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# Polymerization of Ethylene Catalyzed by the System Ta($\eta^5$-$C_5Me_5$)($\eta^4$-diene)($CH_3$)$_2$/MAO: An Isoelectronic Analogue for a Group 4 Metallocene Catalyst

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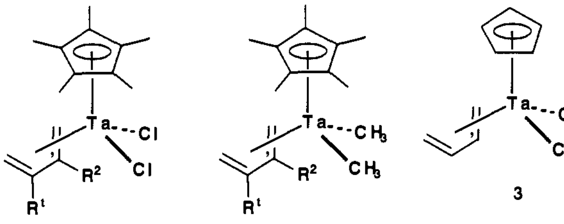
Initiator systems of the type group 4 metallocene/aluminoxane (MAO) have been actively studied for $\alpha$-olefin polymerization.[1-3] Recently, similar catalyst systems with a single-component catalyst such as cationic group 4 metallocenes, the isoelectronic neutral group 3, or lanthanide metallocene hydrides or alkyls were reported.[4-6] Although the polymerization of ethylene has been studied using a catalytic system based on vanadium/alkylaluminum,[7] group 5 metallocene/MAO, *e.g.*, $Cp_2TaCl_2$ or $Cp_2NbCl_2$, was found to have no activity.[8] The group 5 organometallic fragment of the type Cp($\eta^4$-diene)M is isoelectronic to that of group 4 metallocenes $Cp_2M$.[9-11] We have prepared and investigated the reactivity of dialkyls of Cp($\eta^4$-diene)$MR_2$, where M = Nb and Ta.[9b] In this contribution we describe the syntheses and structural characterizations of alkyl tantalum–diene complexes which are thus found to be unique catalyst precursors for the polymerization of ethylene to a polymer ($M_n = \sim 10^{4-5}$) with narrow molecular weight dispersity (MWD).

Halo and alkyl complexes of the type ($\eta^5$-$C_5R_5$)($\eta^4$-diene)$TaX_2$ (R = H and $CH_3$; X = Cl and $CH_3$) in the presence of a large excess of MAO were found to be the catalyst precursors for the polymerization of ethylene (atmospheric pressure), and the results are summarized in Table I. Alkyl complex Cp*($\eta^4$-1,3-butadiene)$TaMe_2$ (Cp* = pentamethylcyclopentadienyl) (**2a**) was prepared by the treatment of Cp*($\eta^4$-1,3-butadiene)$TaCl_2$ (**1a**)[9a,c] with 2 equiv of MeMgI in THF at −78 °C to room temperature. Evaporation of the solvent, extraction of the solid residue with hexane, and recrystallization from a mixture of toluene and hexane gave violet crystals of the dimethyl complex **2a** in 32% yield.[12] Complexes **2b** and **2c** were prepared by the reaction of the corresponding dichloro complexes **1b** and **1c** with 2 equiv of MeMgI, respectively.[12] Similarly, Cp($\eta^4$-1,3-butadiene)$TaMe_2$ (**3**) was prepared by the reaction of Cp($\eta^4$-1,3-butadiene)$TaCl_2$.[13]



1 2 3

a: $R^t = R^2 = H$
b: $R^1 = CH_3$, $R^2 = H$
c: $R^t = R^2 = CH_3$

As a mixture of **2a** (10.6 mg in 19 mL of toluene) and MAO (500 equiv) was gradually warmed from −78 °C to room

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[12] **2a**: 32% yield, mp 162–164 °C dec; $^1$H NMR ($C_6D_6$) $\delta$ −1.08 (m, $H_{1anti}$ and $H_{4anti}$), −0.43 (s, Ta–$CH_3$), 0.09 (m, $H_{1syn}$ and $H_{4syn}$), 1.81 (s, $C_5Me_5$), 6.98 (m, $H_2$ and $H_3$); $^{13}$C NMR ($C_6D_6$) $\delta$ 11.3 ($C_5$*Me*$_5$), 40.0 (Ta–$CH_3$), 56.5 ($C_1$ and $C_4$), 117.0 (*C*$_5$Me$_5$), 119.2 ($C_2$ and $C_3$). **2b**: 50% yield, mp 87–91 °C dec; $^1$H NMR ($C_6D_6$) $\delta$ −1.24 (m, $H_{1anti}$), −0.60 and −0.49 (s, Ta–$CH_3$), −1.03 (m, $H_{4anti}$), −0.35 (m, $H_{1syn}$), 0.17 (m, $H_{4syn}$), 6.60 (m, $H_3$); $^{13}$C NMR ($C_6D_6$) $\delta$ 11.3 ($C_5$*Me*$_5$), 23.3 ($CH_3$), 37.4 and 46.9 (Ta–$CH_3$), 58.0 ($C_1$), 59.7 ($C_4$), 114.0 ($C_3$), 122.3 ($C_2$), 118.9 (*C*$_5$Me$_5$). **2c**: 47% yield, mp 92–94 °C dec; $^1$H NMR ($C_6D_6$) $\delta$ −1.08 (m, $H_{1anti}$ and $H_{4anti}$), −0.68 (s, Ta–$CH_3$), −0.22 (m, $H_{1syn}$ and $H_{4syn}$); $^{13}$C NMR ($C_6D_6$) $\delta$ 11.3 ($C_5$*Me*$_5$), 20.3 ($CH_3$), 44.3 (Ta–$CH_3$), 63.7 ($C_1$ and $C_4$), 116.9 ($C_2$ and $C_3$), 118.5 (*C*$_5$Me$_5$). All complexes gave satisfactory elemental analysis and mass spectra.

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**Table I.** Polymerization of Ethylene Catalyzed by Tantalum–Diene Complexes/MAO[a]

| complex | $t$ (°C) | activity[b] (kg/h·[Ta]mol) | $M_n/10^{4}$[c] | $M_w/M_n$[c] |
|---|---|---|---|---|
| **2a** | 20 | 4.48 | 2.04 | 2.06 |
| **2a** | –20 | 1.18 | 2.55 | 1.08 |
| **2a** | –40 | 0.73 | 0.86 | 1.10 |
| **2b** | 60 | 3.99 | 0.17 | 1.82 |
| **2b** | 20 | 1.60 | 1.23 | 1.65 |
| **2c** | 20 | 5.69 | 1.20 | 2.09 |
| **1a** | 20 | 5.93 | 2.03 | 2.04 |
| **1a** | –20 | 1.51 | 2.03 | 1.16 |
| **1b** | 20 | 1.92 | 1.15 | 1.63 |
| **3** | –20 | 7.07 | 8.18 | 1.40 |
| **3** | –40 | 4.29 | 4.29 | 1.32 |
| **3** | –60 | 0.94 | 1.68 | 1.11 |
| **4**[d] | 0 | 13.03 | 4.88 | 4.39 |

[a] Polymerization reactions were carried out in toluene ($1.44 \times 10^{-3}$ M of [Ta]) in the presence of MAO (500 equiv) for 6 h without other notice. Ethylene (atmospheric pressure) was used. [b] Polymer was methanol-insoluble parts. [c] GPC analysis. [d] Reaction time was 2 h.

temperature under atmospheric pressure of ethylene, the color of the solution changed to yellow. After 6 h at 20 °C, quenching of the reaction by the addition of HCl/MeOH afforded polyethylene (0.71 g, activity = 4.45 kg/h·[Ta]mol). Gel permeation chromatography (GPC) analysis showed the sample to have a relatively narrow molecular weight distribution ($M_n = 2.04 \times 10^4$, $M_w/M_n = 2.06$). Almost the same catalyst property of **1a** ($M_n = 2.03 \times 10^4$, $M_w/M_n = 2.04$) was observed with **2a**.

The catalytic activity for the polymerization of ethylene depends on the structure of the diene. Methyl substitution on the diene unit influenced the catalyst activity of **2**, *i.e.*, 1,3-butadiene ≈ 2,3-dimethyl-1,3-butadiene > isoprene. Thus, activity of the catalyst is controlled by the steric and electronic effect of the diene coordinated to tantalum. The presence of a diene moiety during the catalysis was further supported by the fact that the catalyst system of $Cp^*TaCl_4$/MAO exhibited lower activity for the polymerization of ethylene under similar reaction conditions.[14,15]

When the polymerization of ethylene in the presence of **1a** or **2a**/MAO as catalysts was carried out at lower temperature (–20 °C), the very narrow polydispersities ($M_w/M_n = 1.08$–$1.16$) was observed for high molecular weight polyethylene ($M_n = (2.03$–$2.55) \times 10^4$). Below –20 °C, the polymerization of ethylene by using **2a**/MAO afforded a linear relation in $M_n$ vs time, which suggests that this system has the character of the living polymerization.[16] These polydispersities are extremely narrow compared with that now known to be the narrowest (1.61) of the polyethylene prepared by homogeneous organochromium catalyst $[Cp^*CrMe(thf)_2]^+$.[17]

When Cp was used instead of Cp* ligand, the catalyst activity of **3** for the polymerization of ethylene at –20 °C increased. Moreover, the similar niobium complex CpNb($\eta^4$-2,3-dimethyl-1,3-butadiene)$Cl_2$ (**4**)[9b] in combination with MAO was more active (13.03 kg/h·[Nb]mol at 0 °C) for polymerization of ethylene.

Thus, we demonstrated a catalytic feasibility of group 5–diene complexes for the first time. Further development of the organometallic chemistry of the Cp($\eta^4$-diene)M moiety of group 5 metals is now in progress.

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**Supplementary Material Available:** Experimental details for the preparation of complexes **2** and **3** and polymer characterization (GPC analysis), plot of $M_n$ vs time (4 pages). Ordering information is given on any current masthead page.

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(13) **3**: 33% yield, mp 146–148 °C dec; $^1$H NMR ($C_6D_6$) $\delta$ –0.80 (m, $H_{1anti}$ and $H_{4anti}$), –0.25 (s, Ta–$CH_3$), 0.25 (m, $H_{1syn}$ and $H_{4syn}$), 5.95 (s, Cp), 6.92 (m, $H_2$ and $H_3$); $^{13}$C NMR ($C_6D_6$) $\delta$ 38.0 (Ta–$CH_3$), 51.9 ($C_1$), 110.6 (Cp), 116.8 ($C_2$).

(14) Experimental procedure: to $Cp^*TaCl_4$ (12.2 mg, $2.66 \times 10^{-5}$ mol) suspended in toluene (19 mL) was added MAO (500 equiv) via syringe. After the catalyst mixture was stirred at room temperature for 10 min, ethylene (atmospheric pressure) was introduced. After 6 h at room temperature, polymerization was quenched by the addition of HCl–MeOH, and activity was found to be $7.89 \times 10^{-2}$ kg/h·[Ta]mol.

(15) The cationic alkyltantalum complexes such as $[Cp^*(\eta^4\text{-diene})TaR]^+$ are expected to be a catalytically active species, as already observed for the zirconocene/MAO system.[4,5] The presence of the cationic species in the catalyst system was suggested by the following evidence. The reaction of **2b** with $B(C_6F_5)_3$ in benzene-$d_6$ at room temperature resulted in the formation of a yellow solution of cationic species [$^1$H NMR (benzene-$d_6$) $\delta$ –1.27 (1H, d, $H_{1anti}$, $J = 6.9$ Hz), –1.06 (1H, t, $H_{4anti}$, $J = 7.1$ Hz), –0.56 (6H, br s, $CH_3$), –0.08 (1H, d, $H_{1syn}$), 0.39 (1H, t, $H_{4syn}$), 1.79 (15H, s, Cp*), 2.61 (3H, s, $CH_3$), 6.52 (1H, t, $H_3$)]. This color of the solution corresponds to the color of the solution from **2**/MAO. The cationic complexes were too thermally unstable to be isolated. In contrast to the fact that complexes **1–3** were not the catalyst for polymerization of ethylene, the combination of $B(C_6F_5)_3$ and **2** was not the active catalyst for the polymerization of ethylene (atmospheric pressure) at the same condition (at room temperature) as that shown in Table I for substitution of $B(C_6F_5)_3$ for MAO but became the catalyst for polymerization of ethylene (35 kg/cm$^2$) with rather low activity ($1.8 \times 10^{-2}$ kg/h·[Ta]mol).

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