Macromol. Symp. ***159****, 69–76 (2000)*

Catalytic Diversity of Diene Complexes of Niobium and Tantalum on Polymerizations of Ethylene, Norbornene, and Methyl Methacrylate

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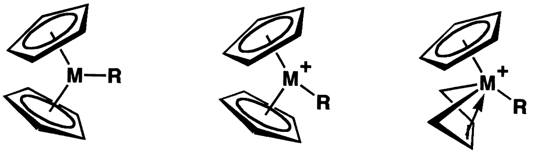
SUMMARY: Half-metallocene diene complexes of niobium and tantalum catalyzed three-types of polymerization: (1) the living polymerization of ethylene by niobium and tantalum complexes, $MCl_2(\eta^4\text{-}1,3\text{-diene})(\eta^5\text{-}C_5R_5)$ (**1-4**; M = Nb, Ta; R = H, Me) combined with an excess of methylaluminoxane; (2) the stereoselective ring opening metathesis polymerization of norbornene by bis(benzyl) tantalum complexes, $Ta(CH_2Ph)_2(\eta^4\text{-}1,3\text{-butadiene})(\eta^5\text{-}C_5R_5)$ (**11**: R = Me; **12**: R = H) and $Ta(CH_2Ph)_2(\eta^4\text{-}o\text{-xylylene})(\eta^5\text{-}C_5Me_5)$ (**16**); and (3) the polymerization of methyl methacrylate by butadiene-diazabutadiene complexes of tantalum, $Ta(\eta^2\text{-RN=CHCH=NR})(\eta^4\text{-}1,3\text{-butadiene})(\eta^5\text{-}C_5Me_5)$ (**25**: R = *p*-methoxyphenyl; **26**: R = cyclohexyl) in the presence of an aluminum compound (**24**) as an activator of the monomer.

Introduction

Olefin polymerization based on metallocene initiator system of Group 4 metallocene/methylaluminoxane (MAO) has been extensively investigated.[1,2] The polymerization using single-component catalysts such as cationic Group 4 metallocenes or isoelectronic neutral Group 3 and lanthanide metallocene hydrides or alkyls has recently been developed.[3-5] Furthermore, the polymerization based on non-metallocene catalysts has opened a new era.[6] The fragments of $MCp(\eta^4\text{-}1,3\text{-diene})$ (M = Nb and Ta) are isoelectronic and isolobal to those of MCp_2 (M = Zr and Hf).[7] This prompted us to prepare the benzyne complex, $Cp^*(\eta^4\text{-buta-}1,3\text{-diene})Ta(\eta^2\text{-}C_6H_4)$ (Cp* = η^5-pentamethylcyclopentadienyl),[8] and the benzylidene complex, $Cp^*(\eta^4\text{-buta-}1,3\text{-diene})Ta(=CHPh)(PMe_3)$,[9] whose structure and reactivity were compared with those of the corresponding metallocene complexes of Group 4 metals as well as those of metallocene-like complexes such as niobium complexes having Nb(NR)Cp fragments.[10] We have investigated the diversity of the diene complexes of niobium and tantalum as catalyst precursors for the olefin polymerization; 14 electron isoelectronic species for Group 3, 4, and 5 metals being schematically shown in Scheme 1. This review briefly focuses on aspects of our past and current research on the polymerization.

CCC 1022-1360/00/$ 17.50+.50/0

Scheme 1: Active 14-electron species

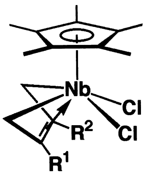


Group 3 Group 4 Group 5

Living Polymerization of Ethylene[11-13]

We used mono-diene complexes of niobium and tantalum, $MCl_2(\eta^5-C_5R_5)(\eta^4\text{-diene})$ (M = Nb and Ta; R = H and Me; diene = buta-1,3-diene, isoprene, 2,3-dimethylbuta-1,3-diene), as catalyst precursors of ethylene polymerization. These complexes have been synthesized by the reaction of $MCl_4(\eta^5-C_5R_5)$ with the corresponding 1,3-diene compounds of magnesium.[14] Treatment of **2a-c** with 2 equiv. of MeMgI afforded dimethyl complexes of tantalum **5a-c**. In the case of the preparation of **6a** and **6c**, we used one-pot reaction of $TaCl_4Cp$ with 2 equiv. of the corresponding methylated allyl Grignard reagent and 2 equiv. of MeMgI in THF, since the corresponding dichloro-diene complexes **4a** and **4c** have low solubility in organic solvent. A niobium dimethyl complex **7** was prepared similarly, but **7** was thermally unstable and decomposed gradually at room temperature to give a nascent carbene complex, which can be trapped by benzophenone to give 1,1-diphenylethylene. Bis(2,3-dimethyl-1,3-butadiene) complexes **8** and **9** were prepared by the reaction of MCl_4Cp^* with two equiv. of Mg(2,3-diemthyl-1,3-butadiene).[14] All diene complexes mentioned above were the active catalyst precursors for ethylene polymerization when combined with 500 equiv. of MAO. Representative results using these mono-diene and bis(diene) complexes are shown in Table 1.

The dichloro and dimethyl complexes **2** and **5** exhibited almost the same catalyst activity, MAO thus inducing both the methylation and the ligand exchange reaction between aluminum and tantalum to lead the formation of cationic species. The most attracting finding is the living nature of the polymerization; for example, using the niobium complexes **1a** and **1c** we obtained polyethylene with the narrowest polydispersity (M_w/M_n = 1.05) to date. Other aspects of the catalysts are that the niobium complexes are superior to the corresponding tantalum complexes and that the bis(diene) complexes were also the active catalyst precursors for the ethylene polymerization.



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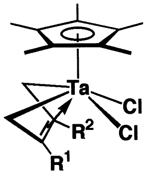

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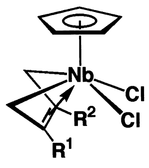

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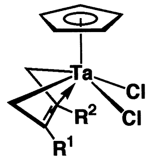

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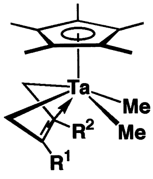

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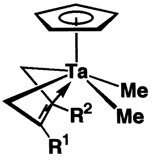

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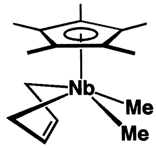

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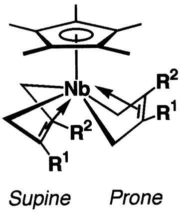

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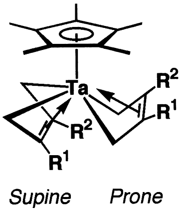

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a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = R^2 = Me$

Table 1. Polymerization of Ethylene Catalyzed by Mono-diene Complexes/MAO.[a]

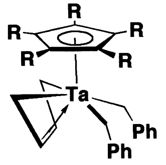
run	complex	time h	temp °C	activity[b] kg/h·[M]mol	$M_n/10^4$	M_w/M_n
1	**1a**	1	-20	10.65	2.36	1.05
2	**1b**	1	-20	1.02	0.51	1.09
3	**1c**	1	-20	12.71	4.10	1.05
4	**2a**	6	-20	1.51	2.03	1.16
5	**4a**	6	-20	7.07	8.18	1.40
6	**5a**	6	-20	1.18	2.55	1.08
7	**8c**	1	-20	12.48	1.42	1.06
8	**9c**	6	-20	0.26	0.54	1.09

[a] Polymerization reactions were carried out in toluene ([M] = 1.44×10^{-3} M) in the presence of MAO (500 equiv.) for 6 hours without other notice.
[b] For the methanol-insoluble parts.

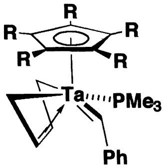
In order to get an insight into the active species, we first examined the reaction of **5b** with 1 equiv. of TfOH in toluene, generating TaCp*(η^4-isoprene)(OSO_2CF_3)Me (**10**) with elimination of 1 equiv. of methane. In the ^1H NMR spectrum of **10**, one set of signals was observed, indicating one of the two non-equivalent methyl groups selectively replaced by the TfO anion. As revealed by a crystallographic study, the complex **10** has the Ta-O covalent bond and thereby did not exhibit any activity in the polymerization. The addition of $B(C_6F_5)_3$ to **5b** generated a cationic species, despite its thermal instability, which catalyzed the polymerization.

Stereoselective ROMP of Norbornene[9,15,16]

We also studied the ring-opening metathesis polymerization (ROMP) of norbornene by using tantalum alkylidene species having Ta(η^5-C_5R_5)(η^4-butadiene) and TaCp*(η^4-*o*-xylylene) fragments,[9,15,16] because isoelectronic titanocene-alkylidene species have successfully been applied for the ROMP of norbornene.[17-19] Bis(benzyl) complexes **11** and **12** were prepared by the reactions of the dichloro complexes **2** and **4**, respectively, with 2 equiv. of benzyl Grignard reagent. The thermolysis of **11** and **12** in the presence of PMe_3 afforded the corresponding benzylidene phosphine complexes **13** and **14**, respectively. The phenyl group of the benzylidene moiety in the complexes **13** and **14** pointed away toward the η^5-C_5R_5 ligand; this *anti*-geometry may play a crucial role in determining the stereochemistry of the double bond of the poly(norbornene).

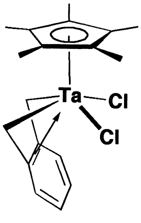


11: R = CH_3
12: R = H



13: R = CH_3
14: R = H

The *o*-xylylene ligand can coordinate to a metal center in η^4-fashion similar to the η^4-1,3-diene ligand. Thus, we anticipated that $Ta(CH_2Ph)_2(\eta^4\text{-}o\text{-}(CH_2)_2C_6H_4)Cp^*$ (**16**), which can be readily synthesized from **15**, initiates the ROMP of norbornene. The thermolysis of **16** produced a phosphine-free benzylidene complex, $Ta(=CHPh)(\eta^4\text{-}o\text{-}(CH_2)_2C_6H_4)Cp^*$ (**17**), whose crystallographic study revealed its *syn*-geometry around the Ta=C bond, being in sharp contrast to the *anti*-one found for **13** and **14**.



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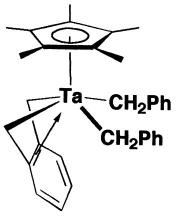

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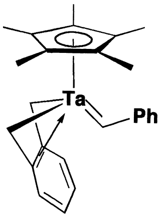

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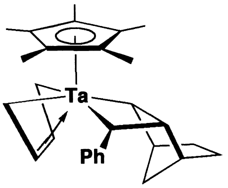
The *cis*-bis(benzyl) complexes **11**, **12**, and **16** together with the benzylidene complex **17** were found to be catalyst precursors for the ROMP of norbornene, whereas the isolated benzylidene-phosphine complexes **13** and **14** had no catalytic activity due to the coordination site occupied by the phosphine ligand. The stereochemistry of the vinylene double bonds of poly(norbornene) was effectively controlled by the catalyst precursor's architecture; **11** gave the polymer with a high *cis*-vinylene double bond (97-99%), while, in sharp contrast, **16** and **17** gave the polymer with a high *trans*-vinylene double bond (92-95%). This preferential difference is attributed to the geometry around the Ta=C bond of the nascent carbene species, *i.e.*, *anti*-rotamer or *syn*-one. The addition of norbornene to each rotamer resulted in the selective formation of metallacyclobutanes **18** and **20**. The metathesis cleavage of **18** affords the alkylidene species **19** along with the *cis*-double bond. The successive polymerization gives rise to the *cis*-poly(norbornene). The similar cleavage of the *o*-xylylene complex **20** leads to the *trans*-double bond and the *anti*-alkylidene species **21**, which turns the *syn*-one **22** before the successive addition of the monomer.



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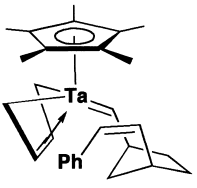

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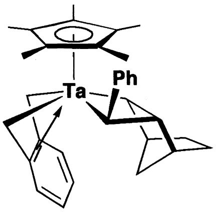
The evidence of metallacyclobutane intermediates was obtained by the crystallographic study for an acenaphthylene complex **23**, in which acenaphthylene added to the Ta=C bond in place of the norbornene and the stereochemistry of the *syn*-rotamer of 17 was retained (eq 1). The Cp complex **12** showed no stereoselectivity in double bond formation, indicating that the Cp and butadiene ligands exert similar steric effects and hence both *anti*- and *syn*-rotamers formed during the propagation.



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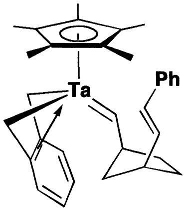

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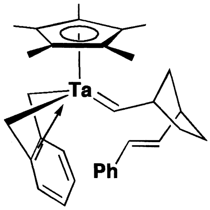

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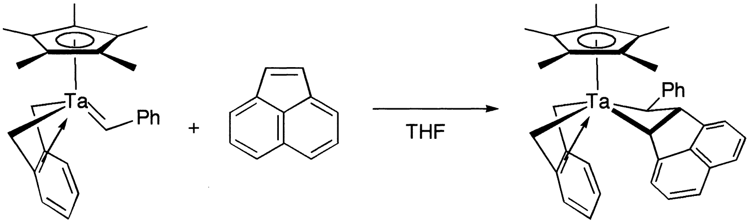


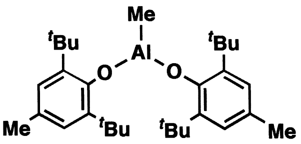
17 **23** (1)

Polymerization of Methyl Methacrylate[20]

The polymerization of functionalized olefins such as methyl methacrylate (MMA) using metallocene complexes of lanthanoid and zirconium has attracted recent interest.[21-28] On the basis of our above findings, it is assumed that half-metallocene-diene complexes of tantalum have the capability of polymerizing the polar monomers because the Group 5 metals are much tolerant to functionalized monomers.

In ethylene polymerization, the bis(diene) complexes of niobium and tantalum became unique catalyst precursors, in which one of the two diene ligands, *supine* and *prone* ones, was readily released upon treatment with MAO. Thus, the bis(diene) tantalum complex **9a** was first examined for the polymerization of MMA (Table 2), but it showed low activity. The polymerization of MMA proceeded much faster when combined with a bulky substituted bis(aryloxo)aluminum compound **24** as an activator of the monomer.[20]

1,4-Diaza-1,3-butadiene (= DAD) ligand is much tolerant to functionalized monomers and thereby the DAD-diene complexes of tantalum[29] were used as the catalyst precursors for the polymerization of MMA. Results summarized in Table 2 indicate that the DAD complexes **25** and **26** are superior in catalytic activity to the bis(diene) complex **9a**.[30] Further investigation to synthesize organometallic species active for the MMA polymerization is now in progress; various MMA complexes of tantalum were quite recently found to be excellent catalyst precursors for the polymerization of MMA.[30]



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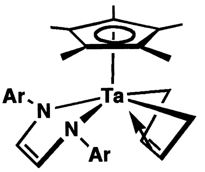

Ar = p-MeO-C_6H_4

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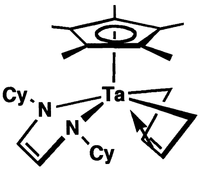

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Table 2. Polymerization of MMA Catalyzed by Diene Complexes of Tantalum.

run	catalyst	additive[a]	temp °C	time min.	yield[b] %	M_n[c] (x 10^4)	M_w/M_n[c]	rr
1	**9a**	-	20	1440	7	-	-	-
2	**9a**	**24**	0	40	98	29.3	2.3	68
3	**25**	**24**	0	40	99	44.2	2.5	73
4	**26**	**24**	0	10	81	14.4	1.5	71
5	**26**	**24**	0	5	99	16.9	1.4	70

[a] [Cat.] : [MMA] = 1 : 100; [Cat.] : [**24**] : [MMA] = 1 : 10 : 100.

[b] Yield = weight of polymer obtained/weight of monomer used.

[c] Measured by GPC calibrated with standard polystyrene samples.

Conclusions

We demonstrated the catalytic diversity of the half-metallocene diene complexes of tantalum which catalyzed three different polymerizations (the living polymerization of ethylene, the stereoselective ROMP of norbornene, and the polymerization of methyl methacrylate) by controlling mutable auxiliary ligands, *i.e.*, chloro or methyl, diene, benzylidene, and 1,4-diaza-1,3-butadiene, bound to the tantalum center

Acknowledgment

I wish to thank my active co-workers and dedicated students listed in the reference section. This work was financially supported by the Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from the Ministry of Education, Science, Sports, and Culture, Japanese government, and also by the Yamada Science Foundation.

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30 Unpublished results.