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A New Ruthenium Complex with an Electron-Donating Aminoindenyl Ligand for Fast Metal-Mediated Living Radical Polymerizations

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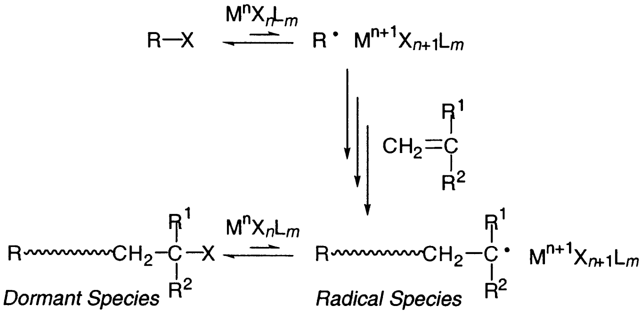
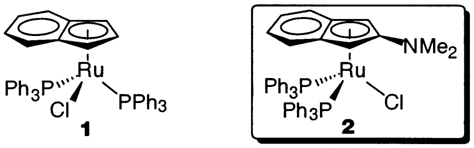
Living radical polymerization is now achieved via various approaches based on the reversible activation of dormant species into growing radicals by stimuli such as heat, light, or catalysis; the dormant species are covalent precursors from which the growing radicals may be generated, reversibly and selectively.[1] Among these approaches, the metal-catalyzed system[1a,b,2−6] owes its wide applicability and fine controllability to the catalyst performance in the equilibria, and therefore the advent of new efficient, active, versatile, and well-defined catalysts is awaited for further developments. The role of the catalysts is to generate the growing radical species from the dormant counterpart reversibly via the single-electron redox cycle accompanying reversible abstraction of the halogens at the dormant polymer terminals, which can react with monomers to undergo propagation only during the activated period (Scheme 1). For control of the polymer chain length, the metal catalysts should induce the reversible process more frequently than the propagation. This leads to a hypothesis that a metal catalyst with a low redox potential or high electron density is suited, because upon activation it should give one electron to the dormant polymer chain.[7−9]

Scheme 1



Ruthenium can take a wide range of oxidation states (from −2 to +8), and its complexes have been employed for various catalytic reactions where the oxidation states are changed efficiently and reversibly.[10] The use of ruthenium complexes for a single electron redox cycle dates back to Kharasch addition reactions with $RuCl_2(PPh_3)_3$.[11] More recently, we have discovered living radical polymerizations of methyl methacrylate (MMA) with the use of this[2] and other related complexes such as a more active indenyl derivative [**1**; $Ru(Ind)Cl(PPh_3)_2$, Ind = η^5-C_9H_7] (Chart 1).[12] One of the features of these half-metallocene complexes is that the anionic cyclopentadiene (Cp′)-based ligands can donate electrons to the metal center via strong interaction, in comparison to neutral ligands that may be labile in some cases. In fact, excellent organic reactions are mediated by ruthenium Cp′ complexes.[10b] Some Cp′ complexes bearing a heteroatom via a bridged alkyl substituent on Cp′ have been synthesized.[13]

Chart 1



This study is thus to design and employ a new ruthenium complex [**2**, $Ru(2\text{-}Me_2N\text{-}Ind)Cl(PPh_3)_2$] with an indenyl ligand that carries an electron-donating dimethylamino group. To our knowledge, there have been no reports on the synthesis and catalysis of a ruthenium complex with such an aminoindenyl ligand. We herein employed the complex **2** for living radical polymerizations of methyl methacrylate (MMA), styrene, and methyl acrylate (MA) to show its high catalytic activity, versatility, and fine reaction controllability.

The complex **2** was prepared from the lithium salt of *N*-(1H-2-indenyl)-*N*,*N*-dimethylamine[14] and $RuCl_2(PPh_3)_3$ in toluene at 90 °C. Figure 1 shows the crystal structures of **2** and its parent form **1**. The aminoindenyl ligand is most probably η^5-coordinated as indicated by the small slip parameter ($\Delta = 0.0320$ Å).[15] The corresponding parameter for **1** ($\Delta = 0.2053$ Å) is clearly larger, which shows a slight distortion of the indenyl ring from η^5- toward η^3-coordination, while much smaller than those for a typical η^3-coordination ($\Delta = 0.69-0.80$ Å).[15] In contrast, the hinge angle[15] was larger in **2** than in **1** (12.6° vs 7.7°). The sum of the three bond angles around the nitrogen atom in **2** was 357.16°, which suggested planar geometry at the nitrogen and that the lone pair was cross-conjugated into the indenyl ring. The bond lengths between the ruthenium and the two phosphorus were 2.3338 and 2.3168 Å, longer than those in **1** (2.3306 and 2.2618 Å, respectively). This may indicate that **2** can readily transform from the original 18-electron form into a more active 16-electorn complex via release of one of the phosphine ligands.

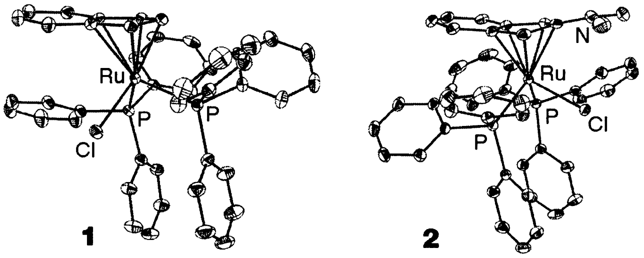


Figure 1. ORTEP diagrams of **1** and **2** (thermal ellipsoids at the 50% level).

For example, cyclic voltammetric analysis of **2** showed a highly reproducible wave corresponding to the Ru(II)/Ru(III) conversions

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in several scans. The redox potential ($E_{1/2}$ = 0.42 V) was lower than those of **1** (0.55 V) and a similar pentamethylcyclopentadienyl complex [RuCp*Cl(PPh$_3$)$_2$ (Cp* = η^5-C$_5$Me$_5$)] (0.46 V).[7,16] This also suggests a high activity of **2** for the Ru(II)-mediated radical-generating reactions.

We employed the new ruthenium complex for living radical polymerization of MMA, where an MMA-dimer chloride, (CH$_3$)$_2$C(CO$_2$CH$_3$)CH$_2$C(CH$_3$)(CO$_2$CH$_3$)Cl (**3**),[17] was used as an initiator in conjunction with Al(O*i*-Pr)$_3$ as an activator or a cocatalyst. The polymerization proceeded faster than that with **1**[12] under the same conditions (Figure 2). The number-average molecular weights (M_n) increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one molecule of the initiator generates one living polymer chain. The molecular weight distributions (MWDs) were narrower than those obtained with **1** (M_w/M_n = 1.07 vs 1.13). The polydisperisty index is one of the narrowest for PMMA obtained by living radical polymerizations[1] even with a low amount of catalyst relative to that of initiator ([**2**]$_0$/[**3**]$_0$ = 0.10). The fast polymerization with fine molecular weight control and narrow MWDs shows that the ruthenium complex is effective in increasing not only the polymerization rate but also the interconversion between the dormant and the activated species.

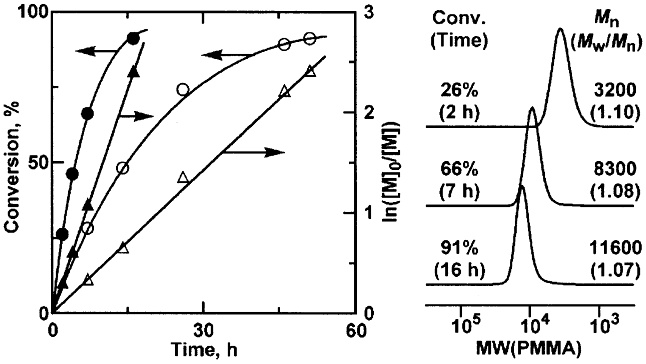

Figure 2. Kinetic plots of the living radical polymerization of MMA with Ru(II) complex **1** (○, △) or **2** (●, ▲) coupled with **3** (initiator)/Al(O*i*-Pr)$_3$ in toluene at 80 °C and size-exclusion chromatograms of the polymers obtained with **2**/**3**/Al(O*i*-Pr)$_3$; [M]$_0$/[**1** or **2**]$_0$/[**3**]$_0$/[Al(O*i*-Pr)$_3$]$_0$ = 4000/4.0/40/40 mM.

A much faster polymerization with **2** can be attained with the use of *n*-Bu$_2$NH as the cocatalyst in place of Al(O*i*-Pr)$_3$ (>90% conversion in 10 h vs 16 h; Figure 2).[18] The complex is active even without additives, but the polymerization was obviously slower (92% conversion in 28 h). A high-molecular weight PMMA (M_n = 95 000) with narrow MWDs (M_w/M_n = 1.09) was obtained within 1 day even at a low catalyst concentration (0.80 mM). Thus, the aminoindenyl complex **2** is highly active in living radical polymerization of MMA with chloride initiators.

Polymerizations of styrene and MA were also investigated with **2** in the presence of Al(O*i*-Pr)$_3$ (Table 1). Importantly, the previously reported ruthenium catalysts have been less suited to monomers that generate less reactive dormant polymer terminals with secondary carbon−halogen linkages.[1a] When the chloride initiator **3** was employed, the styrene polymerization with **2** was faster than with **1** and gave narrower MWDs (entry 1 vs 2). With the use of a bromide initiator [(CH$_3$)$_2$C(CO$_2$C$_2$H$_5$)Br, **4**], narrower MWDs were obtained (entry 3). For MA, the MWDs obtained with **2** were broad for initiator **3** (entry 4), whereas they were narrower with **4** or with an iodide initiator [(CH$_3$)$_2$C(CO$_2$C$_2$H$_5$)I, **5**] (entries 5 and 6, respectively). The relatively broad MWDs of polystyrene and poly(MA) with **3** are due to still slow interconversion with the strong secondary carbon−halogen bonds.

Table 1. Polymerization of Styrene and MA[a]

entry	monomer	catalyst	initiator	time, h	conv, %	M_n	M_w/M_n
1	styrene	**1**	**3**	99	91	11000	1.88
2	styrene	**2**	**3**	33	91	9600	1.26
3	styrene	**2**	**4**	38	91	9000	1.22
4	MA	**2**	**3**	64	94	9600	2.33
5	MA	**2**	**4**	38	92	7700	1.47
6	MA	**2**	**5**	61	95	9400	1.32

[a] [M]$_0$/[initiator]$_0$/[catalyst]$_0$/[Al(O*i*-Pr)$_3$]$_0$ = 4000/40/4.0/40 mM; in toluene at 100 (styrene) or 80 (MA) °C.

In conclusion, a new ruthenium complex (**2**) with an electron-donating aminoindenyl ligand has a low redox potential and is highly active and versatile in living radical polymerization. Catalyst development based on ligand design is being pursued further in our laboratory.

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Supporting Information Available: The synthetic and spectroscopic data of **2**, additional polymerization results, and experimental procedures (PDF) and X-ray crystallographic data (CIF) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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