Dinuclear Ruthenium Ethylene Complexes: Syntheses, Structures, and Catalytic Applications in ATRA and ATRC Reactions

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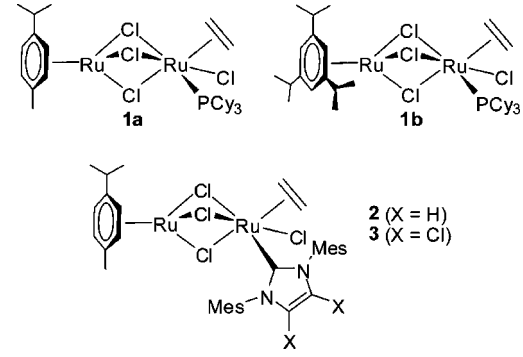
The complexes [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)] (PR_3 = PPh_3, P*n*-Bu_3) were synthesized by reaction of [(*p*-cymene)RuCl(μ-Cl)]$_2$ with the respective phosphine ligand in the presence of ethylene. Structurally related complexes containing the tricyclopentylphosphine ($PCyp_3$) or the isobutylphobane ligand (phobane = 9-phosphabicyclo[3.3.1]nonane) were obtained by reaction of [(arene)RuCl(μ-Cl)]$_2$ (arene = *p*-cymene, 1,3,5-*i*-$Pr_3C_6H_3$) with 2 equiv of [(arene)$RuCl_2$($PCyp_3$)] or [(arene)$RuCl_2$(isobutylphobane)] in the presence of ethylene. The structures of the dinuclear complexes [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PPh_3)] and [(1,3,5-*i*-$Pr_3C_6H_3$)Ru(μ-Cl)$_3$RuCl(C_2H_4)(isobutylphobane)] as well as of the mononuclear precursors [(*p*-cymene)$RuCl_2$(isobutylphobane)], [(1,3,5-*i*-$Pr_3C_6H_3$)$RuCl_2$(isobutylphobane)], and [(*p*-cymene)$RuCl_2$($PCyp_3$)] were determined by single-crystal X-ray analyses. Kinetic analyses of the atom transfer radical addition reaction of CCl_4 to styrene revealed that the catalytic activity of the dinuclear complexes was strongly dependent on the nature of the phosphine ligand but only slightly affected by the nature of the arene ligand. Addition of Mg to the reaction mixture was found to increase the lifetime of the catalyst significantly. With Mg as the cocatalyst, mixed-valence Ru(II)−Ru(III) complexes of the general formula [(arene)Ru(μ-Cl)$_3$$RuCl_2$($PR_3$)] were found to be equally potent catalyst precursors when compared to the Ru(II)−Ru(II) complexes [(arene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)].

Introduction

In 2005, we described the dinuclear ruthenium ethylene complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] (**1a**).[1] It can be obtained by reaction of the commonly used starting material [(*p*-cymene)RuCl(μ-Cl)]$_2$ with PCy_3 in the presence of ethylene. This complex turned out to be an exceptionally active catalyst for atom transfer radical addition (ATRA) reactions[2] with turnover frequencies of up to 1550 h^{-1}.[1] Subsequently, we have shown that the more soluble analogue **1b** can be employed as a catalyst for the controlled atom transfer radical polymerization (ATRP) of methacrylates under very mild conditions.[3] More recently, Delaude and Demonceau have reported that it is possible to prepare the dinuclear complexes **2** and **3** by using N-heterocyclic carbene ligands instead of PCy_3.[4] Interestingly, these complexes showed a very different characteristic in catalytic reactions. Whereas the carbene complexes **2** and **3** catalyzed the ATRP of acrylates with a reduced control compared to the PCy_3 complexes **1**, they were found to be active olefin metathesis catalysts. The PCy_3 complexes **1a** and **1b**, however, are inactive for this type of reaction.

The results described above indicate that an exchange of the PCy_3 ligand for an N-heterocyclic carbene ligand can have a pronounced influence on the catalytic behavior of this type of dinuclear Ru complex. We were thus interested to see how an exchange of the PCy_3 ligand for other phosphine ligands would influence the reactivity. Below, we describe the syntheses and the structures of dinuclear Ru ethylene complexes containing PPh_3, P*n*-Bu_3, $PCyp_3$, or the isobutylphobane ligand. The nature of the phosphine ligand was found to have a strong influence on the catalytic activity in ATRA reactions. Furthermore, we describe a new catalytic procedure, which allows increasing the lifetime of the catalysts substantially. With the new procedure, it was possible to catalyze atom transfer radical cyclization (ATRC) reactions of a diverse set of substrates.



Results and Discussion

Following the synthetic pathway described for complex **1**, we were able to obtain the PPh_3 complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PPh_3)] (**4**) in 86% yield (Scheme 1). The partial pressure of ethylene is a decisive parameter for the success of the reaction: whereas a clean conversion occurred at slightly elevated pressure (3 bar), significant amounts of side products

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(3) Haas, M.; Solari, E.; Nguyen, Q. T.; Gauthier, S.; Scopelliti, R.; Severin, K. *Adv. Synth. Catal.* **2006**, *348*, 439–442.
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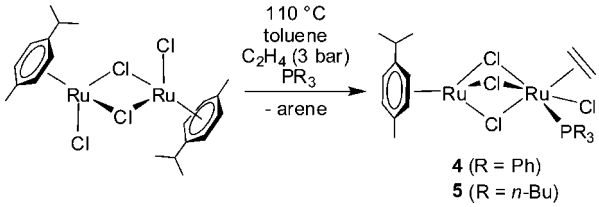
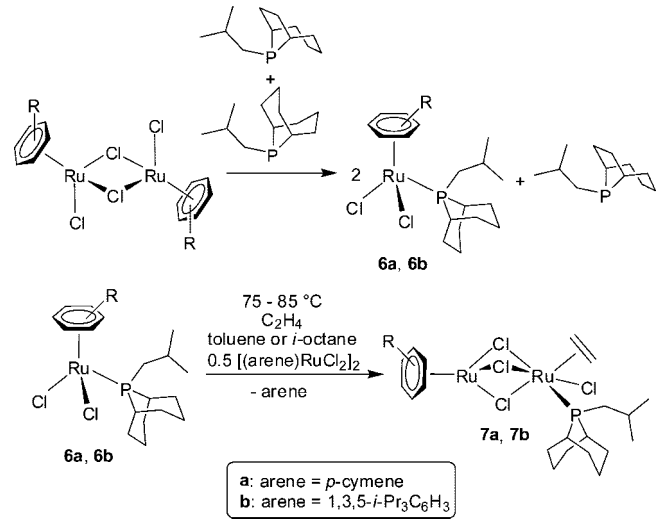
Scheme 1



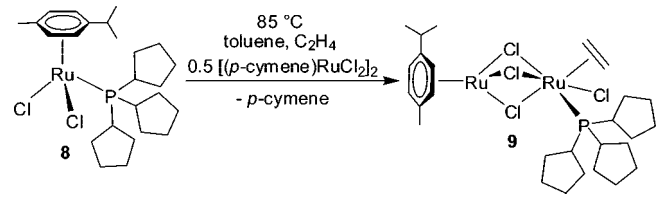
were observed when the reaction was performed under atmospheric pressure. When P*n*-Bu_3 was used instead of PPh_3, two main compounds were formed, even at elevated ethylene pressures. The major compound was the desired product [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(P*n*-Bu_3)] (**5**) (~70% by ^{31}P NMR), but the other compound remained unidentified. It was possible to purify complex **5** by crystallization, but this resulted in a significantly reduced yield (17% yield).

9-Phosphabicyclononane ("phobane")-derived ligands have been known for more than 40 years[5] and have been used industrially in Co-based hydroformylation reactions.[6] Recently, alkylphobane complexes of ruthenium were found to act as robust and active catalysts for olefin metathesis reactions.[7] This has resulted in the commercialization of an isobutylphobane complex by Umicore ("Neolyst M3"). Despite this success, only a few investigations on Ru complexes with phobane ligands have been published.[7,8] Phobane ligands are generally obtained as a mixture of isomers containing 9-phosphabicyclo[3.3.1]-nonane and 9-phosphabicyclo[4.2.1]nonane.[9] This was also true for the isobutylphobane ligand employed for our studies, which contained the [3.3.1] and the [4.2.1] isomer in a ratio of approximately 3:1. For cyclohexylphobane, it had been reported that the [3.3.1] isomer preferentially coordinated to ruthenium carbene complexes, allowing the preparation of isomerically pure compounds.[7b,c] To test whether a similar preference exists for (arene)Ru complexes, we investigated the reaction of [(arene)RuCl(μ-Cl)]$_2$ (arene = *p*-cymene, 1,3,5-*i*-$Pr_3C_6H_3$) with an excess of isobutylphobane (Scheme 2). Indeed, the resulting mononuclear complexes **6a** and **6b** contained exclusively the [3.3.1] isomer. The remaining [4.2.1] isomer was easily removed by washing with hexane.

Scheme 2



Scheme 3



The synthesis of the dinuclear complexes **7a** and **7b** was then accomplished by heating **6a** or **6b** with 0.5 equiv of the respective chloro-bridged dimer [(arene)RuCl(μ-Cl)]$_2$ in the presence of ethylene gas. For the *p*-cymene complex **7a**, a slightly elevated ethylene pressure of 3 bar in combination with toluene as the solvent gave the best results. For the synthesis of the more soluble 1,3,5-*i*-$Pr_3C_6H_3$ complex **7b**, the utilization of isooctane as the solvent turned out to be advantageous, because the product precipitates from the reaction mixture, which facilitates its isolation. Furthermore, this reaction can be performed under lower pressure of ethylene (1.1−1.3 atm measured at 75 °C).

A two-step procedure was also employed to synthesize the tricyclopentylphosphine complex [(*p*-cymene)Ru(μ-Cl)$_3$RuCl-(C_2H_4)($PCyp_3$)] (**9**). First the mononuclear complex **8** was prepared by reaction of [(*p*-cymene)RuCl(μ-Cl)]$_2$ with 2 equiv of $PCyp_3$. Purified **8** was then reacted with [(*p*-cymene)RuCl(μ-Cl)]$_2$ and ethylene (3 bar) in toluene at 80 °C to give complex **9** in 90% yield (Scheme 3).

The complexes **4**−**9** were characterized by NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) and elemental analysis. In addition, the structures of the dinuclear complexes [(*p*-cymene)Ru(μ-Cl)$_3$-RuCl(C_2H_4)(PPh_3)] (**4**) and [(1,3,5-*i*-$Pr_3C_6H_3$)Ru(μ-Cl)$_3$RuCl-(C_2H_4)(isobutylphobane)] (**7b**) as well as of the mononuclear precursors [(*p*-cymene)$RuCl_2$(isobutylphobane)] (**6a**), [(1,3,5-*i*-$Pr_3C_6H_3$)$RuCl_2$(isobutylphobane)] (**6b**), and [(*p*-cymene)-$RuCl_2$($PCyp_3$)] (**8**) were determined by single-crystal X-ray analyses.

The complexes **6a**, **6b**, and **8** show a typical "piano stool" geometry, with two chloro ligands and one phosphine ligand opposite the η^6-bound arene ligands (Figure 1). The bond lengths of the Ru−Cl, Ru−P, and Ru−C bonds are similar to what has been observed for other complexes of the type [(arene)$RuCl_2$(phosphine)] (Table 1).[10]

The dinuclear complexes **4** and **7b** show (arene)$RuCl_2$ fragments, which are connected via three chloro bridges to a

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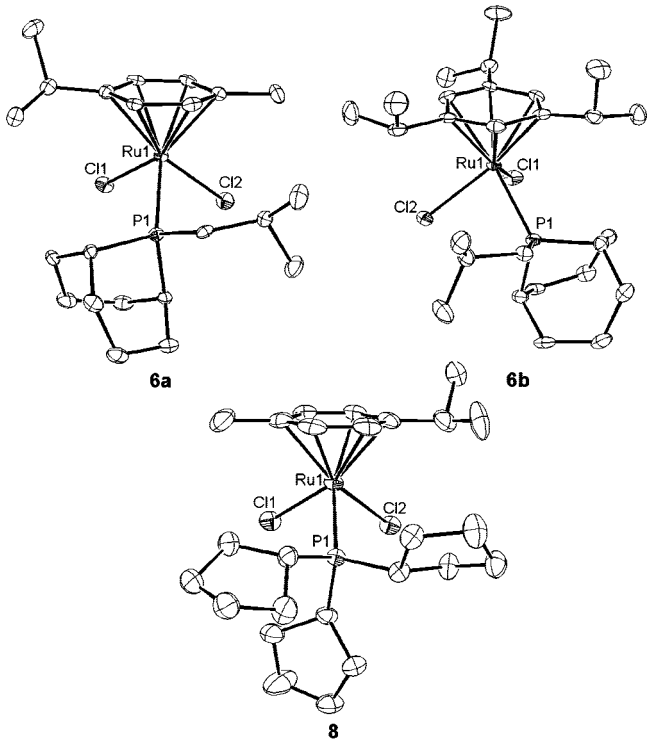


Figure 1. ORTEP representation of the mononuclear complexes **6a**, **6b**, and **8** in the crystal. Thermal ellipsoids are at the 50% probability level. Cocrystallized solvent molecules (1 $CHCl_3$ for **6b**) and hydrogen atoms are not shown for clarity.

Table 1. Selected Distances (Å) and Angles (deg) for the Mononuclear Complexes 6a, 6b and 8

	6a	6b	8
Ru−P	2.3894(7)	2.3895(7)	2.3878(10)
Ru−Cl1	2.4123(7)	2.4273(7)	2.4051(9)
Ru−Cl2	2.4133(7)	2.4078(7)	2.4169(9
Cl1−Ru−Cl2	88.69(3)	87.30(2)	86.81(3)
Cl2−Ru−P	82.45(3)	83.54(2)	89.31(3)
Cl1−Ru−P	94.29(3)	95.21(2)	86.32(3)

$RuCl_2(C_2H_4)PCy_3$ fragment (Figure 2).[11] The Ru−Cl bond distances observed for the terminal chloro ligands (**4**, 2.3830(7) Å; **7b**, 2.3633(12) Å) are shorter than the Ru−Cl bond lengths found for the bridging chloro ligands (2.42−2.57 Å).

For complex **7b**, the crystallographic data showed that 30% of the ethylene binding sites are occupied by a chloro ligand. The chlorinated solvent used for the crystallization process (CH_2Cl_2) is likely responsible for this partial oxidation. At 1.315(2) Å, the carbon−carbon bond of the ethylene ligand of complex **4** is surprisingly short. Typical C−C bond distances of Ru(η^2-C_2H_4) complexes are around 1.41−1.43 Å.[12] It

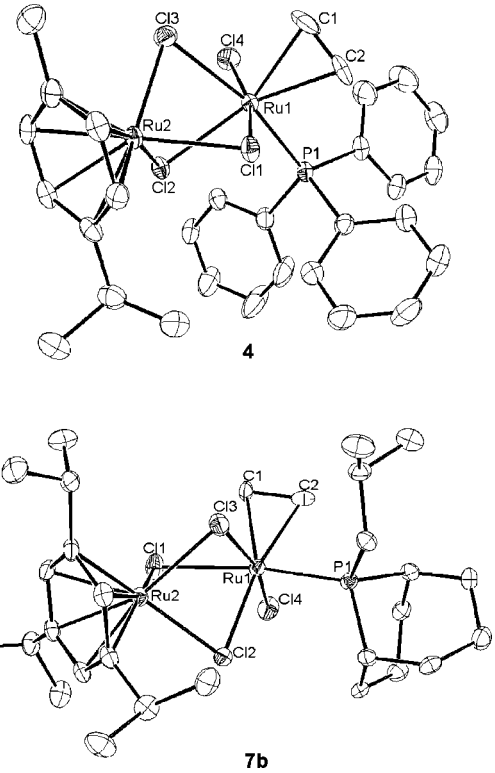
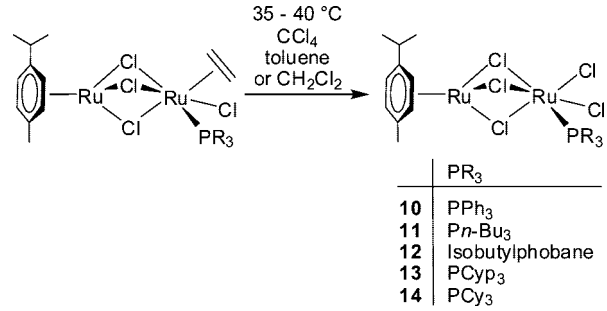


Figure 2. ORTEP drawing of the dinuclear Ru(II)−Ru(II) complexes **4** and **7b** in the crystal. Thermal ellipsoids are at the 50% probability level. Cocrystallized solvent molecules (1 CH_2Cl_2 for **7b**) and hydrogen atoms are omitted for clarity.

Scheme 4



	PR_3
10	PPh_3
11	P*n*-Bu_3
12	Isobutylphobane
13	$PCyp_3$
14	PCy_3

therefore appears likely that the crystals of complex **4** also contain minor amounts (<5%) of a complex in which the ethylene ligand is replaced by a chloro ligand. Such a disorder would lead to a virtual shortening of the ethylene C−C bond. Due to the low amount of this putative side product, it was not possible to resolve this disorder crystallographically.

The fact that crystals of complex **7b** contained ~30% of the Ru(II)−Ru(III) complex [(1,3,5-*i*-$Pr_3C_6H_3$)Ru(μ-Cl)$_3$$RuCl_2$(isobutylphobane)] was evidence that the Ru(C_2H_4) complex can easily be oxidized to a Ru−Cl complex. This assumption is corroborated by our previous observation that CCl_4 is able to oxidize the PCy_3 complex **1a** to give [(*p*-cymene)Ru(μ-Cl)$_3$$RuCl_2(PCy_3)$] (**14**).[1] Since processes of this kind are believed to be involved in catalytic atom transfer radical reactions (see below), we were interested whether we could access Ru(II)−Ru(III) complexes with different phosphine ligands on a preparative scale. Indeed, gentle heating of the ethylene complexes with an excess of CCl_4 gave the new complexes **10**−**13** in good yields (Scheme 4).

The very broad signals of the ^{1}H NMR spectra of **10**−**13** were indicative that the complexes are, as expected, paramag-

(11) For some recent reports about complexes in which two different metal fragments are connected by three halogeno-bridged complexes see: (a) Quebatte, L.; Scopelliti, R.; Severin, K. *Eur. J. Inorg. Chem.* **2006**, 231–236. (b) Gauthier, S.; Scopelliti, R.; Severin, K. *Organometallics* **2004**, *23*, 3769. (c) Gauthier, S.; Quebatte, L.; Scopelliti, R.; Severin, K. *Chem.−Eur. J.* **2004**, *10*, 2811. (d) Gauthier, S.; Quebatte, L.; Scopelliti, R.; Severin, K. *Inorg. Chem. Commun.* **2004**, *7*, 708. (e) Severin, K. *Chem.−Eur. J.* **2002**, *8*, 1514, and references therein.

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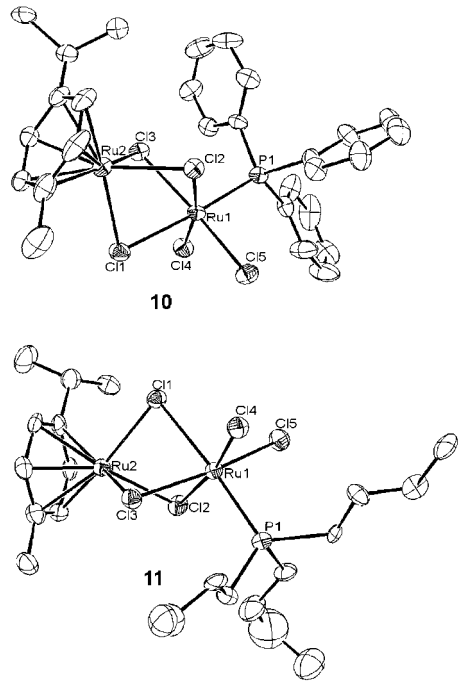
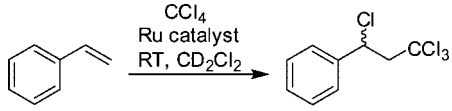


Figure 3. ORTEP representation of the dinuclear Ru(II)−Ru(III) complexes **10** and **11** in the crystal. Thermal ellipsoids are at the 50% probability level. Cocrystallized solvent molecules (1 $CHCl_3$ for **10**) and hydrogen atoms are not shown for clarity.

Scheme 5



netic. The solid state structures of **10** and **11** were determined by single-crystal X-ray crystallography (Figure 3). Overall, the triply chloro-bridged structures are similar to that of the ethylene complexes. The Ru−Cl bond lengths of the bridging chloro ligands (2.40−2.56 Å) are, again, larger than the Ru−Cl bond distance found for the terminal chloro ligand (2.30−2.31 Å).

After having established synthetic protocols for dinuclear Ru complexes with different phosphine ligands, we investigated the ability of these complexes to catalyze atom transfer radical reactions. As a benchmark reaction, we used the addition of CCl_4 to styrene (Scheme 5). Due to the high intrinsic reactivity of CCl_4, this is a relatively easy ATRA reaction, which is often employed as a first test to evaluate the catalytic behavior of novel Ru complexes.[2,13] The reactions were performed at room temperature with a styrene to catalyst ratio of 1000:1. One should note that these are rather demanding conditions, since Ru catalysts are typically tested at 60 °C with a substrate to catalyst ratio of 300:1.[2] All reactions were performed in "wet" CD_2Cl_2 because we had previously observed that traces of water are often beneficial for Ru-catalyzed ATRA reactions.[1,13f,14]

As shown in Figure 4, the complexes **1a**, **4**, **5**, **7a**, **7b**, and **9** display very different rate profiles. With regard to the initial catalytic activity, one can distinguish three groups: the highly active PCy_3 and $PCyp_3$ complexes **1a** and **9**, the moderately active phobane and PPh_3 complexes **7a**, **7b**, and **4**, and the low-activity P*n*-Bu_3 complex **5**. With regard to the final yield, however, the picture is quite different: the yields for the highly active PCy_3 and $PCyp_3$ complexes **1a** and **9** start to level off at around 100 min, whereas the PPh_3 complex **4** displays a sigmoidal rate profile and gives rise to a yield of 97% after 420

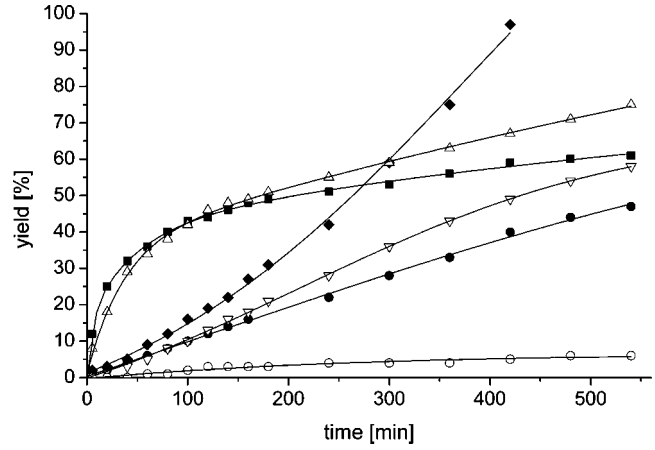
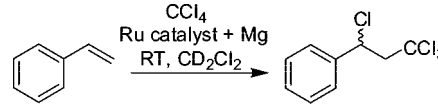


Figure 4. Time course of ATRA reactions between CCl_4 and styrene catalyzed by complex **1a** (■), **4** (♦), **5** (○), **7a** (●), **7b** (▽), or **9** (△). The yields were determined by ^1H NMR spectroscopy using the internal standard 1,4-bis(trifluormethyl)benzene. Conditions: CD_2Cl_2, RT, [catalyst] = 1.38 mM, [styrene] = 1.38 M, [CCl_4] = 5.52 M, [internal standard] = 270 mM.

Scheme 6



min. This points to a deactivation mechanism for the highly active catalysts **1a** and **9** and to an activation mechanism for the PPh_3 complex **4**. It appears likely that a loss of the ethylene ligand is required to activate the dinuclear complexes. The sigmoidal rate profile for reactions with catalyst **4** might be due to a slow displacement of ethylene. In fact, solutions of the PPh_3 complex **4** were found to be stable over a prolonged period of time, whereas the PCy_3 complex **1a** is prone to lose ethylene (^{13}C NMR spectra of **1a** should be recorded under an atmosphere of ethylene).[1] This difference can be explained by the different size and electron-donating properties of the respective phosphine ligand.

The homocoupling of two carbon-based radicals is a possible side reaction during ATRA. This kind of termination reaction leads to an accumulation of Ru(III) complexes and consequently to decreased rates. We have recently demonstrated that the addition of 5 mol % AIBN as an external radical source can dramatically increase the turnover numbers (TON), which can be achieved in ATRA reactions catalyzed by [Cp*RuCl-$(PPh_3)_2$].[15] The role of AIBN is to regenerate the Ru(II) catalysts by reduction of the Ru(III) complex. This technique has

(13) For some selected recent examples see: (a) Lundgren, R. J.; Rankin, M. A.; McDonald, R.; Stradiotto, M. *Organometallics* **2008**, *27*, 254–258. (b) Borguet, Y.; Richel, A.; Delfosse, S.; Leclerc, A.; Delaude, L.; Demonceau, A. *Tetrahedron Lett.* **2007**, *48*, 6334–6338. (c) Richel, A.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2006**, *47*, 2077–2081. (d) Quebatte, L.; Scopelliti, R.; Severin, K. *Eur. J. Inorg. Chem.* **2005**, 3353–3358. (e) Quebatte, L.; Haas, M.; Solari, E.; Scopelliti, R.; Nguyen, Q. T.; Severin, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1084–1088. (f) Quebatte, L.; Scopelliti, R.; Severin, K. *Angew. Chem., Int. Ed.* **2004**, *43*, 1520–1524. (g) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2003**, *44*, 8421–8425. (h) De Clercq, B.; Verpoort, F. *J. Organomet. Chem.* **2003**, *672*, 11–16. (i) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, 11830–11831. (j) De Clercq, B.; Verpoort, F. *Tetrahedron Lett.* **2002**, *43*, 4687–4690. (k) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Eur. J. Org. Chem.* **2001**, 2689–2695. (l) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2000**, *41*, 6071–6074.

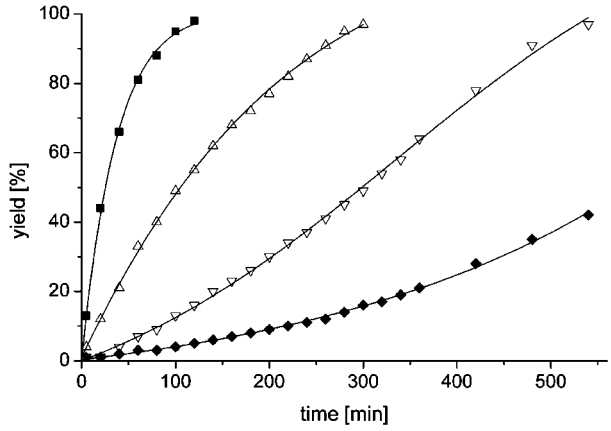


Figure 5. Time course of ATRA reactions between CCl_4 and styrene catalyzed by complex **1a** (■), **4** (♦),**7b** (▽), or **9** (△). The yields were determined by ^{1}H NMR spectroscopy using the internal standard 1,4-bis(trifluormethyl)benzene. Conditions: CD_2Cl_2, RT, [catalyst] = 1.38 mM, [styrene] = 1.38 M, [CCl_4] = 5.52 M, [internal standard] = 270 mM, cocatalyst: 100 mg of activated Mg for a reaction volume of 1000 μL.

subsequently been employed with good success in other Ru-[13a] and Cu-catalyzed[16] ATRA reactions.[17] A drawback of AIBN-cocatalyzed reactions is that AIBN might also act as a radical initiator for polymerizations. Furthermore, AIBN and its decomposition products have to be separated from the ATRA adduct and the reactions cannot be performed at ambient temperature. These limitations can be overcome by using Mg instead of AIBN as the cocatalyst.[14] Mg is easy to separate by filtration, and reductions take place at RT. We have therefore performed a second set of experiments using the complexes **1a**, **4**, **7b**, and **9** in combination with an excess of activated Mg powder as the catalysts. As a test reaction, we have again employed the addition of CCl_4 to styrene (Scheme 6). The time courses of the reactions are depicted in Figure 5.

The addition of Mg powder was found to have a pronounced effect on the catalytic performance. Within 9 h, nearly quantitative yields were observed for reactions catalyzed by **1a**, **7b**, and **9**. Reactions catalyzed by the PPh_3 complex **4**, however, were slower in the presence of Mg. The fastest reactions were observed for the PCy_3 complex **1a**, containing the sterically most demanding phosphine ligand in the series. With this complex, a TON of 980 was obtained after only 2 h.

A potential additional advantage of performing ATRA reactions in the presence of a reducing agent is the possibility to use a metal complex in its oxidized form as the catalyst precursor. This can be beneficial from a practical point of view, because the oxidized complexes are generally less sensitive. We have therefore compared the activity of the Ru(II)−Ru(II) complexes **9** (PCy_3) and **1a** ($PCyp_3$) with that of the corresponding Ru(II)−Ru(III) complexes **13** and **14**. To detect differences in activity, we have used a catalyst to styrene ratio of 1:2000 and a short reaction time of 3 h. The results show that there are only minor differences in catalytic activity (Table 3, entries 1−4). For further studies, we have therefore focused on the more easy to handle Ru(II)−Ru(III) complexes **13** and **14**.

Table 2. Selected Distances (Å) and Angles (deg) for the Dinuclear Complexes 4 and 7b

	4	7b
Ru1−P1	2.2799(7)	2.3061(12)
Ru1−Cl4	2.3830(7)	2.3633(12)
Ru1−C1	2.167(3)	2.173(7)
Ru1−C2	2.203(3)	2.196(12)
C1−C2	1.315(5)	1.412(13)
P1−Ru1−Cl2	91.39(2)	90.85(4)
Cl1−Ru1−Cl4	90.40(2)	86.92(4)
C1−Ru1−P1	109.06(10)	114.4(2)

Table 3. ATRA Reactions Catalyzed by Dinuclear Ru Complexes in the Presence of Mg[a]

entry	olefin	R−Cl	cat.	[cat.]:[olefin]	*t* (h)	conv (%)	yield (%)
1	styrene	CCl_4	**1a**	1:2000	3	77	76
2	styrene	CCl_4	**14**	1:2000	3	65	61
3	styrene	CCl_4	**9**	1:2000	3	39	36
4	styrene	CCl_4	**13**	1:2000	3	53	52
5	*p*-chlorostyrene	CCl_4	**14**	1:1000	5	100	99
6	*p*-chlorostyrene	CCl_4	**13**	1:1000	5	79	76
7	methyl methacrylate	CCl_4	**14**	1:500	24	100	80
8	methyl methacrylate	CCl_4	**13**	1:500	24	100	71
9	1-decene	CCl_4	**14**	1:1000	24	93	78
10	1-decene	CCl_4	**13**	1:1000	24	95	90
11	styrene	$CHCl_3$	**14**	1:300	24	21	10
12	styrene	$CHCl_3$	**13**	1:300	24	81	74
13	styrene	CCl_3CO_2Et	**14**	1:500	24	100	81
14	styrene	CCl_3CO_2Et	**13**	1:500	24	100	78
15	methyl methacrylate	CCl_3CO_2Et	**14**	1:500	24	67	40
16	methyl methacrylate	CCl_3CO_2Et	**13**	1:500	24	70	39

[a] The reactions were performed at room temperature in the presence of activated Mg powder (100 mg) with D_2O-saturated CD_2Cl_2 as the solvent (total volume: 1000 μL, [olefin] = 1.38 M, [CCl_4]:[olefin] = 4:1, $CHCl_3$ as the solvent for the addition of $CHCl_3$, [CCl_3CO_2Et]:[olefin] = 3:1). The conversion is based on the consumption of the olefin and the yield is based on the formation of the product as determined by ^{1}H NMR spectroscopy using the internal standard 1,4-bis(trifluoromethyl)benzene (270 mM).

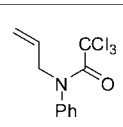
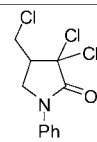
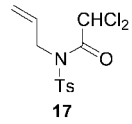
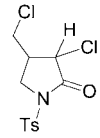
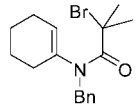
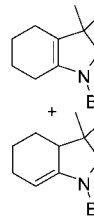
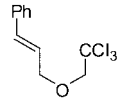
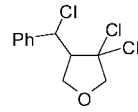
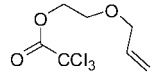
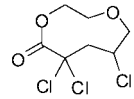
With the Ru(II)−Ru(III) precatalysts **13** and **14**, we investigated a number of other ATRA reactions. Similar to styrene, the CCl_4 adduct of *p*-chlorostyrene was cleanly formed using 0.1 mol % of complex **14** (entry 5). Again, lower yields were observed with the $PCyp_3$ complex **13** (entry 6). The CCl_4 adducts of methyl methacrylate and 1-decene were formed in good yields using 0.1 or 0.2 mol % of the catalysts **13** and **14**, respectively (entries 7−10). For the addition of 1-decene, the $PCyp_3$ complex **13** gave interestingly less side products than the PCy_3 complex **14** (entry 9 vs entry 10).

Chloroform addition reactions with complex **14** proceeded very sluggishly (entry 11). Significantly improved yields were obtained with complex **13** (74% after 24 h; entry 12). These last results clearly indicate that the best catalyst depends on the substrates that are used.

ATRA reactions with α-chlorinated esters are of interest because the products can be cyclized to give lactones.[18,19] We found that good yields can be obtained for the addition of CCl_3CO_2Et to styrene using 0.2 mol % of either **13** or **14** (entries 13 and 14). However, only moderate yields were obtained under similar conditions for CCl_3CO_2Et additions to methyl methacrylate (entries 15 and 16).

(14) Thommes, K.; Içli, B.; Scopelliti, R.; Severin, K. *Chem.−Eur. J.* **2007**, *13*, 6899–6907.
(15) Quebatte, L.; Thommes, K.; Severin, K. *J. Am. Chem. Soc.* **2006**, *128*, 7440–7441.
(16) (a) Eckenhoff, W. T.; Garrity, S. T.; Pintauer, T. *Eur. J. Inorg. Chem.* **2008**, 563–571. (b) Eckenhoff, W. T.; Garrity, S. T.; Pintauer, T. *Inorg. Chem.* **2007**, *46*, 5844–5846.
(17) The addition of AIBN can also be beneficial for Cu-catalyzed atom transfer radical polymerization reactions. See: Braunecker, W. A.; Matyjaszewski, K. *J. Mol. Catal. A* **2006**, *254*, 155–164.
(18) Lee, B. T.; Schrader, T. O.; Martín-Matute, B.; Kauffman, C. R.; Zhang, P.; Snapper, M. L. *Tetrahedron* **2004**, *60*, 7391–7396.
(19) Somech, I.; Shvo, Y. *J. Organomet. Chem.* **2000**, *601*, 153–159.

Table 4. ATRC Reactions Catalyzed by Dinuclear Ru Complexes in the Presence of Mg[a]

Entry	Substrate	Product	Cat.	[Cat.] [mol%]	*t* [h]	*T* [°C]	Conv. [%]	Yield [%]
1	 **15**	 **16**	**1a**	5	5	22	72	61
2	**15**	**16**	**14**	5	5	22	70	61
3	**15**	**16**	**9**	5	5	22	70	58
4	**15**	**16**	**13**	5	5	22	71	60
5[b]	 **17**	 **18** (85:15)	**14**	5	5	22	100	94
6[c]	 **19**	 **20a** + **20b** (1:4)	**14**	1	5	22	100	88
7	 **21**	 **22** (82:18)	**14**	10	24	22	98	92
8[d]	 **23**	 **24**	**14**	10	24	80	18	15

[a] The reactions were performed in CD_2Cl_2 (total volume = 1000 μL, [substrate] = 0.14 M). The conversion is based on the consumption of the olefin and the yield is based on the formation of the product as determined by ^{1}H NMR spectroscopy using 1,4-bis(trifluoromethyl)benzene (50 mM) as the internal standard. [b] Mesitylene was used as the internal standard. [c] One equivalent of NEt_3 with respect to the substrate was added to the reaction mixture. [d] The reaction was performed in d_8-toluene.

Overall, the results summarized in Table 3 show that the combination of the dinuclear Ru(II)−Ru(III) complex **13** or **14** with Mg powder catalyzes ATRA reactions with good efficiency. Remarkably fast conversions and good TONs are observed at room temperature, whereas most Ru-based catalysts described so far require elevated temperatures.[2] Among the few catalysts that can rival the activity of **13** or **14** is our recently developed [Cp*$RuCl_2(PPh_3)$] + Mg catalyst system. ATRA reactions with CCl_3CO_2Et, for example, can be performed with 0.1 mol % of [Cp*$RuCl_2(PPh_3)$] (instead of 0.2 mol % for **13** or **14**).

Atom transfer radical cyclization (ATRC) reactions are intramolecular versions of ATRA reactions, which have been widely used in organic synthesis.[20,21] Ruthenium and copper complexes are frequently used as catalysts for this type of reaction. Cyclizations of *N*-allyl-*N*-alkyltrichloroacetamides have been studied in the groups of Itoh and Nagashima, among others.[20−22] These ATRC reactions can be performed with 5 mol % of [$RuCl_2(PPh_3)_3$] or 30 mol % of CuCl/bipy at elevated temperatures to give the corresponding 5-*exo* atom transfer products in good yield. So far, there are only a few Ru complexes that can catalyze this reaction at room temperature.[14,23,24] To test whether our dinuclear complexes are suitable catalysts for ATRC reactions, we have investigated the cyclization of *N*-allyl-*N*-phenyltrichloroacetamide (**15**). In a first set of experiments, we have again compared the catalytic activity of the Ru(II)−Ru(II) complexes **1a** (PCy_3) and **9** ($PCyp_3$) with that of the corresponding Ru(II)−Ru(III) complexes **13** and **14**

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(21) For selected recent examples see: (a) Bull, J. A.; Hutchings, M. G.; Quayle, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1869–1872. (b) Stevens, C. V.; Van Meenen, E.; Masschelein, K. G. R.; Eeckhout, Y.; Hooghe, W.; D'hondt, B.; Nemykin, V. N.; Zhdankin, V. V. *Tetrahedron Lett.* **2007**, *48*, 7108–7111. (c) Bellesia, F.; Danieli, C.; De Buyck, L.; Galeazi, R.; Ghelfi, F.; Mucci, A.; Orena, M.; Pagnoni, U. M.; Parsons, A. F.; Roncaglia, F. *Tetrahedron* **2006**, *62*, 746–757. (d) De Buyck, L.; Forzato, C.; Ghelfi, F.; Mucci, A.; Nitti, P.; Pagnoni, U. M.; Parsone, A. F.; Pitocco, G.; Roncaglia, F. *Tetrahedron Lett.* **2006**, *47*, 7759–7762. (e) Edlin, C. D.; Faulkner, J.; Helliwell, M.; Knight, C. K.; Parker, J.; Quayle, P.; Raftery, J. *Tetrahedron* **2006**, *62*, 3004–3015. (f) Seigal, B. A.; Fajardo, C.; Snapper, M. L. *J. Am. Chem. Soc.* **2005**, *127*, 16329–16332. (g) Schmidt, B.; Pohler, M. *J. Organomet. Chem.* **2005**, *690*, 5552–5555.

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Table 5. Crystallographic Data for the Complexes 6a, 6b, and 8

	6a	6b	8
empirical formula	$C_{27}H_{47}Cl_2PRu$	$C_{22}H_{37}Cl_2PRu \cdot CHCl_3$	$C_{25}H_{41}Cl_2PRu$
mol wt/g mol^{-1}	574.69	623.82	544.52
cryst size/mm^3	0.43 × 0.33 × 0.29	0.31 × 0.27 × 0.25	0.37 × 0.27 × 0.20
cryst syst	orthorhombic	monoclinic	monoclinic
space group	*Pbca*	$P2_1/c$	$P2_1/n$
a/Å	16.7222(3)	12.7570(3)	10.2138(4)
b/Å	14.4243(4)	15.4559(3)	18.8352(6)
c/Å	22.8272(4)	13.4577(3)	13.6626(5)
α/deg	90	90	90
β/deg	90	92.309(2)	111.811(4)
γ/deg	90	90	90
volume/Å^3	5506.1(2)	2651.31(10)	2440.25(15)
Z	8	4	4
density/g cm^{-3}	1.386	1.563	1.482
temperature/K	140(2)	140(2)	140(2)
absorp coeff/mm^{-1}	0.835	1.166	0.937
θ range/deg	2.95 to 25.03	3.03 to 26.37	2.69 to 26.37
index ranges	−19 → 19, −15 → 15, −27 → 27	−15 → 14, −19 → 19, −16 → 16	−12 → 12, −22 → 23, −17 → 16
no. of reflns collected	31 270	17 520	18 928
no. of indep reflns	4556 [*R*(int) = 0.0421]	5413 [*R*(int) = 0.0406]	4963 [*R*(int) = 0.0538]
absorp corrr	semiempirical from equivalents	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmn	1.00000 and 0.67202	1.00000 and 0.91962	1.00000 and 0.90820
no. of data/restraints/params	4556/0/280	5413/0/271	4963/0/281
goodness-of-fit on F^2	1.057	1.036	1.053
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0274$, $wR_2 = 0.0625$	$R_1 = 0.0306$, $wR_2 = 0.0548$	$R_1 = 0.0393$, $wR_2 = 0.0706$
R indices (all data)	$R_1 = 0.0412$, $wR_2 = 0.0717$	$R_1 = 0.0540$, $wR_2 = 0.0615$	$R_1 = 0.0676$, $wR_2 = 0.0801$
larg diff peak and hole/e Å^{-3}	0.658 and −0.706	0.487 and −0.452	0.559 and −0.381

(Table 4, entries 1−4) in the presence of Mg powder as the cocatalyst. Using 5 mol % of the respective Ru catalyst at room temperature, the cyclization products were obtained in around 60% yield after 5 h. As it was observed for ATRA reactions, there were only minor differences between the Ru(II)−Ru(II) complexes **1a** and **9** and the mixed-valence Ru(II)−Ru(III) complexes **13** and **14**. The nature of the phosphine ligand (PCy_3 vs $PCyp_3$) had likewise a small influence on the final yield. For all further studies, we therefore decided to focus on complex **14** as the catalyst.

Next, we investigated the cyclization of *N*-allyl-*N*-tosyldichloroacetamide (**17**) to give the corresponding *γ*-lactam **18**. Despite the fact that the dichloroacetamide **17** is not a particularly active ATRC substrate,[25] we were able to obtain the product **18** in very good yield after 5 h at room temperature using 5 mol % of complex **14** (entry 5).

The ATRC of α-bromo enamides has been studied by Clarke et al.[26] They found that the cyclization of **19** can be carried out in good yield using CuBr (30 mol %) along with the activating ligand tris(*N*,*N*-2-dimethylamino)ethylamine (30 mol %). It was suggested that **19** undergoes a 5-*endo* cyclization to give a mixture of the *γ*-lactams **20a** and **20b** through a radical-polar crossover mechanism with elimination of HBr.[26c] Using the Ru catalyst **14**, it is possible to perform the reaction at room temperature with a catalyst concentration of only 1 mol % (entry 6).

ATRC reactions of 2,2,2-trichloroethyl ethers such as **21** are of interest because the reaction products can be converted into substituted chlorofurans. This was demonstrated by Ram et al., who have shown that the cyclization of **21** can be achieved using CuCl/bipy (30 mol %) as the catalyst at 80 °C.[27] When complex **14** (10 mol %) was used for the ATRC reaction of **21**, a yield of 92% was obtained at room temperature after 20 h (Table 4, entry 7). Due to the mild reaction conditions, a good diastereoselectivity of 82:18 was achieved.

The synthesis of medium-sized lactones via ATRC of di- or trichloroacetates is challenging due to competing telomerization reactions. So far, mainly Cu-based catalysts have been employed and mostly in high concentrations.[28] For the macrocyclization of the trichloroacetate **23**, however, Cu catalysts were found to give poor yields, and better results were obtained with a Fe(II) complex.[28a] Attempts to cyclize **23** with the dinuclear catalyst **14** gave unfortunately only very low yields of the macrocyclic product **24** (entry 8).

The results described above show that the dinuclear complex **14** is a potent catalyst for ATRC reactions of five- or six-membered-ring systems. In terms of catalytic activity, the **14**/Mg system compares favorably with most Cu- and Ru-based catalysts. As observed for the ATRA reactions, however, it is inferior compared to the best Ru-based system known so far, which is comprised of the half-sandwich complex [Cp*$RuCl_2$(PPh_3)] in combination with Mg.[14] With the latter, for example, the cyclization of the ether **21** can be accomplished with 0.5 mol % [Cp*$RuCl_2(PPh_3)$], whereas 10 mol % are needed for the present catalyst **14**.

In view of the observations of Delaude and Demonceau that the N-heterocyclic carbene complexes **2** and **3** can promote

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Table 6. Crystallographic Data for the Complexes 4 and 7b

	4	7b
empirical formula	$C_{30}H_{33}Cl_4PRu_2 \cdot 1/3CH_2Cl_2$	$C_{27}H_{47}Cl_4PRu_2 \cdot 0.7(C_2H_4) \cdot 0.3Cl \cdot CH_2Cl_2$
mol weight/g mol^{-1}	796.80	861.75
cryst size/mm^3	0.38 × 0.34 × 0.20	0.40 × 0.35 × 0.22
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a/Å	9.5465(2)	17.4584(5)
b/Å	19.3372(3)	18.8627(5)
c/Å	17.5203(3)	10.8896(3)
α/deg	90	90
β/deg	104.265(2)	102.752(3)
γ/deg	90	90
volume/Å^3	3134.57(10)	3497.62(17)
Z	4	4
density/g cm^{-3}	1.688	1.637
temperature/K	140(2)	140(2)
absorp coeff/mm^{-1}	1.432	1.410
θ range/deg	2.62 to 26.37	2.62 to 26.37
index ranges	−11 → 11, −23 → 23, −21 → 21	−21 γ→ 21, −23 → 23, −13 → 10
no. of reflns collected	27464	27639
no. of indep reflns	6343 [R(int) = 0.0291]	7100 [R(int) = 0.0635]
absorp corrr	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmn	1.00000 and 0.85930	1.00000 and 0.85147
no. of data/restraints/params	6343/0/361	7100/ 0/361
goodness-of-fit on F^2	1.048	1.041
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0248$, $wR_2 = 0.0494$	$R_1 = 0.0441$, $wR_2 = 0.0662$
R indices (all data)	$R_1 = 0.0397$, $wR_2 = 0.0563$	$R_1 = 0.0805$, $wR_2 = 0.0768$
larg diff peak and hole/e Å^{-3}	0.480 and •0.466	0.995 and −0.595

olefin metathesis reactions, we have tested the catalytic behavior of the PPh_3 complex **4** and the isobutylphobane complex **7** using styrene as the substrate (0.2 mol % catalyst, 85 °C, toluene). After 2 h, only traces of the metathesis product are obtained. This is in line with the lack of activity reported for the PCy_3 complex **1a**.[4] These results suggest that the presence of N-heterocyclic carbene ligands is a decisive feature for metathesis activity of dinuclear ethylene complexes.

Conclusion

We have described synthetic procedures that allow the preparation of dinuclear complexes of the general formula [(arene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)]. These complexes are potent catalysts for ATRA and ATRC reactions. The catalytic activity was found to be strongly dependent on the nature of the phosphine ligand, but it was only slightly affected by the nature of the arene ligand. By addition of Mg powder to the reaction mixture it was possible to increase the lifetime of the catalyst significantly. With Mg as the cocatalyst, mixed-valence Ru(II)−Ru(III) complexes of the general formula [(arene)Ru(μ-Cl)$_3$RuCl$_2$(PR_3)] were found to be equally potent catalyst precursors when compared to the Ru(II)−Ru(II) complexes [(arene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)]. The fact that the ethylene complexes [(arene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)] are easily converted to the chloro complexes [(arene)Ru(μ-Cl)$_3$RuCl$_2$(PR_3)] by addition of CCl_4 suggests that the radical reactions proceed via an initial loss of ethylene. In reactions with Ru(II)−Ru(III) precatalysts, Mg acts as a reducing agent to generate the same active Ru(II)−Ru(II) species, which then can abstract a halogen atom from the substrate to initiate the reaction. This hypothesis is in line with the generally accepted mechanism for Ru-catalyzed atom transfer radical reactions, which assumes a Ru(II)/Ru(III) redox couple as the key catalytic components.[2] Apart from applications in ATRA and ATRC reactions, it will be interesting to study the reactivity of the dinuclear complexes [(arene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)] toward other substrates. In a recent communication, for example, we have reported that the addition of acetylene to the PCy_3 complex **1a** results in an unusual cleavage of the C≡C triple bond to give a Ru═C═Ru μ-carbide complex.[29] Reactions of [(arene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PR_3)] with other unsaturated small molecules are currently being investigated in our laboratory.

Experimental Section

General Comments. The Ru complexes were prepared under an atmosphere of dry argon using standard Schlenk glassware and vacuum line techniques. The solvents were either dried using a solvent purification system from Innovative Technologies, Inc., or distilled from appropriate drying agents. The ATRA and ATRC reactions were performed inside a glovebox under an atmosphere of dry dinitrogen. NMR data were recorded on a Bruker DPX400 instrument operating at 400 MHz (^{1}H), 101 MHz (^{13}C{^{1}H}), or 162 MHz (^{31}P{^{1}H}). The spectra were referenced internally using the signals from the residual protonated solvents (^{1}H) and the solvent signals (^{13}C), or externally using 85% H_3PO_4 (^{31}P). All spectra were recorded at room temperature. The complexes [(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCy_3)] (**1a**)[1] and [(*p*-cymene)Ru(μ-Cl)$_3$RuCl$_2$(PCy_3)] (**14**), the substrates *N*-allyl-2,2,2-trichloro-*N*-phenylacetamide (**15**),[22g] *N*-allyl-2,2-dichloro-*N*-phenylacetamide (**17**),[22g] *N*-benzyl-2-methyl-2-bromo-*N*-cyclohexyl-1-enylpropionamide (**19**),[26b] [(2,2,2-trichloroethoxy)prop-1-enyl]benzene (**21**),[27] and 2-(allyloxy)ethyl-2,2,2-trichloroacetate (**23**),[28] and ligand $PCyp_3$[30] were prepared according to literature procedures. $RuCl_3(H_2O)_n$ was obtained from Precious Metals Online. Mg powder (>99%) was purchased from Fuka. It was agitated by a stirring bar under an atmosphere of dry dinitrogen for 10 days before use. Isobutylphobane (80% pure by ^{31}P NMR) was used as a mixture of (3,3,1) and (4,2,1) isomers in a 3:1 ratio.

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PPh_3)] (4). In an autoclave, PPh_3 (262 mg, 1.00 mmol) was mixed with [(*p*-cymene)RuCl(μ-Cl)]$_2$ (612 mg, 1.00 mmol) in toluene (60 mL). The autoclave was then pressurized with ethylene (3 bar), and the mixture was heated

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Table 7. Crystallographic Data for the Complexes 10 and 11

	10	11
empirical formula	$C_{28}H_{30}Cl_5PRu_2.CHCl_3$	$C_{22}H_{41}Cl_5PRu_2$
mol weight/g mol^{-1}	895.24	715.91
cryst size/mm^3	0.40 × 0.35 × 0.20	0.23 × 0.18 × 0.14
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	$Pbcn$
a/Å	19.7274(12)	18.0407(7)
b/Å	9.6194(4)	13.7759(5)
c/Å	20.4425(13)	22.9357(8)
α/deg	90	90
β/deg	118.446(8)	90
γ/deg	90	90
volume/Å^3	3410.9(3)	5700.1(4)
Z	4	8
density/g cm^{-3}	1.743	1.668
temperature/K	140(2)	140(2)
absorption coeff/mm^{-1}	1.579	1.594
θ range/deg	2.90 to 26.37	2.57 to 26.37
index ranges	−24 → 24, −11 → 11, −25 → 25	−22 → 22, −14 → 17, −28 → 28
no. of reflns collected	24 315	50 988
no. of indep reflns	6924 [R(int) = 0.0785]	5822 [R(int) = 0.1597]
absorp corrr	semiempirical from equivalents	semiempirical from equivalents
max. and min. transmn	1.00000 and 0.52748	1.00000 and 0.40832
no. of data/restraints/params	6924/0/361	5822/ 144/379
goodness-of-fit on F^2	1.032	1.182
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0602$, $wR_2 = 0.1282$	$R_1 = 0.0738$, $wR_2 = 0.1272$
R indices (all data)	$R_1 = 0.1032$, $wR_2 = 0.1516$	$R_1 = 0.1179$, $wR_2 = 0.1439$
larg diff peak and hole/e Å^{-3}	1.780 and −1.061	1.043 and −0.732

to 110 °C under stirring for 48 h. After cooling to 60 °C, the solution was transferred to a Schlenk flask. Small amounts of decomposed material were removed by filtration through Celite. The solvent was removed under vacuum, and the residue was washed with diethyl ether (2 × 75 mL) and dried under vacuum. An orange-red solid was obtained (660 mg, 86%). Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a solution of **4** in dichloromethane at −20 °C. $C_{30}H_{33}Cl_4Ru_2P$ (768.52). Anal. Calcd for $C_{30}H_{33}Cl_4Ru_2P \times 0.5\ CH_2Cl_2$: C 45.17, H 4.23. Found: C 45.10, H 4.24. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.53−7.61 (m, 6 H, *o*-CH, PPh_3), 7.25−7.38 (m, 9 H, *m*,*p*-CH, PPh_3), 5.28; 5.50 (d, ^3J = 5.7 Hz, 1 H, CH, *p*-cym), 5.31; 5.43 (d, ^3J = 5.6 Hz, 1 H, CH, *p*-cym), 3.89−3.95 (m, 2 H, C_2H_4), 3.34−3.38 (m, 2 H, C_2H_4), 2.76 (sept, ^3J = 6. 9 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.21 (s, 3 H, CH_3, *p*-cym), 1.23 (d, ^3J = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.22 (d, ^3J = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 133.7 (d, $^2J_{C-P}$ = 8.6 Hz, *o*-CH, PPh_3), 133.5 (d, $^1J_{C-P}$ = 48.6 Hz, C*i*, PPh_3), 129.2 (d, $^4J_{C-P}$ = 2.1 Hz, *p*-CH, PPh_3), 127.2 (d, $^3J_{C-P}$ = 9.7 Hz, *m*-CH, PPh_3), 100.4 (s, *C*-CH$_3$); 96.1 (s, *C*-CH(CH$_3$)$_2$), 79.0; 78.9; 78.0; 77.9 (s, CH, *p*-cym), 60.2 (s, C_2H_4), 30.8 (s, C-*C*HMe$_2$), 21.8; 21.7 (s, C-CH(*C*H$_3$)$_2$), 18.3 (s, CH_3, *p*-cym)). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 53.4 (s).

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C$_2$H$_4$)(P*n*-Bu$_3$)] (5). In an autoclave, P*n*-Bu$_3$ (202 mg, 1.00 mmol) was mixed with [(*p*-cymene)RuCl(μ-Cl)]$_2$ (612 mg, 1.00 mmol) in toluene (60 mL). The autoclave was then pressurized with ethylene (3 bar), and the mixture was heated to 110 °C under stirring for 16 h. After cooling to RT, the solution was transferred to a Schlenk flask. The solvent was removed under vacuum, and the residue was dissolved in dichloromethane (20 mL). After addition of hexane (250 mL), the mixture was filtered and the solution was concentrated under vacuum to ∼200 mL. This solution was kept under an ethylene atmosphere at −20 °C. After 24 h, a red-orange microcrystalline material had formed, which was isolated by filtration, washed with hexane, and dried under vacuum (120 mg, 17%). $C_{24}H_{45}Cl_4Ru_2P$ (708.55). Anal. Calcd: C 40.68, H 6.40. Found: C 40.64, H 6.55. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.56; 5.60 (d, ^3J = 5.6 Hz, 1 H, CH, cym), 5.38; 5.39 (d, ^3J = 5.1 Hz, 1 H, CH, *p*-cym), 3.61−3.66 (m, 2 H, C_2H_4), 3.34−3.39 (m, 2 H, C_2H_4), 2.92 (sept, ^3J = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$), 2.29 (s, 3 H, CH_3, *p*-cym), 1.63−1.70 (m, 6 H, P-C*H*$_2$), 1.28−1.48 (m, 18 H, P-CH$_2$-(C*H*$_2$)$_2$-CH$_3$ + CH(C*H*$_3$)$_2$), 0.92 (t, ^3J = 6.9 Hz, 9 H, P-(CH$_2$)$_3$-C*H*$_3$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 100.5 (s, *C*-CH$_3$); 96.2 (s, *C*-CH(CH$_3$)$_2$), 79.0; 78.0; 77.9 (s, CH, *p*-cym), 58.0 (d, $^2J_{C-P}$ = 2.2 Hz, C_2H_4), 31.1 (s, C-*C*H(CH$_3$)$_2$), 25.4 (d, $^3J_{C-P}$ = 4.3 Hz, P-(CH$_2$)$_2$-*C*H$_2$), 24.8 (d, $^1J_{C-P}$ = 28.8 Hz, P-CH$_2$), 24.3 (d, $^2J_{C-P}$ = 12.5 Hz, P-CH$_2$-*C*H$_2$), 22.0; 21.9 (s, C-CH(*C*H$_3$)$_2$), 18.4 (s, CH_3, *p*-cym), 13.4 (s, P-(CH$_2$)$_3$-*C*H$_3$). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 39.2 (s).

[(*p*-cymene)RuCl$_2$(isobutylphobane) (6a)]. Isobutylphobane (900 mg, mixture of isomers) was added to a solution of [(*p*-cymene)RuCl(μ-Cl)]$_2$ (830 mg, 1.35 mmol) in CH_2Cl_2 (35 mL). After heating the mixture for 60 min at 35 °C, the solvent was removed under vacuum. The residue was washed with hexane (3 × 50 mL) and dried under vacuum to give an orange-red solid (1.30 g, 95%). Suitable crystals for X-ray diffraction were obtained by slow diffusion of hexane into a solution of **6a** in chloroform at 0 °C. $C_{22}H_{37}Cl_2RuP$ (504.49). Anal. Calcd for $C_{22}H_{37}Cl_2RuP \times 0.5\ CHCl_3$: C 47.90, H 6.70. Found: C 47.60, H 6.76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (d, ^3J = 5.8 Hz, 2 H, CH, *p*-cym), 5.32 (d, ^3J = 5.8 Hz, 2 H, *CH* (*p*-cym)), 2.70−2.90 (m, 3 H, P-CH$_2$ + C*H*(CH$_3$)$_2$, *p*-cym), 1.50−2.50 (3 m, 18 H, CH + CH$_2$ (phobane); CH_3, *p*-cym), 1.28 (d, ^3J = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$, *p*-cym), 1.07 (d, ^3J = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$, phobane). ^{13}C NMR (101 MHz, $CDCl_3$): δ 106.0 (s, *C*-CH$_3$), 97.1 (s, *C*-CH(CH$_3$)$_2$), 87.6; 85.9 (d, $^3J_{C-P}$ = 4.3 Hz, CH, *p*-cym), 36.1 (d, $^1J_{C-P}$ = 18.7 Hz, P-CH), 30.5 (s, C-*C*H(CH$_3$)$_2$), 28.4 (d + s, P-CH-*C*H$_2$ + P-CH$_2$-CH(*C*H$_3$)$_2$), 27.9 (d, $^1J_{C-P}$ = 20.8 Hz, P-CH-*C*H$_2$), 25.9 (d, $^2J_{C-P}$ = 1 Hz, P-CH$_2$-*C*H(CH$_3$)$_2$), 25.1 (d, $^2J_{C-P}$ = 7.5 Hz, P-CH-*C*H$_2$), 22.4 (s, C-CH(*C*H$_3$)$_2$), 21.8 (d, $^3J_{C-P}$ = 5.4 Hz, P-CH-CH$_2$-*C*H$_2$), 20.8 (d, $^3J_{C-P}$ = 4.4 Hz, P-CH-CH$_2$-*C*H$_2$); 18.0 (s, CH_3, *p*-cym). ^{31}P NMR (162 MHz, $CDCl_3$): δ 7.8 (s).

[(1,3,5-*i*-Pr$_3$C$_6$H$_3$)RuCl$_2$(isobutylphobane)] (6b). Isobutylphobane (240 mg, mixture of isomers) was added to a solution of [(1,3,5-*i*-Pr$_3$C$_6$H$_3$)RuCl(μ-Cl)]$_2$ (238 mg, 316 μmol) in THF (10 mL). After heating the mixture for 20 min at 60 °C, the solvent was removed under vacuum. The residue was washed with hexane (2 × 20 mL) and dried under vacuum to give an orange-brown solid (254 mg, 70%). Suitable crystals for X-ray diffraction were obtained by slow diffusion of hexane into a solution of **6b** in chloroform at 0 °C. $C_{27}H_{47}Cl_2RuP$ (574.62). Anal. Calcd: C 56.44, H 8.24. Found: C 56.54, H 7.92. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.25 (s, 3 H, CH, *i*Pr$_3$C$_6$H$_3$), 2.75−3.10 (m, 5 H, P-CH$_2$ + C*H*(CH$_3$)$_2$, *i*Pr$_3$(C$_6$H$_3$),

1.50−2.50 (3 m, 15 H, CH + CH_2, phobane), 1.36 (d, ^3J = 6.9 Hz, 18 H, CH(CH_3)$_2$, *i*$Pr_3C_6H_3$), 1.14 (d, ^3J = 6.5 Hz, 6 H, CH(CH_3)$_2$, phobane). ^{13}C NMR (101 MHz, $CDCl_3$): δ 109.3 (d, $^{2,3}J_{C-P}$ = 2.5 Hz, *C*-CH(CH_3)$_2$), 80.7 (d, $^3J_{C-P}$ = 3.3 Hz, CH, C_6H_3), 36.0 (d, $^1J_{C-P}$ = 17.3 Hz, P-CH), 30.8 (s, C-*C*H(CH_3)$_2$), 28.7 (s, P-CH_2-CH(*C*H_3)$_2$), 28.6 (d, $^2J_{C-P}$ = 6.4 Hz, P-CH-*C*H_2), 26.2 (d, $^1J_{C-P}$ = 20.3 Hz, P-CH_2), 25.7 (s, P-CH_2-*C*H(CH_3)$_2$), 25.3 (d, $^2J_{C-P}$ = 7.5 Hz, P-CH-*C*H_2); 22.7 (s, C-CH(*C*H_3)$_2$), 21.9 (d, $^3J_{C-P}$ = 5.0 Hz, P-CH-CH_2-*C*H_2), 20.9 (d, $^3J_{C-P}$ = 4.0 Hz, P-CH-CH_2-*C*H_2). ^{31}P NMR (162 MHz, $CDCl_3$): δ 4.8 (s).

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(isobutylphobane)] (7a). In an autoclave, complex **6a** (252 mg, 500 μmol) was mixed with [(*p*-cymene)RuCl(μ-Cl)]$_2$ (153 mg, 250 μmol) in toluene (30 mL). The autoclave was then pressurized with ethylene (3 bar), and the mixture was heated to 85 °C under stirring for 16 h. After cooling to RT, the solution was transferred to a Schlenk flask. The solvent was removed under vacuum, and the residue was washed with hexane (2 × 50 mL) and dried under vacuum. A dark orange-red solid was obtained (270 mg, 77%). $C_{24}H_{41}Cl_4Ru_2P$ (704.51). Anal. Calcd for $C_{24}H_{41}Cl_4Ru_2P$ × 1/2 C_7H_8: C 44.01, H 6.04. Found: C 43.96, H 5.20. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.38; 5.58 (d, ^3J = 5.3 Hz, 1 H, CH, *p*-cym)), 5.31; 5.55 (d, ^3J = 5.7 Hz, 1 H, CH, *p*-cym)), 3.71−3.78 (m, 2 H, C_2H_4), 3.43−3.48 (m, 2 H, C_2H_4), 2.89 (setp, ^3J = 6.9 Hz, 1 H, C−*C*H(CH_3)$_2$), 2.70−2.84; 0.8−2.6 (m, H phobane, C-CH_3, C-CH_2(CH_3)$_2$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 100.4 (s, *C*-CH(CH_3)$_2$), 96.1 (s, *C*-CH_3), 79.3; 77.2; 78.0 (s, CH, *p*-cym), 53 (C_2H_4 under CD_2Cl_2), 34.3 (d, $^1J_{C-P}$ = 21.6 Hz, P-CH), 31.0 (s, C-*C*H(CH_3)$_2$), 29.4 (d, $^2J_{C-P}$ = 5.6 Hz, P-CH-*C*H_2), 29.0 (br s, P-CH-*C*H_2), 28.8 (d, $^2J_{C-P}$ = 2.6 Hz, P-CH-*C*H_2), 27.5 (s), 28.3 (d, $^2J_{C-P}$ = 6.2 Hz), 28.6 (s) (P-*C*H_2-*C*H(CH_3)$_2$; P-CH), 25.3 (d, $^3J_{C-P}$ = 2.6 Hz, P-CH_2-CH(*C*H_3)$_2$), 24.9 (d, $^1J_{C-P}$ = 12.1 Hz, P-CH_2), 23.3 (d, $^3J_{C-P}$ = 2.8 Hz, P-CH_2-CH(*C*H_3)$_2$), 22.0 (d, $^3J_{C-P}$ = 5.0 Hz, P-CH-CH_2-*C*H_2), 21.9 (s, C-CH(*C*H_3)$_2$), 21.8 (s, C-CH(*C*H_3)$_2$), 21.2 (d, $^3J_{C-P}$ = 4.1 Hz, P-CH-CH_2-*C*H_2), 18.4 (s, CH_3, *p*-cym). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 30.3 (s).

[(1,3,5-*i*-$Pr_3C_6H_3$)Ru(μ-Cl)$_3$RuCl(C_2H_4)(isobutylphobane)] (7b). In a 100 mL Schlenk flask, complex **7b** (160 mg, 278 μmol) was mixed with [(1,3,5-*i*-$Pr_3C_6H_3$)RuCl(μ-Cl)]$_2$ (107 mg, 142 μmol) in isooctane (40 mL). The Schlenk flask was connected to a bottle of ethylene, and the suspension was cooled to 0 °C to saturate the solvent with the gas. The closed Schlenk flask was then heated to 75 °C for 24 h. The product was isolated by filtration, washed with hexane (2 × 50 mL), and dried under vacuum to give an orange-brown solid (190 mg, 88%). $C_{29}H_{51}Cl_4Ru_2P$ (774.65). Anal. Calcd for $C_{29}H_{51}Cl_4Ru_2P$ − 1/2 C_2H_4: C 44.21, H 6.49. Found: C 43.84, H 6.43. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.28 (s, 3 H, CH, *i*-$Pr_3C_6H_3$), 3.60−3.67 (m, 2 H, C_2H_4), 3.32−3.39 (m, 2 H, C_2H_4), 2.87 (setp, ^3J = 6.9 Hz, 3 H, C*H*(CH_3)$_2$, *i*-$Pr_3C_6H_3$), 2.62−2.77 (m, 2 H, P-CH_2), 2.26−2.52 (m, 4 H, phobane), 2.02−2.25 (m, 2 H, phobane), 1.37−1.98 (m, 9 H, CH + CH_2, phobane), 1.29 (d, ^3J = 6.9 Hz, 9 H, CH(CH_3)$_2$, *i*-$Pr_3C_6H_3$), 1.28 (d, ^3J = 6.9 Hz, 9 H, CH(CH_3)$_2$, *i*-$Pr_3C_6H_3$), 0.90 (d, ^3J = 6.6 Hz, 3 H, CH(CH_3)$_2$, phobane), 0.79 (dd, ^3J = 6.4 Hz; $^4J_{P-H}$ = 1.1 Hz, 3 H, CH(CH_3)$_2$, phobane). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 103.1 (s, *C*-CH(CH_3)$_2$), 73.8 (s, CH, C_6H_3), 53.5 (d, $^2J_{C-P}$ = 4.0 Hz, C_2H_4 with CD_2Cl_2), 34.3 (d, $^1J_{C-P}$ = 21.3 Hz, P-CH), 31.2 (s, C-*C*H(CH_3)$_2$), 29.3 (d, $^2J_{C-P}$ = 5.6 Hz, P-CH-*C*H_2), 28.9 (d, $^2J_{C-P}$ = 5.7 Hz, P-CH-*C*H_2), 28.7 (d, $^2J_{C-P}$ = 7.1 Hz, P-CH-*C*H_2), 27.5 (s), 28.2 (d, $^2J_{C-P}$ = 6.2 Hz), 28.6 (s) (P-*C*H_2-*C*H(CH_3)$_2$; P-CH), 25.2 (d, $^3J_{C-P}$ = 2.6 Hz, P-CH_2-CH(*C*H_3)$_2$), 24.9 (d, $^1J_{C-P}$ = 12.2 Hz, P-CH_2), 23.2 (d, $^3J_{C-P}$ = 2.6 Hz, P-CH_2-CH(*C*H_3)$_2$), 22.2 (s, C-CH(*C*H_3)$_2$), 21.9 (d, $^3J_{C-P}$ = 4.9 Hz, P-CH-CH_2-*C*H_2), 21.6 (s, C-CH(*C*H_3)$_2$), 21.2 (d, $^3J_{C-P}$ = 4.0 Hz, P-CH-CH_2-*C*H_2). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.6 (s).

[(*p*-cymene)$RuCl_2$(PCyp$_3$) (8)]. P(Cyp)$_3$ (1.06 g, 4.43 mmol) was added to a solution of [(*p*-cymene)RuCl(μ-Cl)]$_2$ (1.13 g, 1.85 mmol) in dichloromethane (40 mL). After stirring for 1 h at RT, the solvent was removed under vacuum, and the residue was washed with pentane/diethyl ether (1:1, 25 mL) and pentane (2 × 50 mL). An orange-red solid was obtained (1.93 g, 95%). Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a solution of **8** in dichloromethane at − 20 °C. $C_{25}H_{41}Cl_2RuP$ (544.55). Anal. Calcd: C 55.14, H 7.59. Found: C 55.06, H 7.83. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.52−5.62 (m, 4 H, CH, *p*-cym), 2.74 (sept, 1 H, ^3J = 6.9 Hz, C*H*(CH_3)$_2$), 2.58−2.76 (m, 3 H, P-CH), 2.04 (s, 3 H, CH_3, *p*-cym), 2.02−1.92 (m, 6 H, C_5H_9), 1.65−1.86 (m, 12 H, C_5H_9), 1.50−1.63 (m, 6 H, C_5H_9), 1.27 (d, 6 H, ^3J = 6.9 Hz, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 105.4 (*C*-CH_3), 93.6 (*C*-CH(CH_3)$_2$), 88.6 (d, $^2J_{C-P}$ = 4.3 Hz, CH, *p*-cym), 84.1 (d, $^2J_{C-P}$ = 5.2 Hz, CH, *p*-cym), 37.2 (d, $^1J_{C-P}$ = 22.7 Hz, P-CH), 30.4 (s, *C*H(CH_3)$_2$), 29.6 (s, P-CH-CH_2-*C*H_2), 25.5 (d, $^2J_{C-P}$ = 9.0 Hz, P-CH-*C*H_2), 22.1 (s, CH(*C*H_3)$_2$), 17.4 (s, CH_3, *p*-cym). ^{31}P NMR (162 MHz, CD_2Cl_2): 25.0 (s).

[(*p*-cymene)Ru(μ-Cl)$_3$RuCl(C_2H_4)(PCyp$_3$)] (9). In an autoclave, complex **8** (272 mg, 500 μmol) was mixed with [(*p*-cymene)RuCl(μ-Cl)]$_2$ (153 mg, 250 mmol) in toluene (30 mL). The autoclave was then pressurized with ethylene (3 bar), and the mixture was heated to 85 °C under stirring for 24 h. After cooling to RT, the solution was transferred to a Schlenk flask. The solvent was removed under vacuum, and the residue was washed with hexane (2 × 50 mL) and dried under vacuum to give a dark orange solid (335 mg, 90%). Microcrystalline material can be obtained by slow diffusion of pentane into a solution of complex **9** in dichloromethane or toluene at − 20 °C. $C_{27}H_{45}Cl_4Ru_2P$ (744.58). Anal. Calcd for $C_{27}H_{45}Cl_4Ru_2P$ × 0.25 CH_2Cl_2: C 42.74, H 5.99. Found: C 42.88, H 5.70. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 5.43; 5.59 (d, ^3J = 4.8 Hz, 1 H, CH, *p*-cym), 5.33; 5.54 (d, ^3J = 5.6 Hz, 1 H, CH, *p*-cym), 4.00−4.04 (m, 2 H, C_2H_4), 3.52−3.56 (m, 2 H, C_2H_4), 2.93 (sept, ^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$), 2.27 (s, 3 H, CH_3, *p*-cym), 2.10−2.22 (m, 3 H, P-CH), 1.4−2.0 (24 H, CH_2 C_5H_9), 1.36 (2d, ^3J = 6.8 Hz, 6 H, CH(CH_3)$_2$). ^{13}C NMR (101 MHz, CD_2Cl_2): δ 100.3 (s, *C*-CH_3), 96.0 (s, *C*-CH(CH_3)$_2$), 79.1; 79.0; 78.2; 78.0 (s, CH, *p*-cym), 59.5 (d, $^2J_{C-P}$ = 2 Hz, C_2H_4), 37.2 (d, $^1J_{C-P}$ = 25.2 Hz, P-CH), 30.8 (s, *C*H(CH_3)$_2$), 29.0 (s, P-CH-*C*H_2), 25.3; 25.0 (d, $^3J_{C-P}$ = 9.0 Hz, P-CH-CH_2-*C*H_2), 21.6; 21.5 (s, CH(*C*H_3)$_2$), 18.2 (s, CH_3). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 43.9 (s).

[(*p*-cymene)Ru(μ-Cl)$_3$$RuCl_2$(P$Ph_3$)] (10). CCl_4 (4 mL) was added to a solution of complex **4** (104 mg, 135 μmol) in dichloromethane (5 mL). The mixture was stirred for 20 h at 40 °C, during which a dark solid precipitated. After removal of the solvent under vacuum, the residue was washed with toluene (3 mL) and pentane (3 × 5 mL) to give a dark brown solid, which was dried under vacuum (90 mg, 86%). Suitable crystals for X-ray diffraction were obtained by slow diffusion of pentane into a solution of **10** in dichloromethane. $C_{28}H_{29}Cl_5Ru_2P$ (775.92). Anal. Calcd for $C_{28}H_{29}Cl_5Ru_2P$ × 1/4 CH_2Cl_2: C 42.57, H 3.73. Found: C 42.82, H 3.62. NMR: silent (paramagnetic).

[(*p*-cymene)Ru(μ-Cl)$_3$$RuCl_2$(P*n*-$Bu_3$)] (11). CCl_4 (3 mL) was added to a solution of complex **5** (50 mg, 71 μmol) in toluene (2 mL). The mixture was stirred for 20 h at 40 °C. After removal of the solvent under vacuum, the residue was dissolved in a minimum amount of toluene and the product was obtained in crystalline form by slow diffusion of pentane into the toluene solution at 0 °C (35 mg, 69%). $C_{22}H_{41}Cl_5PRu_2$ (715.95). Anal. Calcd for $C_{22}H_{41}Cl_5PRu_2$: C 36.91, H 5.77. Found: C 36.94, H 5.55. NMR: silent (paramagnetic).

[(*p*-cymene)Ru(μ-Cl)$_3$$RuCl_2$(isobutylphobane)] (12). Complex **7a** (120 mg, 170 μmol) was dissolved in a mixture of CCl_4 (5 mL) and dichloromethane (5 mL). The mixture was stirred for 16 h at 35 °C. After removal of the solvent under vacuum, the residue was washed with toluene/pentane (1:1, 5 mL) and pentane (2 × 5 mL) and dried under vacuum. A brown-green solid was obtained (99 mg, 82%). $C_{22}H_{37}Cl_5Ru_2P$ (711.91). Anal. Calcd for $C_{22}H_{37}Cl_5Ru_2P$

× 3/4 CH_2Cl_2: C 35.23, H 5.00. Found: C 35.22, H 4.86. NMR: silent (paramagnetic).

[(*p*-cymene)Ru(*μ*-Cl)$_3$RuCl$_2$(PCyp$_3$)] (13). CCl_4 (3 mL) was added to a solution of complex **9** (40 mg, 54 μmol) in toluene (2 mL). The mixture was stirred for 20 h at 40 °C, during which a dark solid precipitated. After removal of the solvent under vacuum, the residue was washed successively with pentane (5 mL), toluene (3 mL), and pentane (2 × 5 mL) and dried under vacuum. A dark brown solid was obtained (37 mg, 91%). $C_{25}H_{41}Cl_5Ru_2P$ (751.98). Anal. Calcd: C 39.93, H 5.50. Found: C 39.88, H 5.82. NMR: silent (paramagnetic).

General Procedure for the ATRA of CCl_4, $CHCl_3$, or CCl_3CO_2Et to Olefins. The desired amount of a CD_2Cl_2 stock solution of the Ru catalyst was added to a 1.5 mL vial containing Mg powder (100 mg). D_2O (20 μL) was added to a freshly prepared CD_2Cl_2 stock solution of the olefin, CCl_4 or CCl_3CO_2Et (or $CHCl_3$ stock solution of the olefin for $CHCl_3$ addition), and the internal standard 1,4-bis(trifluoromethyl)benzene, and the mixture was shaken for 1 min to saturate the solution with D_2O. The desired amount of this stock solution was added to the vial, and the total volume was completed to 1000 μL with CD_2Cl_2 (final conc: [olefin] = 1.38 M, [CCl_4] = 5.52 M or [CCl_3CO_2Et] = 4.14 M, [internal standard] = 270 mM). The resulting solution was stirred at room temperature, and after a given time, a sample (20 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (500 μL), and analyzed by ^{1}H NMR spectroscopy.

Kinetic Investigations. For the kinetic investigations, an analogous procedure was used. The reactions were started in parallel, and after the given times, samples of 20 μL were removed from the reaction mixture. The conversion and yield were determined using ^{1}H NMR spectroscopy.

General Procedure for ATRC Reactions. The desired amount of a CD_2Cl_2 (or a toluene-d_8 stock solution for **23**) stock solution of the Ru catalyst was added to a 1.5 mL vial containing the Mg powder (100 mg). D_2O was added to a freshly prepared CD_2Cl_2 stock solution of the substrates and the internal standard 1,4-bis(trifluoromethyl)benzene (mesitylene for **17**), and the mixture was shaken for 1 min to saturate the solution with D_2O. The desired amount of stock solution was added to the vial, and the total volume was completed to 1000 μL with the respective solvent (final conc: [substrate] = 0.14 M). The resulting solution was stirred at room temperature or at 80 °C. After a given time, a sample (80 μL) was removed from the reaction mixture, diluted with $CDCl_3$ (500 μL), and analyzed by ^{1}H NMR spectroscopy.

Crystallographic Investigations. The relevant details of the crystals, data collection, and structure refinement can be found in Tables 5−7. Diffraction data were collected using Mo Kα radiation on a four-circle kappa goniometer equipped with an Oxford Diffraction Sapphire/KM4 CCD at 140(2) K, and all data were reduced by Crysalis PRO.[31] An absorption correction was applied to all data sets using a semiempirical method.[32] All structures were refined using the full-matrix least-squares on F^2 with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}$ (where a is 1.5 for methyl hydrogen atoms and 1.2 for others). Structure refinement and geometrical calculations were carried out on all structures with SHELXTL.[33] Some disorder problems have been found during the refinement of **11**. All alkyl chains have been treated by means of the split model and their displacement parameters restrained (ISOR card).

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Supporting Information Available: X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.

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