Easily Accessible Ring Opening Metathesis and Atom Transfer Radical Polymerization Catalysts based on Arene, Norbornadiene and Cyclooctadiene Ruthenium Complexes Bearing Schiff Base Ligands

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Abstract: A group of four mixed ligand ruthenium(II)-Schiff base complexes has been synthesized and characterized. These complexes are easily accessible from [$RuCl_2$(*p*-cymene)]$_2$, [$RuCl_2$(NBD)]$_n$, [$RuCl_2$(COD)]$_x$ and salicylaldimine salts. They have been found to serve as good catalyst precursors for ring-opening metathesis polymerization (ROMP) and atom transfer radical polymerization (ATRP) of different vinyl monomers. The catalytic activity and the control over the produced polymer can be dramatically improved after the addition of additives such as Et_2AlCl and (n-Bu)$_2$NH.

Keywords: atom transfer radical polymerization; homogeneous catalysis; ring opening metathesis polymerization; ruthenium compounds

Introduction

Over the last decade, a tremendous amount of scientific research has focused on the development of new catalysts for polymer synthesis. The potential applications of a polymer are determined by its physical and mechanical properties, which are defined by the polymer morphology. The polymer morphology largely depends on the composition and architecture of the polymer. Therefore, the development of well identified catalysts for the polymerization of a wide range of monomers with control over the stereochemistry, molecular weight and co-monomer incorporation has been a long-standing goal. These challenges can be achieved by using a living polymerization process in which there is neither chain transfer nor termination.[1]

In the late 1950's, heterogeneous catalysts based on Mo, Ru, W or Re oxides and halides were capable of breaking the double bond of a cyclic olefin and converting the ring-opened molecule into a polymer with double bonds in the main-chain (Scheme 1a).[2] This process, called ring-opening metathesis polymerization (ROMP), has been studied in great detail since these initial discoveries. It is now known that olefin metathesis reactions are initiated by metal-carbene complexes. Furthermore, since these early heterogeneous catalysts were difficult to characterize, a lot of research has been focused on the development of single-site metal carbene complexes. These compounds, having the general formula: $L_nM{=}CHR$, allow the synthesis of new polymer microstructures with an exceptional precision. Two of the most representative catalysts that have emerged the last 10 years are based on Mo [3] and Ru.[4]

In the early 1990's, Grubbs and coworkers reported on a new class of well-defined ruthenium carbenes of the form $RuCl_2({=}CHPh)(PR_3)_2$ (R = Ph, Cy) which were active in all facets of olefin metathesis.[5] The spectacular tolerance of these late transition complexes towards many functional groups combined with the ease of handling caused by a reasonable stability against oxygen, water and impurities render them as exceedingly practical tools and explain their unrivalled popularity. However, the rather cumbersome synthesis route *via* diazo compounds constituted a certain handicap which resulted in the development of highly active alternative systems.[6]

In the mean time lots of efforts were performed to get control over a radical polymerization process since almost all monomers can undergo free radical polymerization and radical species are exceptional tolerant towards many functional groups. Before the late 1980's it was even unthinkable to realize controlled/"living" radical polymerizations (CRP) because there was no adequate answer to the near diffusion-controlled bimolecular radical coupling and disproportionation reactions. However, the last years have witnessed the rapid growth in the development and understanding of new

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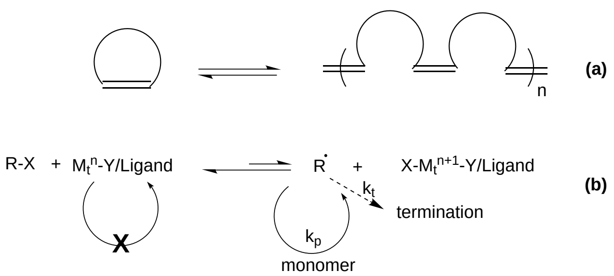


Scheme 1. Equilibrium of ROMP (a) and ATRP (b).

CRP methods.[7] All of these methods are based on a rapid dynamic equilibrium between a minute amount of growing free radicals and a large majority of dormant species. In early examples the dormant species are generated from nitroxide species (e.g., TEMPO) [8] or thioesters that act as degenerative transfer agent.[9]

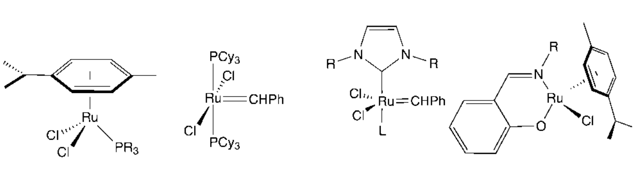
The year 1995 was the start of the transition metal-mediated living radical polymerization or ***a***tom ***t***ransfer ***r***adical ***p***olymerization (ATRP).[10–12] The dynamic equilibrium in ATRP is established through the reversible transition metal-catalyzed cleavage of the covalent carbon-halogen bond in the dormant species (Scheme 1b).

A range of systems has been described using different metal catalysts in conjunction with an activated alkyl halide initiator, e.g., Cu(I), Ru(II), Ni(II), Rh(I) and Fe(II and I).[12]

Recent publications have shown that the multivariate ligand environment around Ru, bearing a large diversity in functional groups provides multifaceted reactive sites, which can be exploited by various substrates and thus can lead to numerous interesting organic products with the same catalyst.[13] In this context the group of Demonceau and we have reported about the excellent ATRP activity of some common "metathesis" catalysts like **1**, **2**, **3** and **4** (Figure 1).[14–15]

Catalyst **1** and **4** show high activity for ROMP after activation with trimethylsilyldiazomethane (TMSD) to generate the active species.[6c,15a,16]

Our earlier investigations about arene-ruthenium-Schiff base complexes prompted us to explore the activity of some new synthesized ruthenium-based systems in the field of ATRP and ROMP without the need for TMSD activation.



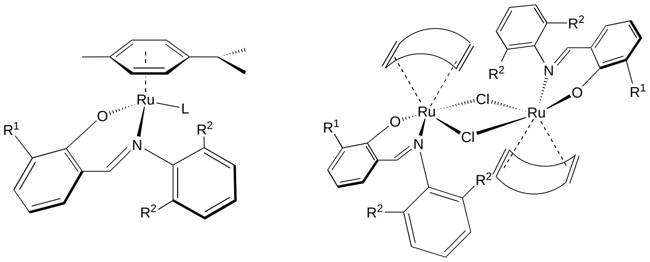
1 **2** **3** R = Cy, *i*-Pr, L = NHC-ligand or PCy_3 **4** R = Me, *t*-But, 2,6-Me-4-BrC_6H_2

Figure 1. Ruthenium catalysts that are active in olefin metathesis and ATRP.

Results and Discussion

A first type of Ru complexes that was synthesized consisted of a Schiff base ligand, a η^6-coordinated *p*-cymene entity and a Cl atom (**5**). This compound can be easily obtained by breaking the (μ-Cl)$_2$ bridge in [$RuCl_2$(*p*-cymene)]$_2$ and abstracting one chloride with the Tl salt of the salicylaldimine ligand at ambient temperature. In a further modification the Cl atom in complex **5** is substituted by a pentafluorophenyl group (**6**) *via* the corresponding Grignard reagent. The strong electron-withdrawing properties of the pentafluorophenyl group have proven efficiency in the Pd-catalyzed olefin polymerization.[17]

To further elaborate the function of the labile arene ligand, the Tl salt of the salicylaldimine was exposed to two new Ru precursors; [$RuCl_2$(NBD)]$_n$ and [$RuCl_2$(COD)]$_x$ (NBD = 2,5-norbornadiene and COD = 1,5-cyclooctadiene), in dichloromethane at room temperature (**7**, **8**).



5 L = Cl
6 L = C_6F_5

7 diolefin = nbd, R^1 = *t*-Bu, R^2 = *i*-Pr
8 diolefin = COD, R^1 = *t*-Bu, R^2 = *i*-Pr

The Raman spectra of complexes **7** and **8** showed two strong bands at 259 and 253 cm^{-1} assignable to ν(RuCl) modes of bridging chlorine atoms. The formation of the neutral 18-electron complexes **7** and **8** is in agreement with the high tendency of arene, COD and NBD complexes to form (μ-Cl)$_n$ (n = 2, 3) structures.[18] Due to the reduced symmetry of **7** and **8** four discrete signals of the C atoms of the norbornadiene and the COD ligand appeared in the ^{13}C NMR spectrum at 145.88, 140.15, 139.84, 135.14 ppm and 84.9, 84.5, 78.1, 79.6 ppm respectively.

In a first set of experiments a ROMP reaction was targeted and therefore catalysts **5**–**8** were mixed in a glass vessel with 225 equivalents of norbornene in 5 mL CH_2Cl_2 at two temperature levels, namely 25 and 85 °C. After 18 h the polymers were precipitated in methanol and dried. The results of these experiments are summarized in Table 1.

From these results it is seen that only catalyst **6** gives detectable conversions at room temperature after a period of 18 h. Rising the temperature to 85 °C has a pronounced effect on the total conversion of all the systems. The pentafluorophenyl catalyst (**6**) is still the most active catalyst (86%) and among the Cl systems the highest conversions are obtained with the cyclo-diolefin coordinated one (69% with **8** and 50% with **7**). The improvement of the catalytic metathesis activity by addition of organoaluminium compounds is well-illustrated in the literature for W, Mo, Ti and Re systems.[2] The most used co-catalysts are Me_3Al, $EtAlCl_2$ and Et_2AlCl. In the current study, the best results are obtained with Et_2AlCl as co-catalyst (Cat/Al = 1/6) and the great impact on the conversion can be seen in Table 1. For catalysts **5** and **6**, quantitative conversions are reached whereas for catalysts **7** and **8**, respectively, conversions of 87% and 88% are obtained. A polymerization with just Et_2AlCl and norbornene was performed as a "blank" reaction but no polymers were detected after 18 h. This observation clearly demonstrates that the combination of a Ru complex (**5**–**8**) and the aluminium compound is responsible for the metathesis activity. The properties of the polyNBE produced with the best performing catalyst are also depicted in Table 1. From these results it is clearly seen that lower molecular weights are obtained when a co-catalyst is used. Furthermore, quite narrow polydispersities are observed at room temperature ($M_w/M_n = 1.11$ and 1.53) whereas at 85 °C typical polydispersity values of 2 are measured. A preference for the *trans*-configuration in the polyalkenamer (75%) is in agreement with previously reported results.[15] The fraction of Ru species that is active during the polymerization is very low. This is indicated by the very low initiator efficiencies that are situated in the range of 1 and 2% for the polymerizations performed at room temperature and between 2 and 5% for the reactions done at 85 °C. Since no carbene entity was present at the start of the reaction it has to be generated *in situ* (self-activation) and this is most probably the reason for the low initiator efficiencies. Et_2AlCl can facilitate this carbene generation since the initiation efficiencies are two times higher but they still remain very low.

The arene ruthenium complex **6** was also treated with 3 equivalents of TMSD to generate a Ru-carbene. However, a conversion of 77% was reached which is not higher than in the case when no activator is used and the polymer exhibits a very broad molecular weight distribution ($M_w/M_n = 3.84$). The broadening of the molecular weight distribution is caused by the generation of multi-reactive sites (those activated *in situ* and those activated by TMSD) and this tendency was previously reported.[15a] These results show that activation of the Schiff base-ruthenium complexes with TMSD is not the ideal technique to create an active ROMP catalyst.

To further explore the catalytic potential of complexes **5**–**8** concerning the ROMP of norbornene, the substrate/catalyst ratio was increased and the results are given in Table 2.

Catalyst **6** preserves best its activity with varying substrate/catalyst ratios and only after 3000 equivalents does the conversion start to decrease. The conversion slightly increases for catalysts **7** and **8**, as the substrate/catalyst ratio is driven up to 900 equivalents norbornene with a maximum conversion of, respectively, 91% and 99%. High molecular weight polymers are generated

Table 1. ROMP of norbornene at two temperatures using catalysts **5**–**8**.

	5	**6**				**7**	**8**
Temperature	Yield [%]	Yield [%]	M_n [× 10^3]	M_w/M_n	*cis/trans*	Yield [%]	Yield [%]
25 °C[a]	< 5	73	2507	1.11	0.44	< 5	< 5
85 °C[a]	35	86	781	2.02	0.43	50	69
25 °C[b]	94	100	1328	1.53	0.39	62	73
85 °C[b]	100	100	451.5	2.06	0.33	87	88

[a] $[norbornene]_0 = 0.8$ M; $[Ru]_0 = 3.56$ mM; 5 mL CH_2Cl_2; 18 h.
[b] $[norbornene]_0 = 0.8$ M; $[Ru]_0 = 3.56$ mM; $[Et_2AlCl]_0 = 21.4$ mM; 5 mL CH_2Cl_2; 18 h.

Table 2. Influence of the norbornene/Ru ratio on the ROMP of norbornene at 85 °C with Et_2AlCl using catalysts **5**–**8**.[a]

	5	**6**				**7**	**8**
Equivalents	Yield [%]	Yield [%]	M_n [× 10^3]	M_w/M_n	*cis/trans*	Yield [%]	Yield [%]
225	100	100	451	2.06	0.33	87	88
450	100	100	1364	1.32	0.32	90	96
900	92	100	1994	1.32	0.49	91	99
1500	86	100	1436	1.42	0.45		
3000	85	98	1341	1.35	0.30		
6000	81	93	1356	1.33	0.32		

[a] $[norbornene]_0 = 0.8$ M; $[Ru]_0 = 3.56$ mM; $[Et_2AlCl]_0 = 21.4$ mM; 5 mL CH_2Cl_2; 18 h.

which remain constant at higher substrate/catalyst ratios and a narrow polydispersity is preserved ($M_w/M_n = 1.35$). This tendency is quite interesting because the initiator efficiency increase from 4.7% (225 equiv.) to 40% (6000 equiv.) indicating that when higher monomer concentrations are used, more active carbene species can be generated.

The evolution of the conversions with the time are depicted in Figure 2 with a norbornene/ruthenium ratio of 800. From Figure 2 it is obvious that catalyst **6** is the most active system since a quantitative conversion is reached after 15 min. ($k_{app} = 99.8 \times 10^{-5}\ s^{-1}$). The polymerization with the COD coordinated system (**8**) proceeds twice as fast as the NBD coordinated congener (**7**) ($k_{app,\mathbf{7}} = 4.1 \times 10^{-5}\ s^{-1}$ and $k_{app,\mathbf{8}} = 8.0 \times 10^{-5}\ s^{-1}$) and leads to the highest conversion of both systems (73% versus 60%).

In order to elucidate the propagating species in this reaction a polymerization was monitored with ^{1}H NMR. For this purpose, 0.1 mmol of catalyst **5** and **6** was transferred into a NMR tube and 1 mL of a norbornene solution was added (0.5 M in CD_2Cl_2). The reaction mixture was monitored during 12 h at room temperature. As soon as the monomer was added a doublet appeared at 23.35 ppm (**6**) and 20.39 ppm (**5**) which can be assigned to the carbene proton. After the reaction, the generated carbene was converted into a Fischer carbene using ethyl vinyl ether [^{1}H NMR: 15.01 (**6**) and 14.90 ppm (**5**)]. The homogeneous catalyst which is an 18-electron complex, catalyzes the polymerization of norbornene, through the loss of a *p*-cymene ligand followed by coordination of norbornene. Finally, a 2,3-hydrogen shift generates a ruthenium carbene species which propagates the ROMP (Scheme 2).[15a] The ruthenium-carbene peak could be integrated for about 1.6% of the total ruthenium in solution. This observation is in agreement with the amount of free *p*-cymene released in solution and with the calculated initiator efficiency of 1.5%. The role of the aluminium compound is not unambiguously clear, we assume that it stabilizes the 14-electron intermediate and facilitates the formation of the carbene.

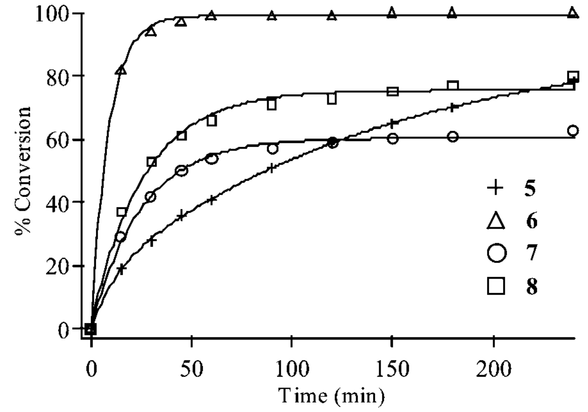
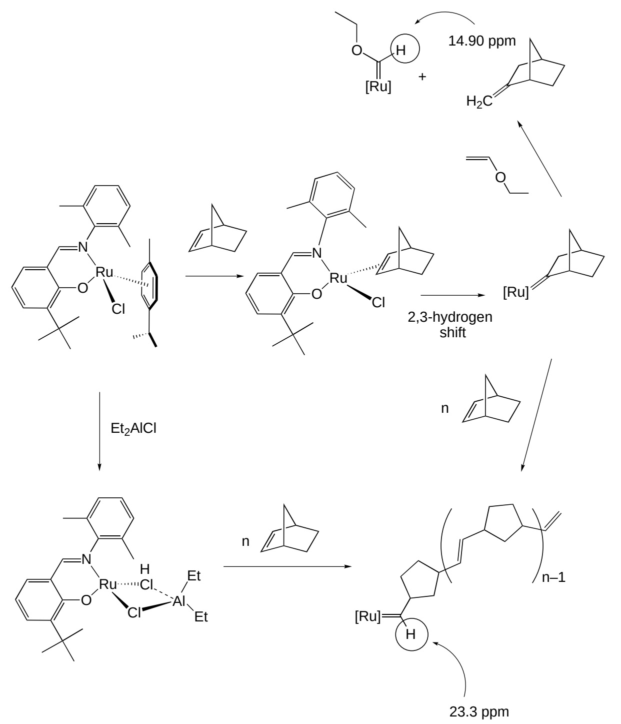


Figure 2. Conversion curve of the ROMP of norbornene using catalysts **5**–**8** (800 equiv. norbornene).



Scheme 2. Possible mechanism for the formation of the initial metal carbene.

To broaden the scope of our study on ruthenium(II)-Schiff base complexes, the catalysts **5**–**8** were also tested for the ATRP of two representative vinyl monomers, namely styrene and methyl methacrylate (MMA) and the results are summarized in Table 3. The initiators were (1-bromoethyl)styrene and 2-bromo-2-methylpropionate, respectively, and this because of the structure analogy with the propagating chain-end.

Complexes **5** and **6** gave moderate yields for the ATRP of styrene (51 and 45%) while they remain almost inactive for promoting the ATRP of MMA (33 and 7%). The other two complexes, **7** and **8**, display a very low activity for both monomers. The properties of the obtained polymers are depicted in Table 4. Quite broad molecular weight distributions are obtained with systems **5** and **6**, indicating a poor control over the polymerization. This tendency was also recognized in the ATRP with Rh-dimer species.[19] The observed low values of the initiator efficiency point to participation of some inevitable side reactions in the overall polymerization process. In general, side reactions are more probable at the beginning of polymerization. At the beginning the formed radicals are still small and therefore mobile enough to escape from a solvent cage shared with their catalyst species counterparts. If initiation is slower relative to propagation and the mobile initiator species combine *via* radical combination, then a loss in initiator efficiency is the result. We already demon-

Table 3. ATRP of MMA and styrene using systems **5**–**8**.[a]

Monomer	Additive	**5**	**6**	**7**	**8**
MMA	None	33	7	10	12
	Al(O-*i*-Pr)	27	86	24	20
	$(n\text{-Bu})_2NH$	44	100	53	56
Styrene	None	51	45	13	12
	Al(O-*i*-Pr)	14	76	60	48
	$(n\text{-Bu})_2NH$	42	100	99	66

[a] Reaction conditions: [Monomer]:[Ru]:[In]:[Additive] = 800:1:2:4, 85 °C (MMA), 110 °C (styrene), 17 h.

strated that changing the substituents on the Schiff base ligand can alter the molecular weight and polydispersity.[15]

It is also known from literature that too bulky substituents on a Schiff base ligand can result in a less-controlled ATRP reaction and since the ligands in **5** and **6** are quite bulky this is maybe the reason for the poor control.[20]

In the case of the dinuclear Ru-catalyst species (**7**, **8**), still another, more facile mechanism of termination of growing radicals can be considered. Potentially, two dormant species can be activated in the same time interval in one solvent cage. Since probability of termination of two free radicals occurring in the same solvent cage is very high, the above event can be regarded as one possible mechanism of the initiator deactivation. Therefore, an *in situ* dissociation of dinuclear catalyst species (which are stable for long times in air) to mononuclear ones could bring a desired increase of the initiator efficiency. We thought that this could be performed by adding appropriate additives to the reaction mixture.

In an attempt to increase the activity and control over the process, $Al(O\text{-}i\text{-}Pr)_3$ and $(n\text{-Bu})_2NH$ were added to the reaction mixture and the results are also depicted in Table 3. These components were chosen based on the promising results of Sawamoto.[10b,21] Addition of 4 equivalents of these activators (catalyst/activator = ¼) has a spectacular influence on the activity of all Ru-catalysts. For instance, for complex **7** the conversion increases from 10 to 53% for MMA and from 13 to 99% for styrene when $(n\text{-Bu})_2NH$ is used. Another remarkable example is complex **6** where quantitative yields are found for both monomers with $(n\text{-Bu})_2NH$. The additive $Al(O\text{-}i\text{-}Pr)_3$ is less effective and this in both cases, as only conversions of 86 (**6**) and 24% (**7**) were obtained for MMA and 76 (**6**) and 60% (**7**) for styrene. The properties of the polymers are depicted in Table 4. From these results it is seen that the molecular weight distribution strongly depends on whether any additive is used. The polydispersities of the formed polymers have very broad polydispersities when no additives are used. For instance the polydispersities of the PMMA produced with catalysts **6** and **7** are, respectively, 1.53 and 1.57 whereas the polydispersities are 2.01 and 3.07 for the polystyrene samples. These values decrease when an additive is used and it is more significant for $(n\text{-Bu})_2NH$. In this way the polydispersities for the PMMA obtained with this additive are 1.51 and 1.50 for systems **6** and **7**, the corresponding values for the polystyrene samples are 1.83 and 1.77. In an analogous way the initiator efficiencies increase from 0.02 to 0.21 (**6**) and from 0.29 to 0.36 (**7**) for the polymerization of MMA. For the polymerization of styrene these discrepancy is very clear for catalyst **6** as the initiator efficiencies increase from 0.30 to 0.85. From these observations it is clear that $(n\text{-Bu})_2NH$ acts as the best additive and can help with stabilizing and generating (for the dinuclear systems) the higher oxidation state. This results in a more efficient initiation process and smaller polydispersities.

Table 4. Properties of the polymers formed via ATRP with catalysts **5**–**8**.

		5			**6**			**7**			**8**		
		M_n [$\times 10^3$][a]	M_w/M_n	*f*[b]	M_n [$\times 10^3$][a]	M_w/M_n	*f*[b]	M_n [$\times 10^3$][a]	M_w/M_n	*f*[b]	M_n [$\times 10^3$][a]	M_w/M_n	*f*[b]
MMA	None	175	1.78	0.08	164	1.53	0.02	14	1.57	0.29	9	1.54	0.53
	Al(O-*i*-Pr)	88	1.73	0.12	126	1.52	0.27	39	1.55	0.25	37	1.53	0.22
	$(n\text{-Bu})_2NH$	112	1.68	0.16	194	1.51	0.21	59	1.50	0.36	49	1.51	0.46
Styrene	None	160	1.95	0.13	62	2.01	0.30	7	3.07	0.78	5	2.80	1.00
	Al(O-*i*-Pr)	80	2.98	0.07	59	1.83	0.54	30	2.22	0.84	23	2.18	0.87
	$(n\text{-Bu})_2NH$	182	1.93	0.10	49	1.83	0.85	53	1.77	0.78	38	1.86	0.73

[a] GPC values determined versus polystyrene and PMMA standards.

[b] f = initiator efficiency = $M_{n,\,theor}/M_{n,\,exp}$ with $M_{n,\,theor} = ([\text{Monomer}]_0/[\text{Initiator}]_0) \times M_{w,\,monomer} \times$ conversion.

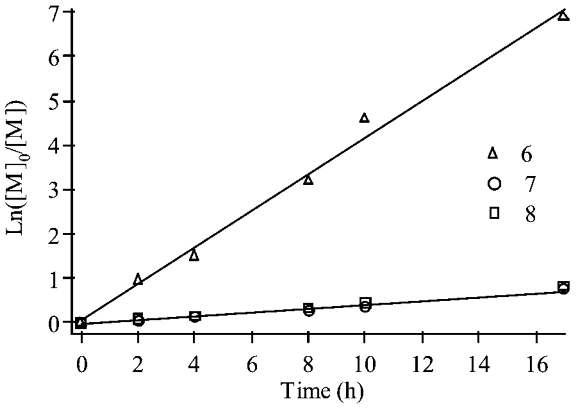


Figure 3. Plot of ln([M]$_0$/[M]) versus time (h) for MMA polymerization mediated by complexes **6–8** at 85 °C. [MMA]$_0$ = 3.74 M, [Ru]$_0$ = 0.00468 M, [In]$_0$ = 0.00928 M, [*n*-Bu$_2$NH]$_0$ = 0.018 M (**6** y = 0.4128x + 0.0482, r^2 = 0.9918; **7** y = 0.0443x – 0.0461, r^2 = 0.9787; **8** y = 0.0438x – 0.025, r^2 = 0.9936).

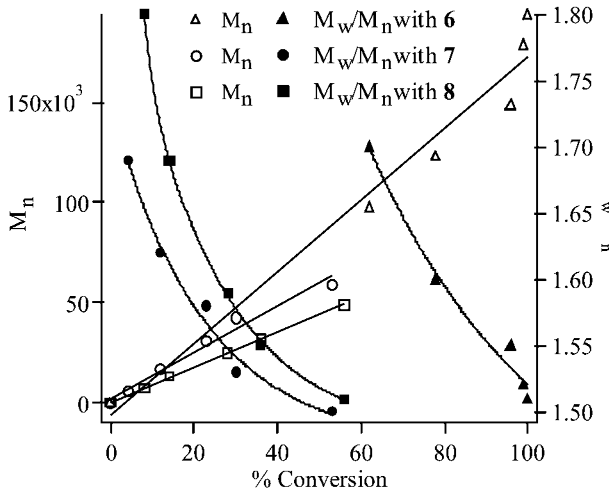


Figure 5. Plot of the PMMA molecular weight versus the monomer conversion mediated by complexes **6–8** at 85 °C. (**6** y = 1785x – 5584, r^2 = 0.96; **7** y = 1140x + 2603, r^2 = 0.976; **8** y = 873x + 394, r^2 = 0.9993).

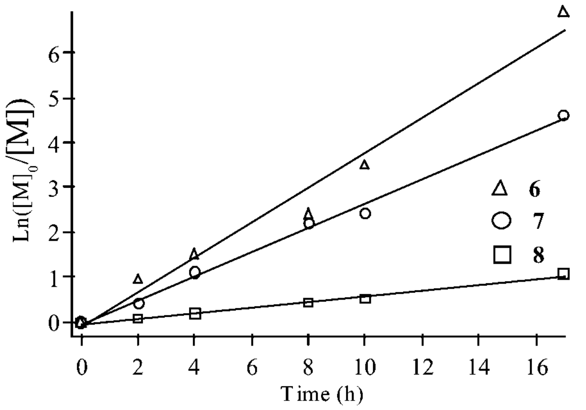


Figure 4. Plot of ln([M]$_0$/[M]) versus time (h) for Styrene polymerization mediated by complexes **6–8** at 110 °C. [St]$_0$ = 3.64 M, [Ru]$_0$ = 0.00455 M, [In]$_0$ = 0.0091 M, [*n*-Bu$_2$NH]$_0$ = 0.018 M. (**6** y = 0.3898x – 0.1133, r^2 = 0.9767; **7** y = 0.077x + 0.021, r^2 = 0.9977; **8** y = 0.0629x – 0.0413, r^2 = 0.9882).

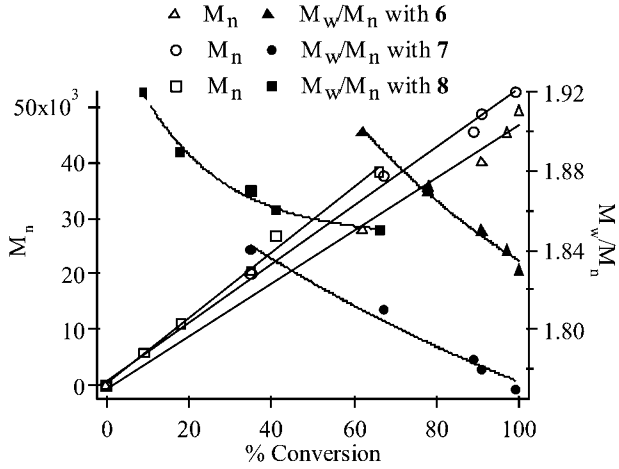


Figure 6. Plot of the PS molecular weight versus the monomer conversion for styrene polymerization mediated by complexes **6–8** at 110 °C. (**6** y = 472x – 598, r^2 = 0.9915; **7** y = 521x – 954, r^2 = 0.9956; **8** y = 586x + 560, r^2 = 0.9938).

In the case where (*n*-Bu)$_2$NH is added to the reaction mixture, a linear time dependence of ln([M]$_0$/[M]$_t$) is obtained for the polymerization of MMA (Figure 3) and styrene (Figure 4) with complexes **6–8**. This is consistent with a controlled polymerization and first order in monomer concentration. The linear relationship between M$_n$ and the conversion (Figures 5 and 6) for both monomers with catalyst **6–8** is also in agreement with a controlled process with a constant number of growing chains. Furthermore, the molecular weight distribution (M$_w$/M$_n$) decreased as the polymerization proceeded, indicating that the radicals are long-lived.

The presence of radical intermediates was proven by a total inhibition of the polymerization after addition of 5 equivalents of galvinoxyl. Furthermore, ^{13}C NMR analysis showed that the polymers thus obtained were predominantly syndiotactic (rr:rm:mm = 64:33:3). This tacticity is similar compared to the structure of PMMA radically prepared, for instance, with AIBN.[22]

Conclusion

In conclusion, we succeeded in synthesizing a new class of ruthenium-based catalysts which exhibit good activity in the ROMP of norbornene. The complexes consists of a labile group, e.g., *p*-cymene, norbornadiene and 1,5-cyclooctadiene, a bidentate Schiff base ligand and a substituent of the type Cl or pentafluorophenyl. The highest ROMP activity is reached with the pentafluorophenyl catalyst (**6**) which polymerized norbornene at room temperature without the presence of an initial carbene species. The formed polymers possess a high molecular weight with a narrow molecular weight distribution. Carefully observations indicated that the propagating carbene is generated *in situ* directly from the monomer. The conversions for ROMP can be dramatically improved by adding Et_2AlCl. These complexes showed also moderate to high activity for ATRP of MMA and styrene, especially when they are activated with *n*-Bu_2NH. Under these conditions the pentafluorophenyl catalyst showed the highest activity and best control over the formed polymers.

Furthermore, the fact that these catalysts exhibit good activities in both ROMP and ATRP reactions will make it possible to combine the ROMP and the ATRP methodologies to make block-copolymers with different properties.

Experimental Section

General

All reactions and manipulations were performed under an argon atmosphere using conventional Schlenck-tube techniques. Argon gas was dried by passage through P_2O_5 (Aldrich 97%). ^1H NMR (299.89 MHz) and ^{13}C NMR (75.41 MHz) spectra were recorded on a Varian Unity 300 spectrometer. NMR chemical shifts are reported downfield from tetramethylsilane (TMS) as the internal standard. Elemental analyses were carried out on a Carlo-Erba EA 1110. The molecular weights and the molecular weight distributions of the polymers were determined by gel permeation chromatography ($CHCl_3$, 25 °C) using a Shimadzu CLASS-VP™ system equipped with three serial placed columns (PSS SDV: 30 cm, $\varnothing = 8$ mm, 10^3, 10^4, 10^5 Å) and the calibration was performed using polystyrene standards. IR spectra were taken with a Mattson 5000 FTIR spectrometer. Dichloromethane was dried over CaO, toluene and THF were dried over sodium/benzophenone. These solvents were distilled and stored over molecular sieves (MS 4 Å) under an argon atmosphere. $CDCl_3$ and C_6D_6 were dried over MS 4 Å and stored under argon.

$[RuCl_2(p\text{-cymene})]_2$, $RuCl_2(NBD)_n$ and $RuCl_2(COD)_x$ were prepared according to the literature.[23–25] Norbornene was dried over sodium, vacuum transferred and stored under argon.

Polymerization Procedure

In a typical ROMP experiment 0.005 mmol of the catalyst solution (0.1 M in toluene) was transferred into a 15 mL vessel containing the exact amount of monomer solution in dichloromethane. The reaction mixture was then stirred at 85 °C for different time periods. To stop the polymerization reaction, 2–3 mL of an ethyl vinyl ether/BHT solution was added and the solution stirred till the deactivation of the active species was complete. The solution was poured into 50 mL methanol (containing 0.1% BHT) and the polymers were precipitated and dried in vacuum overnight.

In a typical ATRP experiment 0.0117 mmol of catalyst was placed in a glass tube (in which the air was expelled by three vacuum-nitrogen cycles) containing a magnetic stirring bar and capped by a three-way stopcock. Then the monomer and initiator were added so that the molar ratios [catalyst]/[initiator]/[monomer] were 1/2/800. All liquids were handled under argon with dried syringes. The reaction mixture was then heated for different time periods at the reaction temperature which was 85 °C for MMA and 110 °C for styrene. After cooling, the reaction mixture was diluted in chloroform and poured in 50 mL *n*-heptane (MMA) or 50 mL methanol (styrene) under vigorous stirring. The precipitated polymer was filtered and dried in vacuum overnight.

General Procedure for the Preparation of the Schiff Base Ligand

3-*tert*-Butyl-2-hydroxybenzaldehyde (1.712 mL, 10 mmol), 2,6-diisopropylaniline (1.885 mL, 10 mmol) and a few droplets of formic acid were stirred in refluxing ethanol (35 mL, p.a.) during 6 h. Then the mixture was concentrated by evaporating the solvent under vacuum, and cooled to -20 °C which causes precipitation of the ligand. The crystals were filtered off and dried under vacuum. Yield: 93%. ^1H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 12.36$ (s, 1H, OH), 9.19 (s, 1H, C*H*=N), 7.34–6.67 (m, 6H, arom), 2.96 (sept, 2H, *i*-Pr), 1.56 (s, 9H, *t*-Bu), 1.31 (d, 12H, *i*-Pr); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 167.4$ (s, *C*=N), 160.3 (s, *C*-OH), 146.0 (s, *C*-N), 138.8 (2C, *i*-Pr), 137.5, 130.4, 125.3, 123.0, 118.6, 118.3, 109.2 (arom), 34.9 (3C, *t*-Bu), 28.0 (1C, *t*-Bu), 25.4 (s, 4C, *i*-Pr), 23.2 (s, 2C, *i*-Pr). IR (KBr): $\nu = 3365$, 3031, 2850-2925, 1620, 1569, 1523, 1491, 1467, 1385, 1365, 1113, 930, 660, 450 cm^{-1}.

General Procedure for the Preparation of Thallium Salts

1 g (3 mmol) Schiff base was dissolved in the appropriate solvent (15 mL THF for 5 and 6 and CH_2Cl_2 for 7 and 8) and 5 mL of a TlOEt solution (0.6 M in THF) was slowly added *via* cannula at room temperature. Immediately after the addition, a yellow turbidity is seen and the mixture was stirred for 2 h at room temperature. Filtration of the solid under a nitrogen atmosphere gave the thallium salts in quantitative yields. The salts were immediately used in the next step without further purification.

General Procedure for the Preparation of Ru Schiff Base Complex 5

0.92 g $[RuCl_2(p\text{-cymene})]_2$ (1.5 mmol) was dissolved in THF (15 mL) and subsequently 10 mL of a Tl salt solution (0.3 M in THF) were slowly added. The reaction mixture was stirred at room temperature for 10 h. The generated TlCl was filtered off and washed with cold THF. After evaporation of the solvent, the crude residue was recrystallized from CH_2Cl_2/pentane (-70 °C) to give complex 5 as red-brown solid; yield: 84%. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ (aldimine) $= 7.69$ (s, 1H, C*H*=N), 7.07–6.12 (m, 6H), 2.99 (sept, 2H, *i*-Pr), 1.40 (s, 9H, *t*-Bu), 1.28 (d, 12H, *i*-Pr); δ (*p*-cymene) = 5.10, 4.55, 4.46, 4.39 (all d, 1H), 2.72 (sept, 1H, *i*-Pr), 1.60 (s, 6H), 1.09 (d, 6H, *i*-Pr). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (aldimine) = 161.4, 152.9, 138.96, 133.36, 130.85, 125.74, 123.43, 118.7, 114.42, 35.34, 28.42, 26.52, 23.47; δ (*p*-cymene) = 104.14, 93.64, 86.38, 83.74, 80.69, 78.61, 30.20, 22.40, 17.86. IR (KBr): ν = 3050, 3032, 2956, 2923, 2853, 1920, 1672, 1594, 1536, 1467, 1447, 1376, 1347, 757 cm^{-1}; anal. calcd. for $RuC_{33}H_{44}NOCl$: C 65.27, H 7.30, N 2.31%; found: C 65.40, H 7.52, N 2.49%.

General Procedure for the Preparation of Ru Schiff Base Complex 6

0.92 g [$RuCl_2$(*p*-cymene)]$_2$ (1.5 mmol) was dissolved in THF (15 mL) and subsequently 10 mL of a Tl salt solution (0.3 M in THF) were slowly added. The reaction mixture was stirred at room temperature for 10 h. The formed TlCl was filtered off and washed with cold THF. The filtrate was cooled in an ice bath and 6 mL (3 mmol) of a pentafluoromagnesium chloride solution (0.5 M in ether) was added dropwise to the stirred solution. The temperature was gradually increased to room temperature where it held with stirring for 4 hours. The formed $MgCl_2$ was filtered off and washed with THF. After evaporation of the solvent, the crude residue was recrystallized from CH_2Cl_2/pentane (–70 °C) to give complex 6 as black solid; yield: 68%. ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (aldimine) = 7.71 (s, 1H, C*H*=N), 6.99–6.14 (m, 6H), 2.77 (sept, 2H, *i*-Pr), 1.46 (s, 9H, *t*-Bu), 1.30 (d, 12H, *i*-Pr); δ (*p*-cymene) = 5.20, 4.72, 4.58, 4.36 (all d, 1H), 2.61 (sept, 1H, *i*-Pr), 1.62 (s, 6H), 1.10 (d, 6H, *i*-Pr). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (aldimine) = 161.4, 152.9, 138.96, 133.36, 130.85, 125.74, 123.43, 118.7, 114.42, 35.34, 28.42, 26.52, 23.47; δ (*p*-cymene) = 104.14, 93.64, 86.38, 83.74, 80.69, 78.61, 30.20, 22.40, 17.86; δ (pentafluorophenyl) = 109.94, 136, 51, 133.19, 147.73. IR (KBr): ν = 3050, 3032, 2956, 2923, 2853, 1920, 1648, 1605, 1537, 1503, 1465, 1433, 1410, 1376, 1347, 1263, 1078, 1030, 801, 749, 720, 566 cm^{-1}; anal. calcd. for $RuC_{39}H_{44}F_5NO$ (738.84): C 63.40, H 6.02, N 1.90%; found: C 63.88, H 6.64, N 2.34%.

General Procedure for the Preparation of Ru Schiff Base Complexes 7 and 8

The appropriate Ru-precursor (0.79 g [$RuCl_2$(NBD)]$_n$, 0.84 g [$RuCl_2$(COD)]$_x$, 3 mmol Ru) was dissolved in CH_2Cl_2 (15 mL) and subsequently 10 mL of a Tl salt solution (0.3 M in CH_2Cl_2) were slowly added. The reaction mixture was stirred at room temperature for 10 h and the TlCl was filtered off. After evaporation of the solvent an oily substance remained which was washed with cold CH_2Cl_2; yield: 63%.

Complex 7: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (aldimine) = 7.70 (s, 1H, C*H*=N), 7.14–6.66 (m, 6H), 2.70 (sept, 2H, *i*-Pr), 1.34 (s, 9H, *t*-Bu), 1.27 (d, 12H, *i*-Pr); δ (NBD) = 6.59 (d, 1H), 6.47 (d, 1H), 4.1 (s, 1H), 3.98 (s, 1H), 3.91 (s, 1H), 3.86 (s, 1H), 1.82 (s, 2H). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (aldimine) = 160.98, 151.36, 140.15, 135.14, 130.91, 126.68, 123.88, 120.52, 113.92, 34.49, 31.17, 27.84, 24.59; δ (NBD) = 145.88, 140.15, 139.84, 135.14, 72.7, 54.94, 50.10. IR (KBr): ν = 3098, 3025, 3032, 2956, 2923, 2853, 1920, 1672, 1594, 1536, 1467, 1409, 1310, 1240, 1180, 1160, 1085, 1035, 1000, 941, 863, 805, 757 cm^{-1}; anal. calcd. for $Ru_2C_{60}H_{76}N_2O_2Cl_2$ (1130.32): C 63.76, H 6.78, N 2.48%; found: C 63.93, H 7.13, N 2.98%.

Complex 8: ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ (aldimine) = 7.69 (s, 1H, C*H*=N), 7.07–6.12 (m, 6H), 2.99 (sept, 2H, *i*-Pr), 1.40 (s, 9H, *t*-Bu), 1.28 (d, 12H, *i*-Pr); δ (*p*-cymene) = 5.10, 4.55, 4.46, 4.39 (all d, 1H), 2.72 (sept, 1H, *i*-Pr), 1.60 (s, 6H), 1.09 (d, 6H, *i*-Pr). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ (aldimine) = 161.4, 152.9, 138.96, 133.36, 130.85, 125.74, 123.43, 118.7, 114.42, 35.34, 28.42, 26.52, 23.47; δ (*p*-cymene) = 104.14, 93.64, 86.38, 83.74, 80.69, 78.61, 30.20, 22.40, 17.86. IR (KBr): ν = 3050, 3032, 2956, 2923, 2853, 1920, 1672, 1594, 1536, 1467, 1447, 1376, 1347, 757 cm^{-1}; anal. calcd. for $Ru_2C_{62}H_{84}N_2O_2Cl_2$ (1162.39): C 64.06, H 7.28 N 2.41%; found: C 64.56, H 7.79, N 2.89%.

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References

[1] M. Szwarc, *Nature* **1956**, *251*, 1168.

[2] K. J. Ivin, J. C. Mol, *Olefin metathesis and metathesis polymerization*, Academic Press, San Diego, **1997**.

[3] a) R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* **1990**, *112*, 3875; b) R. R. Schrock, R. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan, A. H. Liu, *J. Am. Chem. Soc.* **1988**, *110*, 1423.

[4] a) S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974; b) S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858.

[5] a) P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039; b) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100; c) A. Kinishita, N. Sakakibara, M. Mori, *J. Am. Chem. Soc.* **1997**, *119*, 12388; d) A. Fürstner, K. Langemann, *Synthesis* **1997**, 792.

[6] a) A. Fürstner, M. Piquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315; b) H. Katayama, F. Ozawa, *Chem. Lett.* **1998**, 67; c) A. Demonceau, A. W. Stumpf, E. W. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127.

[7] a) K. Matyjaszewski, *Controlled Radical Polymerization*, American Chemical Society: Washington, DC, Vol. 685, **1998**; b) K. Matyjaszewski, *Controlled/Living Radical Polymerization: Progress in ATRP, NMP and RAFT*, American Chemical Society, Washington, DC, Vol. 768, **2000**.

[8] D. H. Solomon, E. Rizzardo, P. Cacioli, *U. S. Patent* 4,581,429.

[9] C. L. Moad, G. Moad, E. Rizzardo, S. H. Tang, *Macromolecules* **1996**, *29*, 7717.

[10] a) M. Kato, M. Kamigaito, M. Sawomoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721; b) T. Ando, M. Kato, M. Kamigaito, M. Sawamoto, *Macromolecules* **1996**, *29*, 1070.

[11] a) J. S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc*. **1995**, *117*, 5614; b) J. S. Wang, K. Matyjaszewski, *Macromolecules* **1995**, *28*, 7901.

[12] a) M. Sawomoto, M. Kamigaito, *Chemtech* **1999**, *29*, 30; b) K. Matyjaszewski, J. Xia, *Chem. Rev*. **2001**, *101*, 2921; c) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689.

[13] T. Naota, H. Takaya, S. I. Murahashi, *Chem. Rev*. **1998**, *98*, 2599.

[14] a) B. De Clercq, F. Verpoort, *Tetrahedron Lett*. **2001**, *42*, 8959; b) F. Simal, S. Delfoss, A. Demonceau, A. F. Noels, K. Denk, F. Kohl, T. Weskamp, W. A. Herrmann, *Chem. Eur. J.* **2002**, *8*, 3047; c) F. Simal, L. Delaude, D. Jan, A. Demonceau, A. F. Noels, *Polym. Prep* **1999**, *40*, 336; d) T. Opstal, F. Verpoort, *New J. Chem*. **2003**, *2*, 257.

[15] a) B. Declercq, F. Verpoort, *J. Mol. Cat. A: Chemical* **2002**, *180*, 67; b) B. De Clercq, F. Verpoort, *Macromolecules* **2002**, *35*, 8943.

[16] A. W. Stumpf, E. Saive, A. Demonceau, A. F. Noels, *J. Chem. Soc. Chem. Commun*. **1995**, 1127.

[17] A. Sen, *Pure Appl. Chem*. **2001**, *73*, 251.

[18] a) A. C. da Silva, H. Piotrowski, P. Mayer, K. Polborn, K. Severin, *Eur. J. Inorg. Chem.* **2001**, 685; b) F. H. Jardine, in *Progress in Inorganic Chemistry*, vol. 31, (Ed.: S. J. Lippard), John Wiley & Sons, New York, **1984**, p 265; c) T. Arthur, J. A. Stephenson, *J. Organomet. Chem.* **1981**, *208*, 369.

[19] T. Opstal, J. Zedník, J. Sedláček, J. Svoboda, J. Vohlídal, F. Verpoort, *Collect. Czech. Chem. Commun*. **2002**, *67*, 1858.

[20] D. M. Haddleton, M. C. Crossman, B. H. Dana, D. J. Duncalf, A. M. Heming, D. Kukulj, A. J. Shooter, *Macromolecules* **1999**, 32, 2110.

[21] S. Hamasaki, M. Kamigaito, M. Sawamoto, *Macromolecules* **2002**, *35*, 2934.

[22] F. A. Bovey, *Acc. Chem. Res.* **1968**, *1*, 175.

[23] M. A. Bennet, A. K. Smith, *J. Chem. Soc. Dalton Trans.* **1974**, 233.

[24] E. W. Abel, M. A. Bennett, G. Wilkinson, *J. Chem. Soc.* **1959**, 3178.

[25] M. A. Bennett, G. Wilkinson, *Chem. Ind. (London)* **1959**, 1516.