0.0288 g, 0.0414 mmol), AIBN (0.034 g, 0.207 mmol), chalcone (0.862 g, 4.14 mmol), CCl₄ (1.6 mL, 16.56 mmol), and 1.3 mL toluene- d_8 . The reaction was stirred at 85 °C under nitrogen for 48 h. The reaction mixture was cooled to room temperature and purified by chromatography on silica gel (toluene) yielding **19** as a pale yellow crystalline solid in 29% yield (0.44 g). ¹H NMR (CDCl₃, 400 MHz) of major isomer: δ 4.8 (d, 1H, CHCCl₃, ³*J*_{HH} = 10.0 Hz); 5.2 (d, 1H, CHCCl₃, ³*J*_{HH} = 10.0 Hz); 6.5–7.0 (m, 10H, PPh₃); minor isomer: δ 4.55 (d, 1H, CHCCl₃, ³*J*_{HH} = 8.0 Hz); 5.4 (d, 1H, CHCl₃, ³*J*_{HH} = 8.0 Hz); 6.5–7.0 (m, 10H, Ph). ¹³C{¹H} NMR (CDCl₃, 100 MHz) major diastereomer: 62.14 (<u>C</u>HCl), 66.51 (<u>C</u>HCCl₃), 95.55 (<u>C</u>Cl₃), 128.68–129.09 (8 Ar–C); 129.60 (1 Ar–C), 133.89 (1 Ar–C), 137.71

(<u>C</u>-CHCl), 138.10 (<u>C</u>-CO), 193.62 (<u>C</u>=O); minor diastereomer: 61.89 (<u>C</u>HCl), 65.18 (<u>C</u>HCCl₃), 96.64 (<u>C</u>Cl₃), 128.90–129.15 (8 Ar-C); 129.79 (1 Ar-C), 134.17 (1 Ar-C), 137.34 (<u>C</u>-CHCl), 137.63 (<u>C</u>-CO), 191.98 (<u>C</u>=O). APPI-MS: *m/z* Calc. 362.08. Found: 363.12% for [**5**-H]⁺. M.P.: 77–85 °C. X-ray quality crystals were obtained by slow evaporation of hexane solution of **19**.

2.3.2. Synthesis of 1,3,3,3-tetrachloro-1,2-diphenylpropane (20)

To a Schlenk flask with Teflon cap was added Cp*Ru(P-TA)(PPh₃)Cl (0.0288 g, 0.0414 mmol), AIBN (0.034 g, 0.207 mmol), cis-stilbene (740 $\mu\text{L},\,4.14$ mmol), CCl_4 (1.6 mL, 16.56 mmol), and 750 μ L toluene- d_8 . The reaction was stirred at 85 °C under nitrogen for 3 days. The reaction mixture was cooled to room temperature and purified via column chromatography (5% toluene/hexane) yielding **20** as a pale yellow crystalline solid in 43% yield (0.6 g). ¹H NMR (CDCl₃, 400 MHz) major diastereomer: δ 4.17 (d, 1H, CHCCl₃, ${}^{3}J_{HH}$ = 4.8 Hz); 5.91 (d, 1H, CHCl, ${}^{3}J_{HH}$ = 4.8 Hz); 7.0–7.6 (m, 10H, Ph); minor diastereomer: δ 4.48 (d, 1H, CHCCl₃, ${}^{3}J_{HH}$ = 4.0 Hz); 5.76 (d, 1H, CHCl, ${}^{3}J_{HH}$ = 4.0 Hz); 7.0–7.6 (m, 10H, Ph). ¹³C{¹H} NMR (CDCl₃, 100 MHz) major diastereomer: 62.29 (CHCl), 71.60 (CHCCl₃), 100.90 (CCl₃), 127.8-128.6 (8 Ar-C), 128.90 (1 Ar-C), 131.23 (1 Ar-C), 134.47 (C-CHCl), 140.09 (C-CHCCl₃); minor diastereomer: 62.47 (CHCl), 72.36 (CHCCl₃), 101.05 (CCl₃), 127.9-128.6 (8 Ar-C), 129.08 (1 Ar-C), 131.22 (1 Ar-C), 135.39 (C-CHCl), 138.98 (C-CHCCl₃). APPI-MS: *m/z* Calc. 334.07. Found: 334.11%. M.P.: 62-70 °C. X-ray quality crystals were obtained by slow evaporation of a hexane solution of 20.

3. Results and discussion

3.1. Catalytic activity

We investigated the efficiency of complexes 1-3 towards the addition of trichloroethyl acetate to styrene (Table 2, entries 1–3). These reactions proceeded very efficiently at 60 °C and the desired 1:1 adduct **12** was obtained in quantitative yields within 1–2 h. Com-

Table 2

Atom transfer radical addition of CCl₃CO₂Et to styrene catalyzed by complexes 1-11.^a

plexes **1** and **2** exhibited high reactivity with turnover frequencies (TOF, defined as mol-product/mol-catalyst/h, calculated at 50-65% conversion of styrene) of 251.6 and 132.1 h⁻¹, respectively. Contrary to what was observed for the addition of CCl₄, *p*-TsCl, and CHCl₃ to styrene [16], the activity of Cp*Ru(PTA)(PPh₃)Cl **1** (TOF = 251.6 h^{-1}) was slightly higher than that of $Cp^*Ru(PPh_3)_2Cl \ 3$ (TOF = 226 h⁻¹), (Table 2, entries 1 and 3). Encouraged by these results, we also tested the catalytic activity of the Dp, Cp, Ind, and Tp counterparts 4-11 (Table 2, entries 4-12). As observed previously [16], the order of reactivity was proportional to the electron-donating ability of the ancillary ligand Cp', with the exception of Dp complexes 4 and 8 which were slightly less efficient as compared to their Ind counterparts **5** and **9**, respectively, $(Cp^* > Dp < Ind > Cp > Tp)$. Among the catalytic systems (1–11) employed, the Tp-derivatives 7 and 11 were found to be the least active with only 21-28% product formation after 24 h at 80 °C (Table 2, entries 7 and 12). In the absence of Ru no reaction was observed indicating that AIBN is not able to catalyze the reaction under these conditions, Table 2 entry 13.

The catalytic performance of PTA complexes was found to be similar to that of their PMe₃ analogues, except for Cp*Ru(P-Me₃)(PPh₃)Cl (**2**) which displayed lower activity in comparison with Cp*Ru(PTA)(PPh₃)Cl (**1**) (Fig. 2). The Cp*Ru(PTA)(PPh₃)Cl catalyzed reaction obtained a 99% conversion within 80 min, as compared to the 4 h completion time for (**2**). The decrease in activity was also manifest in the lower TOF of **2** (132.1 h⁻¹) versus **1** (251.6 h⁻¹), Table 2 entries 1 and 2. The high activity of the Cp* complexes may be related to the steric bulk and higher electron donating ability of the Cp* ancillary ligand which would stabilize the coordinatively unsaturated 16 e⁻ ruthenium center (Scheme 2) [16,28]. Compound **2** with the more electron donating PMe₃ ligand (relative to PTA or PPh₃) may be too electron rich dropping activity slightly.

As shown in Scheme 2 triphenylphosphine likely dissociates prior to the start of catalysis. Some evidence for this dissociation was observed in a series of kinetics plots for the addition of CCl₃CO₂Et to styrene catalyzed by CpRu(PPh₃)(PMe₃)Cl at various PPh₃ concentrations (Fig. 3). In the absence of excess of PPh₃ there



Entry	Catalyst	Temp. (°C)	Time (h)	$TOF^{b}(h^{-1})$	Yield ^c (%)
1	$Cp^*RuCl(PTA)(PPh_3)$ (1)	60	1.5	251.6	99
2	$Cp^*RuCl(PMe_3)(PPh_3)$ (2)	60	2	132.1	98
3	$Cp^*Ru(PPh_3)_2Cl(3)$	60	1.5	226.0	98 (61)
4	$DpRuCl(PTA)(PPh_3)$ (4)	60	3.25	40.6	98
5	IndRuCl(PTA)(PPh ₃) (5)	60	3.5	61.6	99
6	$CpRuCl(PTA)(PPh_3)$ (6)	60	4	34.7	98
7	$TpRuCl(PTA)(PPh_3)$ (7)	80	24	-	21
8	$DpRuCl(PMe_3)(PPh_3)$ (8)	60	3.25	51.7	98
9	$IndRuCl(PMe_3)(PPh_3)(9)$	60	5	54.5	99
10	$CpRuCl(PMe_3)(PPh_3)$ (10)	60	4	38.6	99
11 ^d	$CpRuCl(PMe_3)(PPh_3)$ (10)	60	4	14.8	59
12	$TpRuCl(PMe_3)(PPh_3)$ (11)	80	24	-	28
13 ^e	-	60	30	-	-

^a All reactions were performed in toluene- d_8 , using 1 mol% catalyst and 5 mol% AIBN.

^b TOF is defined as mol-product/mol-cat/h, calculated at 50-65% conversion of styrene.

^c Yield is determined by ¹H NMR spectroscopy of product vs. internal standard. The isolated yield is given in parenthesis.

^d Without AIBN.

^e Without Ru catalyst with 5 mol% AIBN.



Fig. 2. Kinetics plots for the addition of CCl_3CO_2Et to styrene catalyzed by $1 \mod % Cp^*Ru(PMe_3)(PPh_3)Cl$ (\blacklozenge) or $1 \mod % Cp^*Ru(PTA)(PPh_3)Cl$ (\blacktriangle) followed by 1H NMR spectroscopy.



Scheme 2. General mechanism for $Cp'Ru(L)(PPh_3)Cl$ catalyzed ATRA reaction (where L = PTA, PMe_3, PPh_3).

is no discernable induction period. At early time after the addition of 10 or 20 mol% PPh₃ an induction period was apparent. This induction period was not easily observed in the Cp* systems because the reaction is much faster (Fig. 4). Interestingly the induction period does not increase as [PPh₃] was increased from 10 to 20 mol%. More surprising was that the addition of PPh₃ increased the rate of reaction as evidenced by the steeper slope in kinetics plots of conversion versus time (Figs. 3 and 4). The rate increase is observed with both CpRu(PPh₃)(PMe₃)Cl (Fig. 3) and Cp*Ru(PPh₃)(PMe₃)Cl (Fig. 4) and is evidenced by a steeper slope in both catalysts with addition of PPh₃. At high [PPh₃] (20 mol%) a significant decrease in yield was observed for CpRu(PPh₃)(P- Me_3)Cl, Fig. 3. These plots indicate that PPh₃ has both an inhibitory and promotive effect on catalysis. At this stage we assume that the promotive effect comes from excess triphenylphosphine stabilizing the catalyst from decomposition. Triphenylphosphine dissociation from the Cp* system appears quite fast (no induction period observed) so there is little effect on overall yield with the addition of PPh₃. Triphenylphosphine dissociation from the Cp system is



Fig. 3. Kinetics plots for the addition of CCl_3CO_2Et to styrene followed by ¹H NMR spectroscopy and catalyzed by 1 mol% CpRu(PPh₃)(PMe₃)Cl comparing the reaction with no added PPh₃ (\blacklozenge), with 10 mol% PPh₃ (\blacksquare), and 20 mol% PPh₃ (\blacktriangle).

much slower (as observed by the long induction period); therefore, large amounts of PPh_3 have a negative impact on the overall yield of the reaction.

Severin and co-workers [15] proposed that AIBN allows the reduction of the Ru(III)-X back to the active Ru(II) catalyst (Scheme 2). In the absence of AIBN the addition of CCl₃CO₂Et to styrene is much slower (TOF = 14.8 h⁻¹; Table 2, entry 11) than in the presence of 5 mol% AIBN (TOF = 33.6 h⁻¹; Table 2, entry 10). The percent conversion after 4 h for the CpRu(PPh₃)(PMe₃)Cl catalyzed addition of ethyl trichloroacetate to styrene without AIBN is 59% compared to 99% conversion obtained in the presence of 5 mol% AIBN. Fig. 5 shows the effect of [AIBN] on the addition of CCl₃CO₂Et to styrene catalyzed by CpRu(PPh₃)(PMe₃)Cl. Similar to what we have reported previously for these compounds [16] as the AIBN concentration is increased from 1 to 10 mol% the rate of reaction increases. Above 10 mol% AIBN the reaction rate plateaus (i.e. the rate at 10 mol% is the same as 15 mol%).

The reactivity of the compounds described here (except for the Tp complexes **7** and **11**) are high relative to those reported in the



Fig. 4. Kinetics plots for the addition of CCl₃CO₂Et to styrene followed by ¹H NMR spectroscopy and catalyzed by 1 mol% Cp*Ru(PPh₃)(PMe₃)Cl comparing the reaction with no added PPh₃ (\blacklozenge), with 10 mol% PPh₃ (\blacksquare), and 20 mol% PPh₃ (\blacktriangle).



Fig. 5. Kinetics plots for the addition of CCl₃CO₂Et to styrene catalyzed by 1 mol% CpRu(PPh₃)(PMe₃)Cl at various [AIBN]: (\blacklozenge) no added AIBN, (\blacksquare) 1 mol% AIBN, (\blacktriangle) 5 mol% AIBN, (\blacklozenge) 10 mol% AIBN, and (*) 15 mol% AIBN.

literature. For example, the CCl₃CO₂Et adduct of styrene was obtained in 60% yield after 24 h with 1 mol% RuCl₂(PPh₃)₃ at 75 °C [11]. For the same reaction, 5 mol% Grubb's catalyst $P(Cy_3)_2$. Cl₂Ru=CHPh afforded a 57% yield at 75 °C over 48 h [29]. It is noteworthy that the CCl₃CO₂Et-styrene adducts are synthetically interesting precursors as they can be cyclized to form lactones [18]. ATRA addition of the more difficult substrate CH₂ClCO₂Et to styrene was explored with the most active compounds **1**, **2**, and **3**, Scheme 3. Due to poor reactivity, the reaction temperature was increased to 85 °C. After 24 h, the monoadduct **13** was obtained in modest yields with all three catalysts. Although the conversion of styrene was high (>85%), only 21–28% of the addition product **13** was formed, presumably due to competing polymerization/oligomerization reactions. The reactions proceeded rather



Scheme 3. Addition of CH₂ClCO₂Et to styrene catalyzed by Ru complexes 1-3.

slowly in comparison to the addition of the more halogenated ester CCl_3CO_2Et , for which the same set of catalysts afforded quantitative yields at 60 °C (Table 2, entry 1, 2, and 3). Similar results have been reported previously for the $RuCl_2(PPh_3)_3$ catalyzed addition of CCl_3CO_2Et and CH_2CICO_2Et to styrene [11]. Using Cp* complexes 1–3, the reactivity of the halogenated substrates we have looked at is $CCl_3CO_2Et \sim CHCl_3 > TsCl > CH_2CICO_2Et$ [16].

3.1.1. Addition of CCl₄ to terminal olefins

The substrate scope was further extended for catalyst precursors **1**, **2**, and **3** by exploring the addition of CCl₄ to a variety of terminal olefins: 1-hexene, 1-decene, and *n*-butyl acrylate. With 1-hexene, the CCl₄-adduct was obtained in 90–99% yield within 4-7 h at 60 °C (Table 3, entries 1-3). The Cp*Ru(PTA)(PPh₃)Cl catalyzed addition of CCl₄ to 1-hexene proceeded rapidly (TOF $202 h^{-1}$) as compared to the PMe₃ and PPh₃ analogues (53.3 and $100 h^{-1}$, respectively). This is contrary to the results obtained for CCl₄ addition to styrene where Cp*Ru(PPh₃)₂Cl displayed highest activity [14a,16]. The total turnovers (TTOs) obtained with all three catalysts were impressive; with catalyst loadings of 0.001 mol% (5 mol% AIBN), Cp*Ru(PTA)(PPh₃)Cl (1) exhibited a TTO of 79000 in 48 h, Cp*Ru(PMe₃)(PPh₃)Cl (2) provided a TTO of 88000 after 48 h, and $Cp^*Ru(PPh_3)_2Cl$ (3) was the most active with a TTO of 92000 after 40 h. These are the highest TTOs reported to date. Prior to this work, the highest TTO reported for ATRA was 44000 for the addition of CCl₄ to 1-hexene [15]. With 1-decene, a difficult substrate for ATRA [10a,b,14a], the monoadduct 15 was obtained in greater than 90% yield in under 4 h (Table 3, entries 4–6). *n*-Butyl acrylate, an easily polymerizable substrate, also underwent a fast and clean monoaddition with CCl₄ affording the 1:1 adduct 16 in >90% yield within 2.5–3.5 h (Table 3, entries 7–9). With 1-decene and *n*-butyl acrylate, the reactivity of complexes **1**, **2** and **3** was comparable.

Due to the exceptional activity of $Cp^*Ru(PPh_3)_2Cl(3)$ for ATRA reactions, we performed the addition of CCl_4 to 1-hexene, 1-decene, and *n*-butyl-acrylate with complex **3** at room temperature. Unlike CCl_4 addition to styrene where the reaction goes to completion at room temperature [16], only 30–40% yield was observed in all three cases after ~10 min with no further reaction observed at longer times. The short lifetime of the catalyst at room temperature is presumably due to the lack of AIBN activation at room temperature (AIBN reverses catalyst deactivation).

3.1.2. Addition of CCl₄ to internal olefins

It has been reported that the reaction of internal olefins with CCl_4 occurs with the preferential addition of the Cl atom to the benzylic carbon [11,25]. We obtained similar results for the addition of CCl_4 to *trans*- β -methyl styrene, benzylidene acetone, and chalcone (Table 4, entries 1–9). The reaction of *trans*- β -methyl styrene under the same experimental conditions afforded **17** in 91–95% yield after 5–7 h (Table 4, entries 1–3). The monoadduct **17** was obtained as a mixture of *anti/syn* isomers (~3:1). The α , β -unsaturated ketones (benzylidene acetone and chalcone) were less prone to undergo the addition of CCl₄, yielding only 39–53% of **18** and **19** after 24 h at 60–85 °C (Table 4, entries 4–9). The addition of CCl₄ to *cis*-stilbene afforded **20** as a mixture of two diastereomers in moderate yields after 24 h at 85 °C (Table 4, entries 10–12).

Interestingly, only subtle differences in the activities of catalytic systems **1**, **2** and **3** were observed with all four internal olefins employed. The more electron rich internal olefins were found to be more active with *trans*- β -methyl styrene > benzylidene acetone » chalcone » *cis*-stilbene. For *trans*- β -methyl styrene, all three catalysts yielded >90% of the 1:1 adduct; however, <60% yield was obtained with the less electron rich benzylidene acetone, chalcone, and *cis*-stilbene. Chalcone and *cis*-stilbene were the least active substrates requiring higher temperature (85 °C) relative to the

Entry	Catalyst	Olefins	Time (h)	Product	Yield ^b (%)
1	1	\wedge	4	Cl	93
2	2	$n-C_4H_9$	7		99
3	3	hexene	4.5	n-C ₄ H ₉ CCl ₃	92
				14	
4	1	\diamond	3.5	Cl	94
5	2	$n - C_8 H_{17}$	2.75		92
6	3	decene	3.5	<i>n</i> -C ₈ H ₁₇ CCl ₃	89
				15	
7	1	0	2.5	0	97
8	2	a u 🗍	2.5	с и – Й	99
9	3	C ₄ H ₉ 0	3.5	C4H9 0 CCl3	94
		<i>n</i> -butyl acrylate		Cl 16	



^a All reactions were performed in toluene-*d*₈ at 60 °C using 1 mol% catalyst and 5 mol% AIBN.

^b Yield is determined by ¹H NMR spectroscopy of product vs. internal standard.

Table 4		
Atom transfer radical addition of CC_4 to internal olefins catalyzed by $Cp^*Ru(PTA)(PPh_2)Cl(1)$). $Cp^*Ru(PMe_2)(PPh_2)Cl(2)$.	and Cp*Ru(PPh ₂) ₂ Cl (3).

Entry	Catalyst	Olefins	Temp. (°C)	Time (h)	Product	Yield ^b (%)
1 2 3	Cp*Ru(PPh ₃) ₂ Cl Cp*Ru(PTA)(PPh ₃)Cl Cp*Ru(PMe ₃)(PPh ₃)Cl	transmethyl styrene	60 60 60	5 6 7	$\bigcup_{\substack{CCl_3\\CCl_3}}$	94 (77:23) ^c 95 (77:23) ^c 91 (76:24) ^c
4 5 6	Cp*Ru(PPh ₃) ₂ Cl Cp*Ru(PTA)(PPh ₃)Cl Cp*Ru(PMe ₃)(PPh ₃)Cl	O Benzylidene acetone	60 60 60	24 24 24	$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \end{array} \\ \end{array} \\$	49 (83:17) ^c 53 (87:13) ^c 39 (85:15) ^c
7 8 9	Cp*Ru(PPh ₃) ₂ Cl Cp*Ru(PTA)(PPh ₃)Cl Cp*Ru(PMe ₃)(PPh ₃)Cl	Chalcone	85 85 85	24 24 24	Cl O CCl ₃ 19	41 (70:30) ^c 58 (80:20) ^c 44 (73:27) ^c
10 11 12	Cp*Ru(PPh ₃) ₂ Cl Cp*Ru(PTA)(PPh ₃)Cl Cp*Ru(PMe ₃)(PPh ₃)Cl	<i>cis</i> -Stilbene	85 85 85	24 24 24		$\begin{array}{c} 43 \ (74:26)^d \\ 41 \ (73:27)^d \\ 28 \ (61:39)^d \end{array}$

^a All reactions were performed in toluene-d₈ using 1 mol% catalyst and 5 mol% AIBN, CCl₄/olefin is 4:1.

^b Yield is determined by ¹H NMR spectroscopy of product vs. internal standard.

^c The ratio of anti/syn isomers was determined from the ¹H NMR spectrum.

^d The diastereomeric ratio was determined from the ¹H NMR spectrum.

other substrates (60 °C). Despite the superior catalytic performance of **3** for the ATRA of CCl₄ to styrene [14,16], the activity of **3** towards the addition of CCl₄ to the aforementioned substrates was in general lower than that of **1** and **2**. Complex **2** was slightly more active for addition of CCl₄ to benzylidene acetone (53% yield) versus 49% and 39% for **1** and **3**, respectively. For the addition of CCl₄ to chalcone, **2** was also the most active providing a 58% yield versus 41% and 44% for **1** and **3**, respectively. The reaction of *cis*-stilbene with CCl₄ provided the lowest yields with **1** and **2** the most active with yields of 43% and 41%, respectively; **3** was again the least active at 28% yield. These results indicate that the rate of the reaction varies with small changes to the catalyst, but also with the nature of the substrate.

Compounds **17–20** contain two stereogenic centers; a mixture of diastereomers with predominantly *trans* product was obtained for **17**, **18**, and **19**. Using catalysts **1**, **2**, and **3** only minor variations in diastereomeric ratio were observed. The diastereomeric ratios for **17** (~75:25) and **18** (~85:15) (Table 4, entries 1–6) were slightly higher than previously reported for **17** (2:1) and **18** (64:36) [11,25]. In the case of the chalcone–CCl₄ adduct (**19**), both % yield and isomeric ratio for the Cp*Ru(PTA)(PPh₃)Cl catalyzed reaction were slightly higher than those of PMe₃ and PPh₃ analogues. The differences in stereoselectivity may be due to differences in the sterics of the catalysts. PTA being the smallest of the ligands used, but in the middle with respect to electronics, provides the highest diastereoselectivity.



Fig. 6. Thermal ellipsoid (50% probability) representation of the RR diastereomer of 19 with the atomic numbering scheme, both the RR and SS enantiomers are present in the structure.



Fig. 7. Thermal ellipsoid (50% probability) representation of the *SS* diastereomer of **20** with the atomic numbering scheme, hydrogen atoms have been omitted for clarity, both the *RR* and *SS* enantiomers are present in the structure.

3.2. Structures of addition products 19 and 20

The solid-state structures of **19** and **20** were determined by X-ray crystallography. Crystals suitable for X-ray diffraction were obtained by slow evaporation of hexane solutions of **19** and **20**. Thermal ellipsoid representations of **19** and **20** are depicted in Figs. 6 and 7, respectively, along with atomic numbering schemes. The regioselectivity of CCl₄ addition to chalcone is confirmed from the structure of **19**. As expected, Cl atom is bonded to the benzylic carbon. The structure of major diastereomer of the chalcone–CCl₄ adduct is shown in Fig. 6. The figure contains only the *RR* configuration; however, the crystals are racemic with both *RR* and *SS* enantiomers present. In the case of *cis*-stilbene–CCl₄ adduct, the structure of major diastereomer with (*SS*)-configuration is depicted in Fig. 7, both the *SS* and *RR* enantiomers are present in the crystal.

4. Conclusion

In summary, we have presented here the activity of readily available and air-stable ruthenium mixed-phosphine complexes bearing PTA or PMe₃ ligands in the ATRA of chlorinated esters and carbon tetrachloride to a variety of olefins. The rate of addition of CCl₃CO₂Et was observed to be much faster than that of CH₂ClCO₂Et. The olefinic substrates employed in this study proved to be less reactive than styrene regardless of the catalytic system. Excess phosphine (PPh₃) plays both a promotive and inhibitory role in catalysis, which is not completely understood. The activities of Cp*Ru(PTA)(PPh₃)Cl (**1**) and Cp*Ru(PMe₃)(PPh₃)Cl (**2**) were comparable to that of Cp*Ru(PPh₃)₂Cl (**3**), which is the current standard in Kharasch chemistry.

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Appendix A. Supplementary material

CCDC 830022 and 830023 contain the supplementary crystallographic data for **19** and **20**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.11.008.

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