Living Polymerization

Atom-Transfer Radical Reactions under Mild Conditions with $[\{RuCl_2(1,3,5\text{-}C_6H_3iPr_3)\}_2]$ and PCy_3 as the Catalyst Precursors**

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The complex $[RuCl_2(p\text{-cymene})(PCy_3)]$ (**1**) has emerged as a versatile catalyst precursor for synthetically important transformations such as ring-closing[1] and ring-opening olefin-metathesis reactions[2] and atom-transfer radical polymerizations (ATRP).[3] An attractive feature of this catalyst is the fact that it can be prepared in situ from commercially available $[\{RuCl_2(p\text{-cymene})\}_2]$ (**2**) and PCy_3. Somewhat surprising was the observation by Demonceau and co-workers that complex **1**—despite its good activity in ATRP reactions—fails to catalyze atom-transfer radical additions

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(ATRA) of CCl_4 to olefins,[4] although ATRP and ATRA are mechanistically very similar.[5] Herein, we show that by replacing the (p-cymene)ruthenium complex **2** with the trisisopropylbenzene complex $[\{RuCl_2(1,3,5\text{-}C_6H_3i\text{Pr}_3)\}_2]$ (**3**) it is possible to catalyze both ATRP and ATRA reactions under exceptionally mild conditions with high efficacy.

Activation of **1** is thought to proceed by a thermally or photochemically induced replacement of the arene ligand.[1–3,6] We reasoned that a sterically more demanding π ligand might facilitate this replacement due to steric congestion with the PCy_3 ligand. The commonly used hexamethylbenzene complex $[\{RuCl_2(C_6Me_6)\}_2]$ was not considered because of its low solubility and because it had been reported that the reaction with PCy_3 does not give the monomeric complex $[RuCl_2(C_6Me_6)(PCy_3)]$.[7] Instead, we focused on the trisisopropylbenzene complex **3**, which can be obtained easily from **2** by arene exchange.[8]

First, we investigated the ATRP of methyl methacrylate (MMA) by using ethyl 2-bromo-2-methylpropionate as the initiator and a mixture of **3** and PCy_3 as the catalyst precursors (**3**/PCy_3/initiator/MMA = 1:2:4:1600). The reaction was carried out at a temperature of only 50 °C, which is significantly below the 80–85 °C commonly employed for ruthenium-catalyzed MMA polymerizations.[3,9,10] After 24 h, PMMA could be isolated in 90 % yield. The polymer was found to have a very narrow molecular-weight distribution of $\bar{M}_w/\bar{M}_n = 1.19$ ($\bar{M}_n$ and $\bar{M}_w$ are the number-average and weight-average molecular mass, respectively; $\bar{M}_n = 35\,000$, initiation efficiency $f = 1.03$).[11] Furthermore, a linear relationship of $\ln([M]_0/[M])$ versus time was observed ($[M]$ is the concentration of the monomer; see the Supporting Information), which suggests that polymerization had occurred in a controlled fashion. A radical mechanism is supported by the observed tacticity of rr:rm:mm = 63:30:7 and the fact that the reaction was completely inhibited by galvinoxyl. A comparison of the initial turnover frequencies (TOF)[12] revealed that under these mild conditions, the new catalyst **3**/PCy_3 (TOF = 59 h^{-1}) is one order of magnitude more active than the previously reported system **2**/PCy_3 (TOF = 5 h^{-1}), which was considered to be one of the most active Ru-based catalyst systems described so far.[13] Ethyl methacrylate can likewise be polymerized by **3**/PCy_3 at 50 °C in a controlled fashion (yield after 24 h: 89 %, $\bar{M}_n = 40\,200$, $\bar{M}_w/\bar{M}_n = 1.10$, $f = 1.01$).[11] Reactions with butyl acrylate as the monomer gave also a very high yield (99 %) but revealed a bimodal molecular-weight distribution ($\bar{M}_n = 158\,500$, $\bar{M}_w/\bar{M}_n = 3.36$, $f = 0.32$).[14] Reactions with styrene, on the other hand, gave only low amounts of polymer (yield: 9 %). It should be noted, however, that the ATRP of styrene is generally carried out at temperatures above 100 °C.[9]

Encouraged by the success of the new catalyst system in ATRP reactions, we investigated the ATRA of CCl_4 and of $CHCl_3$ to styrene. Again, the catalyst was prepared in situ by mixing **3** with two equivalents of PCy_3 (**3**/styrene/$CHCl_3$ or CCl_4 = 1:300:450). Two reactions were carried out in toluene at 40 °C: one in the presence of a light source of moderate intensity, the other in the dark. Reactions with CCl_4 gave nearly zero conversions, whereas a conversion of 65 % (yield: 63 %) was observed after 24 h for reactions with $CHCl_3$ that had no influence from a light source. These results were surprising in view of the higher intrinsic reactivity of CCl_4 but in accordance with the observation that complex **1** is not able to promote the addition of CCl_4 to styrene.[4]

The time course of reactions between styrene and $CHCl_3$ catalyzed by complex **3** in the presence of one and two equivalents of PCy_3 is depicted in Figure 1 ([**3**] = 1 mol %).

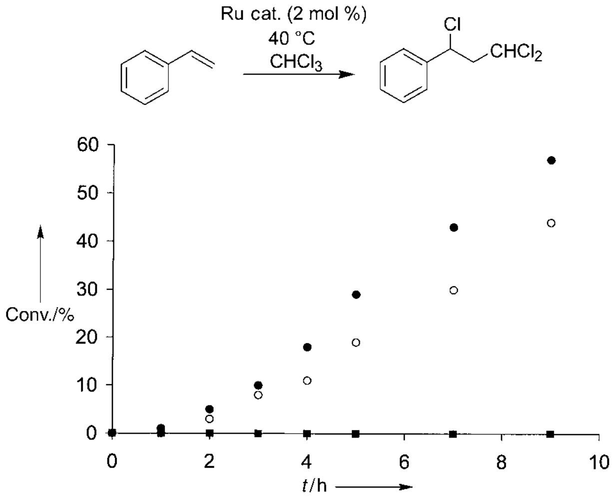


Figure 1. Time course of reactions between styrene and $CHCl_3$ catalyzed by **3** + 2 PCy_3 (●), **3** + 1 PCy_3 (○), and **2** + 2 PCy_3 (■). Reaction conditions: **2** or **3**/styrene/$CHCl_3$ = 1:100:150; [**2**] or [**3**] = 13.8 mM, toluene, 40 °C, no light. The conversion is based on the consumption of styrene as determined by GC.

An induction period is clearly visible, which indicates that catalyst activation must take place. A Ru/PCy_3 ratio of 1:1 is advantageous, although the reaction rates at a later stage of this reaction (4–9 h) are similar to the reaction rates observed when substoichiometric amounts of PCy_3 are present. As in the case of the polymerization reactions, the nature of the π ligand was found to be crucial: reactions performed with the p-cymene complex **2** instead of the trisisopropylbenzene complex **3** gave zero conversion.[15]

To test the scope and the limitations of the new catalyst system, **3**/PCy_3, we investigated ATRA reactions with different olefins (Table 1). The $CHCl_3$ adducts of the aromatic olefins p-chlorostyrene, p-methoxystyrene, 1-vinylnaphthalene, and styrene (entries 1–4) were obtained in yields of between 69 and 95 % with a ruthenium catalyst concentration of 2–6 mol % at 40 °C (entries 1–3) or 60 °C (entry 4). It should be noted that for a Ru-based catalyst, synthetically useful yields above 80 % have been described only for the carbene complex $[RuCl_2(CHPh)(PCy_3)_2]$ (2.5–7.5 mol %, 65–80 °C).[16] Using a substrate/**3** ratio of 1000:1, we were able to obtain the $CHCl_3$ adduct of styrene in 57 % yield after two weeks. This corresponds to 285 turnovers per ruthenium atom, which is, to the best of our knowledge, the highest value ever reported.[17] MMA is a less suited substrate because polymerization becomes a significant side reaction, in accordance with the results described above (entry 5).

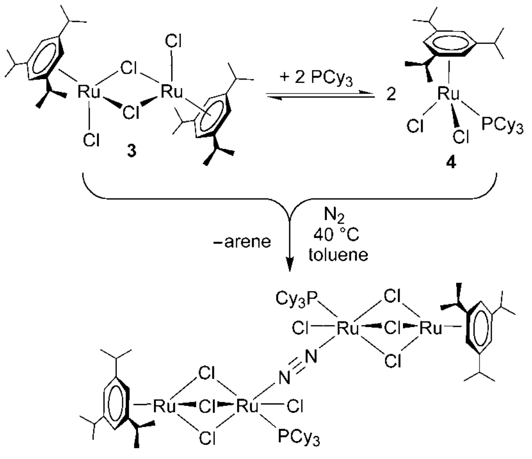
To obtain more information about the mode of activation for reactions with the new catalyst system, we examined

Table 1: ATRA reactions catalyzed by **3**/PCy_3 or by **5**.

Entry	Cat.	Substr. A	Substr. B	T [°C]	t [h]	Conv./Yield [%]
1	**3**/PCy_3	styrene	$CHCl_3$	40	48	95/91[a]
2	**3**/PCy_3	*p*-chlorostyrene	$CHCl_3$	40	48	93/84[a]
3	**3**/PCy_3	*p*-methoxystyrene	$CHCl_3$	40	48	98/95[b]
4	**3**/PCy_3	1-vinylnaphthalene	$CHCl_3$	60	48	73/69[b]
5	**3**/PCy_3	MMA	$CHCl_3$	40	48	92/15[a]
6	**5**	styrene	$CHCl_3$	40	1	25/19[c]
7	**5**	styrene	$CHCl_3$	40	48	88/93[c]
8	**5**	styrene	CCl_4	40	2	99/98[d]
9	**5**	MMA	CCl_4	40	5	89/65[d]
10	**5**	1-decene	CCl_4	40	5	67/66[d]

[a] **3**/PCy_3/olefin/$CHCl_3$ = 1:2:100:150, [**3**] = 13.8 mM; [b] **3**/PCy_3/olefin/$CHCl_3$ = 3:6:100:150, [**3**] = 41.4 mM; [c] **5**/olefin/$CHCl_3$ = 1:200:300; [**5**] = 6.9 mM; [d] **5**/olefin/CCl_4 = 1:600:900; [**5**] = 2.3 mM. All reactions were performed in toluene. The conversion (conv.) is based on the consumption of the olefin and the yield is based on the formation of product as determined by GC or ^1H NMR spectroscopy after the time given.

solutions of **3** and PCy_3 in [D_8]toluene by ^1H and ^{31}P NMR spectroscopy. At room temperature, an equilibrium between **3**, PCy_3, and the monomeric complex [$RuCl_2(1,3,5\text{-}C_6H_3iPr_3)(PCy_3)$] (**4**) was rapidly established, with 25% of the ruthenium being present in the form of **3** and 75% in the form of the monomer **4** (Scheme 1). This reaction was followed by slow liberation of the arene ligand. At 40°C, this displacement proceeded with a half-life of $t_{1/2} = 5$ h. When the reaction mixture was allowed to cool to room temperature, an orange, crystalline complex precipitated. This compound was identified as the tetranuclear complex **5** based on elemental and crystallographic analysis.[18] For comparison, the reaction between the *p*-cymene complex **2** and PCy_3 was investigated. In this case, the equilibrium was found to be completely on the side of the monomeric complex **1**, and arene displacement required significantly harsher reaction conditions ($t_{1/2} = 13$ h, 60°C). When the heating was stopped after 12 h, an orange complex precipitated. Again, the results of the elemental analysis suggested that a tetranuclear dinitrogen complex (**6**) of low solubility had formed.



Scheme 1. In the presence of PCy_3, the dimeric complex **3** is in equilibrium with the monomeric complex **4**. Partial loss of the arene ligand leads to the formation of the tetranuclear complex **5**.

Complex **5** represents the first structurally characterized product of an arene-displacement reaction with [{$RuCl_2$(arene)}$_2$] and PCy_3 (see Figure 2). A plausible mechanism of formation is the liberation of trisisopropylbenzene from **4** to generate [$RuCl_2(PCy_3)$]$_n$, which subsequently reacts with unconverted **3** and N_2 to give the mixed, chloro-bridged complex **5**.[19] The two {$(1,3,5\text{-}C_6H_3iPr_3)Ru(\mu\text{-}Cl)_3RuCl(PCy_3)N$} fragments are related by a crystallographic inversion center. The dinitrogen ligand bridges the fragments in a nearly linear fashion (Ru1-N1-N1A = 174.9(3)°) and the N–N bond length of 1.120(4) Å is similar to that reported for other complexes with Ru-N≡N-Ru units.[20] The Ru–Cl (Ru1/Ru2–Cl1/Cl2/Cl3 = 2.41–2.53 Å, Ru1–Cl4 = 2.3759(6) Å) and the Ru–P (2.3121(7) Å) bond lengths are within the expected range.

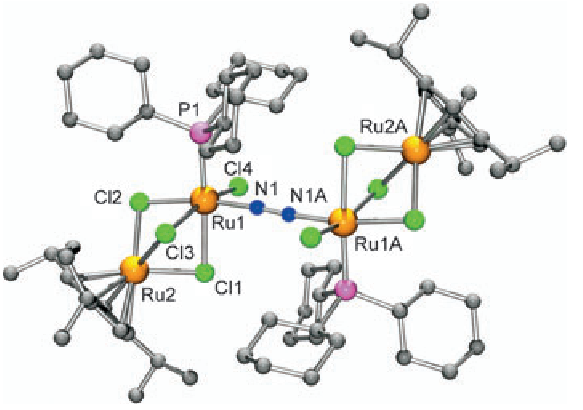


Figure 2. Molecular structure of complex **5** in the crystal. The hydrogen atoms and the solvent molecules are omitted for clarity.

The tetranuclear complex **5** is a very active ATRA catalyst. For the addition of $CHCl_3$ to styrene, for example, a yield of 19% was observed after only one hour at 40°C (Table 1, entry 6). The final yield after 48 h was similar to that found for **3**/PCy_3 (entry 7). Interestingly, complex **5** can also effect the addition of CCl_4 to olefins (entries 8–10). The observed TOFs are comparable to those of the best ATRA catalysts described so far, despite the low reaction temperature.[21] In this context it is interesting to note that two other complexes containing a {Ru–N≡N–Ru} structural motif were reported to catalyze atom-transfer radical reactions.[21a,22] For both complexes it was suggested that catalyst activation proceeds by a CCl_4-induced loss of the N_2 ligand, and a similar mode of activation appears likely for reactions with **5**.

Since the mixture of **3** and PCy_3 was inactive for CCl_4 additions, CCl_4 seemed to interfere with catalyst activation. Control experiments showed that this is indeed the case. CCl_4 was found to react immediately with PCy_3 to give a trichloromethylphosphonium salt.[23] The phosphine is thus removed from the equilibrium between **3** and **4**, thus preventing the formation of the catalytically active ruthenium complex.

In summary, we have demonstrated that a mixture of complex **3** and PCy_3 can be used to efficiently catalyze atom-transfer radical reactions at exceptionally low temperatures. Less than 0.07 mol% of complex **3** is required to quantitatively polymerize methacrylates in a controlled fashion at 50 °C. For the ATRA of the notoriously difficult substrate $CHCl_3$ to aromatic olefins, synthetically useful yields of $>80\%$ can be obtained with only 1–3 mol% of complex **3** at 40 °C. We have evidence that catalyst activation proceeds by a PCy_3-induced substitution of the arene ligand, and for the first time a product of such a reaction has been structurally characterized.

Experimental Section

Synthesis of complex **5**: Complex **3** (100 mg, 133 μmol) was added to a solution of PCy_3 (37.3 mg, 133 μmol) in toluene (10 mL). The solution was stirred for 4 h at 40 °C and then allowed to cool to room temperature. After one week, orange crystals formed, which were collected and washed with pentane (yield: 78.3 mg, 70%). Elemental analysis calcd (%) for $C_{66}H_{114}Cl_8N_2P_2Ru_4 \cdot 2\,C_6H_5CH_3$: C 51.39, H 7.01, N 1.50; found: C 51.53, H 6.95, N 1.15. The same complex was obtained in reactions with a **3**/PCy_3 ratio of 1:2, but the yields were lower. NMR spectra were not recorded owing to the low solubility of **5** in benzene or toluene. In chlorinated solvents the decomposition of **5** was observed.

General polymerization procedure: The monomer and a solution of the initiator in toluene (ethyl 2-bromo-2-methylpropionate for acrylates and 1-bromoethylbenzene for styrene; 0.1M) were added to a Schlenk tube that contained the ruthenium complex **2** or **3** (6.25 μmol) and PCy_3, such that the molar ratios [Ru]/[initiator]/[monomer] were 1:2:800. *n*-Octane (50 μL) was added as the internal standard for GC measurements. Immediately after the components had been mixed, the tube was placed in a thermostatted oil bath (50 °C), which was shielded from light. After a given period of time, the mixture was cooled and diluted with THF (6 mL). The polymer was then precipitated with hexane (acrylates) or with methanol (styrene), isolated, and dried under vacuum. Remaining traces of catalyst were removed by dissolving the polymer in toluene and by adding silica gel. After the silica gel had been removed, the solvent was removed by evaporation and the polymer was dried in vacuum. All reactions were performed under an atmosphere of dry nitrogen and with freshly distilled substrates and solvents. The molecular weights and the molecular-weight distributions of the polymers were determined by gel permeation chromatography (DMF, 60 °C) with PMMA standards. The conversions were determined by GC and the yields by mass.

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