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[5] In a separate experiment, we confirmed that 1-(2-ethyl-3-methylquinolin-6-yl)ethanone (0.20 mmol) reacted with tripropylamine (1.0 mmol) in the presence of $RuCl_3 \cdot nH_2O$ (0.02 mmol) and PPh_3 (0.06 mmol) in dioxane (5 mL) at 180 °C for 40 h to afford 1-(2-ethyl-3-methylquinolin-6-yl)pentan-1-one in 51 % yield, and $SnCl_2 \cdot 2H_2O$ proved to be unnecessary for the alkylation.

[6] For example, ^{1}H NMR (400 MHz) analysis of the crude reaction mixture of **1a** and **2a**, after usual workup prior to separation, showed no signal for the methine proton of an α,α-dialkylated ketone.

[7] Treatment of equimolar amounts of **1b** and **2a** under the usual conditions gave 2-methyl-1-phenylhexan-1-one (**3f**) in only 5 % yield, and the yield of **3f** was not improved at much longer reaction times.

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Half-Metallocene Tantalum Complexes Bearing Methyl Methacrylate (MMA) and 1,4-Diaza-1,3-diene Ligands as MMA Polymerization Catalysts**

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Well-defined organometallic complexes were recently reported to be single-site catalysts for the polymerization of various monomers.[1] While enolate complexes of zirconium,[2–5] yttrium,[6] and samarium,[7, 8] as well as aluminum enolate complexes with Schiff base[9] or porphyrin[10] ligands, have been reported to be active initiators for the polymerization of polar olefinic monomers such as methyl acrylate (MA) and methyl methacrylate (MMA), enolate complexes of other transition metals have not been utilized. We sought a new metal enolate complex that can initiate polymerization of these polar monomers. Since Group 5 metals tolerate polar functional groups and are less oxophilic than the metals of Groups 3 and 4, we chose half-metallocene complexes of tantalum, cationic alkyl and alkylidene derivatives of which have already been applied in the living polymerization of ethylene[11] and stereoselective ring-opening metathesis polymerization of norbornene[12]. Here we report a novel tantalum initiator system and a new approach to generating catalytically active enolate species from monomer-coordinated complexes. We prepared and characterized new half-metallocene complexes of tantalum with MMA and 1,4-diaza-1,3-butadiene (DAD)[13, 14] ligands, and the tantalum–MMA complexes, upon addition of one equivalent of $AlMe_3$, were found to be catalysts for the polymerization of MMA.

Scheme 1 shows the preparation of tantalum–MMA complexes from [Cp*$TaCl_4$] (**1**; Cp* = η^5-C_5Me_5). Reduction of **1** with sodium amalgam in toluene followed by addition of MMA afforded the MMA complex [Cp*$TaCl_2$(η^4-*supine*-MMA)] (**2**), which was alternatively prepared by treatment of the dinuclear Ta^{III} complex [{Cp*$TaCl_2$}$_2$] (**3**)[15] with MMA. The structure of **2**[16] (Figure 1) is essentially the same as that of [Cp*$TaCl_2$(η^4-*supine*-MA)].[17] Reaction of **2** with one equivalent of the dilithium salt of 1,4-bis(*p*-methoxyphenyl)-1,4-diaza-1,3-butadiene (*p*-$MeOC_6H_4$-DAD) or the dilithium salt of 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (Cy-DAD) in THF afforded the half-sandwich DAD complexes of tantalum **4** and **5**, respectively. The ^{1}H NMR spectra of **4** and **5** displayed two doublets at $\delta = 6.67$ and 6.84 ($J = 3.4$ Hz) for **4**

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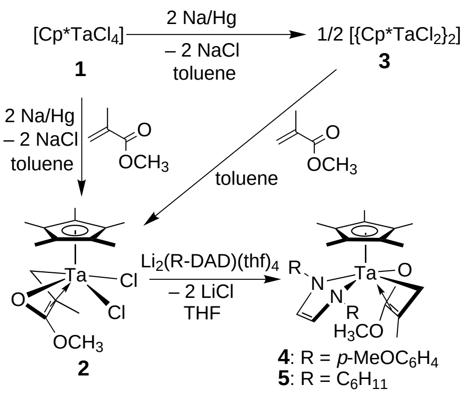


Scheme 1. Synthesis of **4** and **5**.

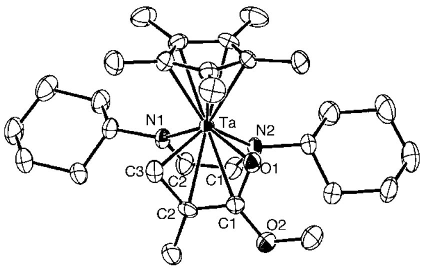


Figure 2. Molecular structure of **5**. Selected bond lengths [Å] and angles [°]: Ta-O1 2.116(4), Ta-C1 2.527(7), Ta-C2 2.460(7), Ta-C3 2.207(7), Ta-N1 2.098(6), Ta-N2 2.101(6), O1-C1 1.310(10), C1-C2 1.372(8), C2-C3 1.49(1); O1-Ta-C3 78.2(2), N1-Ta-N2 75.0(2), MMA fold angle: 111.8(3), DAD fold angle: 159.7(2).

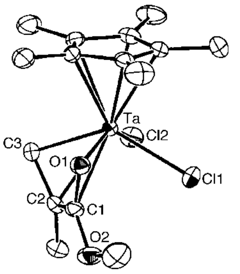


Figure 1. Molecular structure of **2**. Selected bond lengths [Å] and angles [°]: Ta-O1 2.043(3), Ta-C1 2.419(5), Ta-C2 2.403(5), Ta-C3 2.174(5); O1-Ta-C3 76.3(2), Cl1-Ta-Cl2 85.39(5), MMA fold angle: 104.2(3).

and $\delta = 6.44$ and 6.71 ($J = 2.4$ Hz) for **5** due to magnetically inequivalent N=CH protons of the DAD ligand. These chemical shifts together with the characteristic intense red color due to a ligand-to-metal charge-transfer band ($\lambda_{max} = 512$ nm for **4**; 534 nm for **5**) suggest that the DAD ligand adopts an η^2-*N,N′*-enediamido structure.[18, 19] Figure 2[20] clearly shows that the half-metallocene tantalum fragment is coordinated by an η^2-*N,N′*-enediamido Cy-DAD ligand and an η^4-*supine*-MMA ligand. The nitrogen atoms of the Cy-DAD ligand [sums of angles: 359.7° (N1) and 359.9° (N2)] have a trigonal-planar coordination sphere so that the filled p_π orbitals of the nitrogen atoms interact laterally with the empty d_π orbital of the tantalum center.

Table 1 summarizes the results of the polymerization of MMA with tantalum MMA complexes as catalyst precursors and alkylaluminum compounds as cocatalysts. The MMA complexes **4** and **5** without the cocatalyst did not have any catalytic activity, and complex **2** in the presence of one equivalent of $AlMe_3$ also exhibited no catalytic activity (entry 1). The catalyst system of highest activity was the combination of **5** and one equivalent of $AlMe_3$ at −20 °C; the polymerization was completed within 10 min to give a PMMA with very narrow polydispersity ($M_w/M_n = 1.10$; entries 10 and 11).[21] Polymerization with **5**/$AlMe_3$ at −30 °C was much slower and proceeded in a living fashion (entries 12 and 13); the M_n of the polymers increased linearly with increasing percentage monomer consumption (Figure 3). The obtained

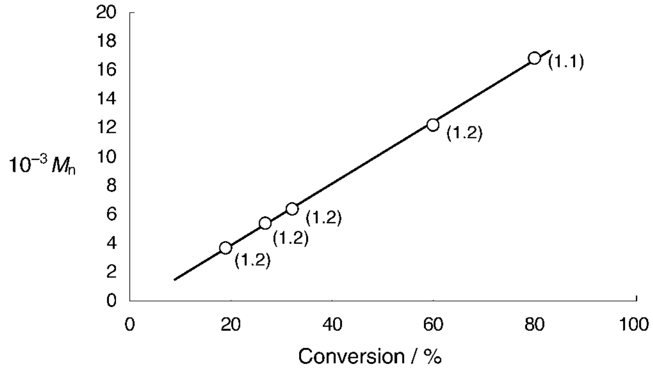


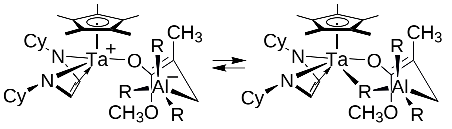
Figure 3. Molecular weight of PMMA, prepared with **5** and one equivalent of $AlMe_3$ as catalyst system at −30 °C versus percentage conversion. The M_w/M_n value for each data point is given in parenthesis.

Table 1. Polymerization of methyl methacrylate with catalysis by tantalum–MMA complexes.[a]

Entry	Precatalyst	Activator	T [°C]	t [min]	Yield[b] [%]	$M_n \times 10^{-3}$[c]	M_w/M_n[c]	Tacticity[d] (mm/mr/rr)
1	**2**	$AlMe_3$	0	300	0	–	–	–
2	**4**	$AlMe_3$	25	300	0	–	–	–
3	**4**	$AlMe_3$	0	90	22	15.6	1.75	1/25/74
4	**4**	$AlMe_3$	0	300	74	34.8	1.83	2/25/73
5	**4**	$AlMe_3$	−20	300	4.2	90.4	1.39	2/25/73
6	**5**	$AlMe_3$	25	300	0	–	–	–
7	**5**	$AlMe_3$	0	60	99	22.0	1.3	2/24/74
8	**5**	$AlEt_3$	0	300	99	20.0	3.0	3/31/66
9	**5**	$AlEt_2Cl$	0	600	0	–	–	–
10	**5**	$AlMe_3$	−20	5	82	18.8	1.11	2/27/71
11	**5**	$AlMe_3$	−20	10	99	21.9	1.10	2/25/73
12	**5**	$AlMe_3$	−30	10	32	6.3	1.20	1/24/75
13	**5**	$AlMe_3$	−30	40	99	24.9	1.23	1/21/78
14	**7**	$AlMe_3$	0	600	0	–	–	–

[a] Polymerizations were conducted in toluene with [precatalyst] = 23.4 mM and [precatalyst]/[activator]/[monomer] = 1/1/100. [b] Yield = weight of polymer obtained/weight of monomer used. [c] Determined by GPC analysis with a polystyrene standard. [d] Determined from ^1H NMR spectra recorded in $CDCl_3$ at 35 °C.

M_n values are approximately twice those calculated on the basis of $[MMA]_0/[initiator]_0$; it is possible that this is due to decomposition of the unstable active species **6** before polymerization is initiated. Increasing the polymerization temperature affected the catalytic activity; at 0 °C the activity of **5** decreased (entry 7) and at 25 °C no polymerization occurred (entry 6). The catalyst system based on **4** was less active than that containing **5** (entries 3–5), and it also exhibited no activity at 25 °C (entry 2); this may be attributable to the electronic effect of the DAD ligand. Such temperature effects can be attributed to the thermal stability of the catalytically active enolate species that is formed on addition of $AlMe_3$ to these MMA complexes. In the case of **5**, the effect of the cocatalyst was examined; both $AlMe_3$ and $AlEt_3$ satisfactorily activated the catalyst precursor (entries 7 and 8), while $AlEt_2Cl$ resulted in no activation (entry 9).



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Controlled experiments gave an insight into the active enolate species. Addition of one equivalent of $AlMe_3$ to **5** in [D$_8$]toluene at room temperature afforded the dimethyl complex [Cp*TaMe$_2$(η^4-Cy-DAD)] (**7**), which was completely inactive in the polymerization of MMA (entry 14) but catalyzed the polymerization of ethylene in the presence of an excess of MAO. On the other hand, addition of one equivalent of $AlMe_3$ to **5** at −20 °C gave the heterodimetallic enolate species **6** together with the dimethyl complex **7** (less than 15%). Compound **6** was tentatively characterized by means of the ^1H NMR spectrum in [D$_8$]toluene, which displayed two broad signals at $\delta = 5.33$ and 6.26 due to the inequivalent N=CH groups of the Cy-DAD ligand and two AlMe signals at $\delta = 0.05$ and 0.45 in a ratio of 1:2. These observations suggest that one of the AlMe groups interacts with the electron-deficient metal center. This enolate species was thermally unstable, and was converted to the dimethyl complex **7** after 1 h at 0 °C. This is in good accordance with the temperature effects observed for the polymerization. Similar insertions of alkylaluminum compounds into zirconocene diene complexes to give heterodimetallic compounds were reported by Erker et al.[22]

In summary, we have demonstrated a new method to generate enolate species from monomer-coordinated tantalum complexes. Tantalum–MMA complexes on treatment with one equivalent of $AlMe_3$ effectively catalyzed the polymerization of MMA. The investigation of the mechanism and the preparation and application of catalyst precursors with other monomers as ligands are under way.

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