cis-iso-Specific Polymerization of Norbornenes by a Unique Combination of Cp* and 1,3-Butadiene Ligands on Tantalum: Crystal Structures of $Cp^*(\eta^4\text{-}C_4H_6)Ta(CH_2Ph)_2$ and $Cp^*(\eta^4\text{-}C_4H_6)Ta(=CHPh)(PMe_3)$[†]

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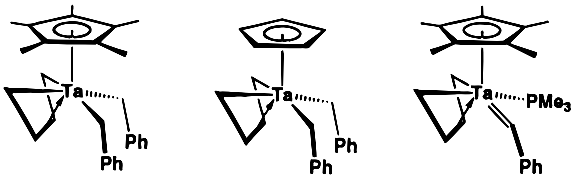
Received January 16, 1996[⊗]

*Summary: cis-iso-Specific homogeneous ring-opening metathesis polymerization of norbornenes is achieved by using the catalyst precursor $Cp^*(\eta^4\text{-}C_4H_6)Ta(CH_2Ph)_2$ (**2**). Thermolysis of **2** generates a benzylidene species, which is trapped by PMe_3 to give a benzylidene complex $Cp^*(\eta^4\text{-}C_4H_6)Ta(=CHPh)(PMe_3)$ (**4**). The crystal structures of **2** and **4** are determined by X-ray analysis.*

Ring-opening metathesis polymerization (ROMP) has been achieved by using well-defined metal−carbene complexes as catalysts.[1−8] Among these, the carbene complexes that have one or two cyclopentadienyl ligands are found to be important for their unique catalytic features.[9,10] The coordination of a 1,3-diene to a TaCp* fragment (Cp* = pentamethylcyclopentadienyl) gives a 14 electron fragment that stabilizes various reactive species such as benzyne,[11] carbene,[12] and cationic alkyls.[12] Moreover we have exploited the monocyclopentadienyl diene complexes of niobium and tantalum as catalyst precursors for the living ethylene polymerization.[12−14] Here we report *cis-iso*-specific homogeneous ring-opening metathesis polymerization of norbornenes[15−17] using the catalyst precursor $Cp^*(\eta^4\text{-}C_4H_6)Ta(CH_2Ph)_2$ (**2**) (Chart 1) and the isolation and characterization of a new benzylidene complex $Cp^*(\eta^4\text{-}C_4H_6)Ta(=CHPh)(PMe_3)$ (**4**) from thermolysis of **2** in the presence of PMe_3.

Chart 1



2 **3** **4**

Complex **2** was prepared in 83% yield by reaction of $Cp^*(\eta^4\text{-}C_4H_6)TaCl_2$ (**1**)[18] with 2 equiv of benzyl Grignard reagent in THF. The monomeric four-legged piano-stool structure of **2** was confirmed by spectral data[19] as well as X-ray analysis (Figure 1).[20] When a mixture of **2** and norbornene (100 equiv.) in toluene or THF was heated (45 or 65 °C), the polymerization of norbornene is induced. Poly(norbornene) was obtained by precipitation with methanol. The observed M_n and M_w/M_n values

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[†] This paper is dedicated to the late Professor H. Takaya (Kyoto University) for his excellent achievements, great contribution, and leadership in organometallic chemistry.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

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(15) For poly(norbornene), four stereospecific polymers are possible. The cis-syndiotactic one has been obtained by using $ReCl_5$-based heterogeneous catalyst.[16] The trans-isotactic-rich poly(norbornene)s have been reported.[17]

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(19) Spectral data for **2**−**4** are presented in the Supporting Information.

(20) **2**: $C_{28}H_{35}Ta$, fw = 552.53, crystal size 0.6 × 0.5 × 0.3 mm, triclinic, space group $P\bar{1}$ (No. 2) with $a = 10.054(2)$ Å, $b = 14.062(3)$ Å, $c = 8.795(2)$ Å, $\alpha = 104.47(1)°$, $\beta = 99.63(2)°$, $\gamma = 81.04(2)°$, $V = 1178.6(4)$ Å^3, $Z = 2$, $d_{calcd} = 1.557$ g cm^{-3}, 5757 reflections ($2\theta_{max} = 60.1°$, $2\theta-\omega$ scan, 23 °C), $R = 0.028$, and $R_w = 0.031$.

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S0276-7333(96)00023-4 CCC: $12.00

Table 1. Polymerization of Norbornene and 7-Methylnorbornene Catalyzed by 2 and 3

run	compd	monomer[a]	temp, °C	solv	S/C[b]	time, h	yield,[c] %	M_n[d]	M_w/M_n[d]	cis,[e] %
1	**2**	NBN	45	toluene	100	50	30	4000	2.36	97
2	**2**	NBN	45	THF	100	50	35	4100	2.00	97
3	**2**	NBN	45	toluene	100	100	54	5600	1.93	98
4	**2**	NBN	45	THF	100	100	60	5200	1.92	98
5	**2**	NBN	65	toluene	100	30	84	8900	1.63	97
6	**2**	NBN	65	THF	100	30	94	8600	1.88	97
7	**2**	NBN	65	none	1000	87	43	32300	2.04	99
8	**3**	NBN	60	toluene	100	32	42	3400	2.46	50
9	**2**	MeNBN	60	toluene	65	40	22[f]	bimodal		99
10	**2**	MeNBN	60	THF	66	40	19[f]	bimodal		99
11	**3**	MeNBN	50	toluene	100	100	96[f]	16100	1.60	13

[a] Monomer: NBN = norbornene; MeNBN = 7-methylnorbornene. [b] S/C: the ratio of norbornenes/catalyst. [c] Methanol-insoluble fraction. [d] GPC analysis in THF versus polystyrene standards. Theoretical M_n value is less than the experimental one.[9,21] [e] Stereochemistry of the double bond of the polymer was determined by ^{1}H-NMR.[9,10,22] [f] Chemical yields are estimated based on *anti*-7-methylnorbornene.

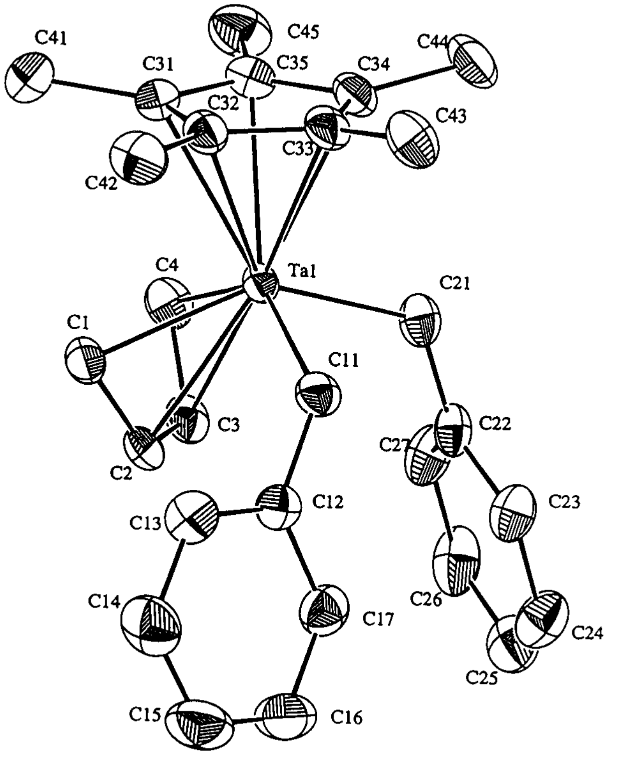
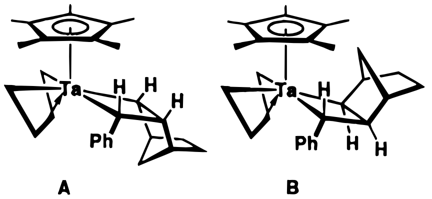


Figure 1. ORTEP drawing of complex **2** with the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta–C(11) 2.249(4), Ta–C(21) 2.277(4), Ta–C(1) 2.263(4), Ta–C(2) 2.392(4), Ta–C(3) 2.389(4), Ta–C(4) 2.265(4), C(1)–C(2) 1.425(6), C(2)–C(3) 1.375(6), C(3)–C(4) 1.425(7); Ta–C(11)–C(12) 130.4(3), Ta–C(21)–C(22) 126.8(3), C(11)–Ta–C(21) 94.5(2).

are summarized in Table 1. The catalytic activity for the polymerization of norbornene depends critically on temperature. The polymerization at 65 °C proceeded faster than that at 45 °C. The polymerization at 65 °C gave a high molecular mass polymer ($M_n = 3.2 \times 10^4$).

The stereochemistry of the double bond proved by ^{1}H NMR spectroscopy to be highly cis (>97%).[9,10] The ^{1}H NMR spectrum of the polymer displayed a doublet at δ 6.46 with a coupling constant of 10.9 Hz, indicating that the initiation proceeded selectively to give (*Z*)-PhCH=CH– as one of the end groups. Since the tacticity of poly(norbornene) could unfortunately not be determined, we used 7-methylnorbornene as a monomer to determine the tacticity of the polymer. The polymerization of a 1:1 mixture of *syn*- and *anti*-7-methylnorbornene by using **2** as a precursor proceeded smoothly at 60 °C to give *cis* (99%) and *isotactic* (88%) poly(*anti*-7-methylnorbornene).[15,22,23]

Chart 2



Norbornene adds to a metal–carbene bond of an anti rotamer to give an all-cis tantalacyclobutane intermediate **A** (Chart 2); the Cp* ligand is sufficiently bulky to disfavor a syn rotamer as well as the geometry **B**. Bond fission in the all-cis complex **A** leads to an anti rotamer and forms a cis double bond at the chain end of the polymer. The fact that the all-cis and isotactic polymer is formed might be a consequence of the successive insertion of norbornene to the anti rotamer on the same side. If the addition proceeded alternatively at one face of the syn rotamer and then at the other, the resulting polymer is cis and syndiotactic. When a Cp analogue, Cp(η^4-C_4H_6)Ta($CH_2Ph)_2$ (**3**),[19] was used as an initiator of the polymerization of norbornene, an atactic polymer (cis/trans = 1/1) was formed. We assume that the bulkiness of unsubstituted Cp and butadiene ligands in a benzylidene species derived from thermolysis of **3** are comparable with each other and thus a monomer attacks a Ta=C bond to give an all-cis or a trans metallacycle. The latter gives a trans double bond in the polymer backbone. Rather broad polydispersities observed for the polymerization of norbornenes might be attributed to the gradual formation of the catalyst in addition to the decay of the intermediate during the polymerization.

Benzylidene complex **4**[19] was isolated in 55% yield by thermolysis of **2** in toluene in the presence of PMe_3 at 48 °C for 16 h. The pathway for formation of **4** involves smooth α-hydrogen abstraction followed by elimination of toluene. A doublet resonance at δ 9.67 (J_{P-H} = 5.9 Hz) in the ^{1}H NMR spectrum of **4** is assignable to the α-benzylidene proton, indicating the presence of a single alkylidene rotamer. The Cα benzylidene resonance of

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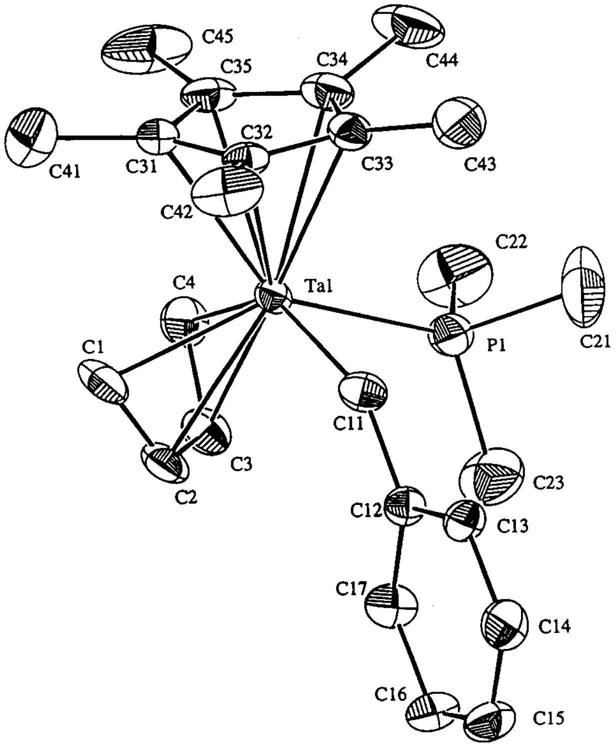

Figure 2. ORTEP drawing of complex **4** with the numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ta−C(11) 2.044(8), Ta−P 2.612(2), Ta−C(1) 2.291(7), Ta−C(2) 2.404(7), Ta−C(3) 2.394(7), Ta−C(4) 2.288(8), Ta−CP 2.147, C(1)−C(2) 1.39(1), C(2)−C(3) 1.37(1), C(3)−C(4) 1.42(1), C(11)−C(12) 1.47(1); Ta−C(11)−C(12) 147.8(5), P−Ta−C(11) 81.7(2), C(1)−Ta−CP 107.2, C(4)−Ta−CP 113.3, C(11)−Ta−CP 110.5, P−Ta−CP 115.4 (CP = the centroid of cyclopentadienyl ring).

4 was observed at δ 237.3 (J_{C-H} = 112 Hz, J_{C-P} = 19 Hz). The chemical shift is comparable to those of benzylidene complexes of tantalum (δ 220−246) such as $Cp_2Ta(=CHPh)(CH_2Ph)$[24] and $Cp^*Ta(=CHPh)(CH_2Ph)_2$.[25]

Figure 2 shows an ORTEP drawing of **4**, which has a four-legged piano stool geometry comprised of C(1), C(4), C(11), and a phosphorus atom.[26] Structural features of **4** are essentially the same as that of benzylidene complexes of vanadium and niobium bearing 14 electron metallocene-like fragment such as $M(\eta^5\text{-}C_5R_5)[N\text{-}C_6H_3\text{-}2,6\text{-}(^iPr)_2]$ (**5**, M = V, R = H;[27] **6**, M = Nb, R = Me[28]). The bond distance of Ta−C(11) [2.044(8) Å] is shorter than those of Ta−C single bonds in **2** [2.249(4) and 2.277(4) Å] and is comparable to that found for **6** [2.026(4) Å]. The orientation of a phenyl group in complex **4** is the same as that of complexes **5** and **6**. The Ta−C(11)−C(12) angle of 147.8(5)° is larger than those of Ta−C(sp^3)−C(Ph) in **2** [130.4(3) and 126.8(3)°] and is indicative of an undistorted alkylidene ligand.

Some reactions of **4** were carried out preliminarily. Reaction of **4** with 3-pentanone afforded 1-phenyl-2-ethyl-but-1-ene in 57% yield.[29] This reactivity corresponds to that found for the Schrock-type carbene complexes.[30,31] Treatment of **4** with methanol and 3,3-dimethyl-1-butyne produced the protonated products $Cp^*(\eta^4\text{-}C_4H_6)Ta(CH_2Ph)(OMe)$ and $Cp^*(\eta^4\text{-}C_4H_6)Ta(CH_2Ph)(C{\equiv}CCMe_3)$, respectively.[29] Complex **4** was found to be inactive as the catalyst for ROMP of norbornene at 65 °C for 30 h.

A *cis*- and *iso*-specific ROMP catalyst was realized using a unique combination of bulky Cp* and nonbulky butadiene ligands on a tantalum center. Further studies of the mechanistic relationship between α-olefin polymerization and ROMP as well as the scope of our catalyst system are being pursued.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236106 from the Ministry of Education, Science, and Culture of Japan.

Supporting Information Available: Text giving experimental details for the preparation of **2**−**4**, reactions of **4**, and the polymerization of norbornene and 7-methylnorbornene, tables listing final positional parameters, final thermal parameters, X-ray parameters, and bond distances and angles for **2** and **4**, and figures showing NMR spectra (24 pages). Ordering information is given on any current masthead page.

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(26) **4**: $C_{24}H_{36}PTa$, fw = 536.47, crystal size 0.30 × 0.25 × 0.25 mm, triclinic, space group $P\bar{1}$ (No. 2) with a = 10.546(2) Å, b = 13.200(3) Å, c = 8.531(2) Å, α = 105.57(2)°, β = 96.83(4)°, γ = 92.99(5)°, V = 1131.4(9) Å^3, Z = 2, d_{calcd} = 1.575 g cm^{-3}, 5435 reflections ($2\theta_{max}$ = 55.0°, 2θ-ω scan, 23 °C), R = 0.027, and R_w = 0.035.

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