4544 *Organometallics* **2004,** *23,* 4544−4546

# Olefin Polymerization Catalyzed by Titanium−Tungsten Heterobimetallic Dinitrogen Complexes[1]

Hiroshige Ishino,[†] Shin Takemoto,[†] Kenji Hirata,[†] Yuka Kanaizuka,[†]
Masanobu Hidai,*,[†] Masaaki Nabika,[‡] Yoshinori Seki,[‡] Tatsuya Miyatake,[‡] and
Noriyuki Suzuki[§]

*Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan, Petrochemical Research Laboratory, Sumitomo Chemical Co. Ltd., Sodegaura, Chiba 299-0295, Japan, and RIKEN, Wako, Saitama 351-0198, Japan*

*Received July 22, 2004*

*Summary: A new family of highly active olefin polymerization catalysts based on titanium−tungsten heterobimetallic dinitrogen complexes, $[Cp'TiCl_2(\mu\text{-}N_2)WCl(L)_4]$ (**1**; L = $PMe_2Ph$, 1/2 $R_2PCH_2CH_2PR_2$; R = Et, Ph), has been developed, in which the tungsten dinitrogen fragment acts as a novel metallonitrogen ligand to the catalytically active titanium center. Alkylation of **1d** (Cp′ = $C_5Me_5$, L = 1/2 $Et_2PCH_2CH_2PEt_2$) with MeLi gave di- and trimethyl derivatives **2d** and **3d**, which were structurally characterized.*

Polymerization of olefins catalyzed by soluble, well-defined transition metal complexes has been one of the most attractive subjects in organometallic chemistry.[2] In particular, monocyclopentadienyl titanium catalysts containing amide, phosphinimide, and aryloxy ligands have extensively been studied, and some of them are now employed commercially.[3,4] On the other hand, some examples of olefin polymerization by using heterobimetallic complexes have been reported where bis(cyclopentadienyl)M (M = Zr, Hf) moieties are connected to other transition metals such as Mo,[5a,b] Fe,[5c,d,f] Co,[5f] Rh,[5e−h] and Ni[5a] via cyclopentadienyl or phosphido ligands. However, significant enhancement in catalytic activity has rarely been observed.[5c,d,g]

During our long-standing study on chemical nitrogen fixation by transition metal complexes,[6] we have recently synthesized the titanium−tungsten heterobimetallic bridging dinitrogen complexes **1a** and **1b** (Figure 1) having a half-sandwich titanium fragment from the reaction of tungsten dinitrogen complexes $[W(N_2)_2(L)_4]$ (L = $PMe_2Ph$, 1/2 dppe; dppe = $Ph_2PCH_2CH_2PPh_2$) with $CpTiCl_3$.[7] We have now found that the heterobimetallic complexes of this class are excellent catalyst precursors for copolymerization of ethylene and 1-hexene. Preliminary results are described here.

Copolymerization of ethylene and 1-hexene was studied using the titanium−tungsten heterobimetallic dinitrogen complexes **1a**−**1g** as catalyst precursors, in which several new complexes, **1c**−**1g**, were synthesized from similar reactions. The constrained geometry catalyst $[(t\text{-}BuNSiMe_2C_5Me_4)TiCl_2]$ (CGC)[2] was chosen as a reference in the copolymerization because it also contains both cyclopentadienyl and nitrogen-based ligands on titanium.

Table 1 summarizes the polymerization results in which $Al(i\text{-}Bu)_3$ and $[Ph_3C][B(C_6F_5)_4]$ were used as cocatalysts. The heterobimetallic dinitrogen complex **1a** showed a very high catalytic activity of 376 kg mmol $(cat)^{-1}$ $h^{-1}$. The copolymers produced have relatively high molecular weights ($M_w = 77 \times 10^4$) and unimodal molecular weight distribution ($M_w/M_n = 2.2$), indicating that the copolymers were produced by a single active species. It should be noted that the catalytic activity of **1a** was more than 3 times as high as that of CGC under the same conditions, although the 1-hexene content was one-third of that observed in CGC.

Complexes **1c**−**1e** with depe ($Et_2PCH_2CH_2PEt_2$) ligands also exhibited high catalytic activity. Complex

---

* Corresponding author. E-mail: hidai@rs.noda.tus.ac.jp.

[†] Tokyo University of Science.

[‡] Sumitomo Chemical Co., Ltd.

[§] RIKEN.

(1) Preparation and Properties of Molybdenum and Tungsten Dinitrogen Complexes. Part 72. Part 71: Arita, C.; Seino, H.; Mizobe, Y.; Hidai, M. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 561−567.

(2) (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143−187. (b) Bristovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447. (c) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205−1221. (d) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223−1252. (e) Kaminsky, W.; Laban, A. *Appl. Catal., A* **2001**, *222*, 47−61.

(3) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S.-Y. (Dow Chemical Co., USA) Eur. Pat. Appl. EP 416815, 1991. (b) Canich, J. A. M.; Turner, H. W. (Exxon) World Pat. WO 9212162, 1992. (c) Chen, Y.-X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649−3657.

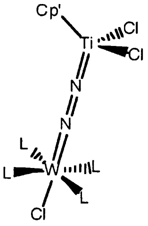
(4) (a) Nomura, K.; Oya, K.; Komatsu, T.; Imanishi, Y. *Macromolecules* **2000**, *33*, 3187−3189. (b) Gielens, E. E. C. G.; Tiesnitsch, J. Y.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 1652−1654. (c) Chen, Y.-X.; Fu, P.-F.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 5958−5963. (d) Katayama, H.; Nabika, M.; Imai, A.; Miyashita, A.; Watanabe, T.; Johohji, H.; Oda, Y.; Hanaoka, H. (Sumitomo Chem. Co., Japan) World Pat., WO 9703992, 1997. (e) Stephan, D. W.; Stewart, J. C.; Guérin, F.; Spence, R. E. v. H.; Xu, W.; Harrison, D. G. *Organometallics* **1999**, *18*, 1116−1118.

(5) (a) Lindenberg, F.; Shribman, T.; Sieler, J.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1996**, *515*, 19−25. (b) Koch, T.; Blaurock, S.; Hey-Hawkins, E.; Galan-Fereres, M.; Plat, D.; Eisen, M. S. *J. Organomet. Chem.* **2000**, *595*, 126−133. (c) Mitani, M.; Oouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Macromol. Chem. Phys.* **1996**, *197*, 1815−1822. (d) Mitani, M.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2967−2976. (e) Yan, X.; Chernega, A.; Green, M. L. H.; Sanders, J.; Souter, J.; Ushioda, T. *J. Mol. Catal. A: Chem.* **1998**, *128*, 119−141. (f) Green, M. L. H.; Popham, N. H. *J. Chem. Soc., Dalton Trans.* **1999**, 1049−1059. (g) Yamaguchi, Y.; Suzuki, N.; Mise, T.; Wakatsuki, Y. *Organometallics* **1999**, *18*, 996−1001. (h) Takeuchi, D.; Kuwabara, J.; Osakada, K. *Organometallics* **2003**, *22*, 2305−2311.

(6) (a) Hidai, M.; Mizobe, Y. In *Molybdenum and Tungsten. Their Roles in Biological Processes*, Vol. 39 of Metal Ions in Biological Systems; Sigel, A., Sigel, H., Eds.; Marcel-Dekker: New York, 2002; pp 121−161. (b) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540−542. (c) Hidai, M.; Ishii, Y. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 819−831.

(7) Ishino, H.; Nagano, T.; Kuwata, S.; Yokobayashi, Y.; Ishii, Y.; Hidai, M. *Organometallics* **2001**, *20*, 188−198.

10.1021/om049447x CCC: $27.50
Publication on Web 09/01/2004



| complexes | L | Cp' |
|---|---|---|
| **1a** | 1/2 dppe | $C_5H_5$ |
| **1b** | $PMe_2Ph$ | $C_5H_5$ |
| **1c** | 1/2 depe | $C_5H_5$ |
| **1d** | 1/2 depe | $C_5Me_5$ |
| **1e** | 1/2 depe | $C_5H_4Me$ |
| **1f** | 1/2 depe | Indenyl |
| **1g** | 1/2 dppe | $C_5Me_5$ |

**Figure 1.** Heterobimetallic dinitrogen complexes.

**Table 1. Copolymerization of Ethylene and 1-Hexene Catalyzed by Heterobimetallic Dinitrogen Complexes with $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$[a]**

| entry | catalyst | activity[b] | $M_w$[c] × $10^{-4}$ | $M_w/M_n$ | 1-hexene content[d] |
|---|---|---|---|---|---|
| 1 | **1a** | 376 | 77 | 2.2 | 2.84 |
| 2 | **1b** | 9 | 41 | 3.0 | 1.71 |
| 3 | **1c** | 388 | 25 | 1.8 | 3.21 |
| 4 | **1d** | 416 | 58 | 2.1 | 2.15 |
| 5 | **1e** | 252 | 28 | 2.0 | 3.64 |
| 6 | **1f** | 60 | 21 | 2.1 | 1.68 |
| 7 | **1g** | 136 | 92 | 6.0 | 1.44 |
| 8 | CGC | 120 | 38 | 4.2 | 8.49 |

[a] Conditions: toluene 198 mL, 1-hexene 2 mL, ethylene 0.6 MPa, 60 °C, 1 h, catalyst 0.025 $\mu$mol, $Al(i\text{-}Bu)_3$ 0.25 mmol, $[Ph_3C][B(C_6F_5)_4]$ 1.0 $\mu$mol. [b] kg mmol(cat)$^{-1}$ h$^{-1}$. [c] Determined by GPC with polystyrene standards. [d]mol %, determined by $^{13}C$ NMR spectroscopy.

**Table 2. Copolymerization of Ethylene and 1-Hexene Catalyzed by Heterobimetallic Dinitrogen Complexes and MMAO Cocatalyst[a]**

| entry | catalyst | activity[b] | $M_w$ × $10^{-4}$ | $M_w/M_n$ | 1-hexene content |
|---|---|---|---|---|---|
| 9 | **1a** | 160 | 158 | 3.1 | 0.70 |
| 10 | **1c** | 100 | 63 | 3.1 | 1.45 |
| 11 | **1d** | 510 | 50 | 2.2 | 1.83 |
| 12 | **1e** | 148 | 48 | 2.9 | 1.27 |
| 13 | CGC | 0.8 | 64 | 3.2 | 2.55 |

[a] Conditions: toluene 198 mL, 1-hexene 2 mL, ethylene 0.6 MPa, 60 °C, 1 h, catalyst 0.025 $\mu$mol, MMAO 1.0 mmol. [b] kg mmol(cat)$^{-1}$ h$^{-1}$.

**1b**, on the other hand, showed significantly lower activity probably due to the lability of monodentate $PMe_2Ph$ ligands on tungsten. The relatively lower activity of **1f** and **1g** might be caused by the steric crowding around the titanium center.

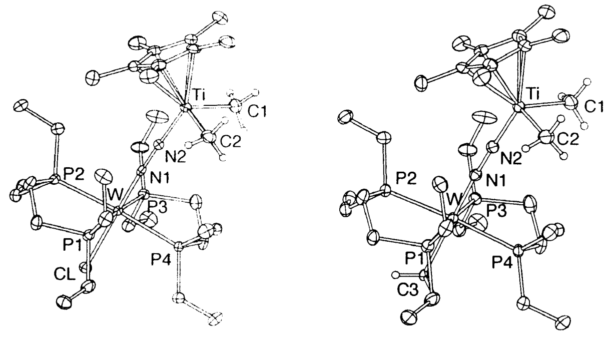
Modified methylaluminoxane (MMAO)[8] can also be used as an effective cocatalyst (Table 2). In this case, the polymerization activity of **1a** was about 200 times as high as that of CGC. Although the relative order of activity in the series of catalysts is not the same as that in the polymerization with the $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ cocatalyst, an exceptionally high catalytic activity of 510 kg mmol(cat)$^{-1}$ h$^{-1}$ was observed for complex **1d**.[9] It is noteworthy that **1d** exhibited a high activity even at relatively high reaction temperatures, around 150 °C, at least during several minutes (346 kg mmol(cat)$^{-1}$ h$^{-1}$, $M_w = 10.7 \times 10^4$ with $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$; 204 kg mmol(cat)$^{-1}$ h$^{-1}$, $M_w = 10.7 \times 10^4$ with MMAO).

The catalytic activity of **1d** for ethylene homopolymerization was investigated and compared to that of CGC (Table 3). Complex **1d** exhibited higher activity than CGC for both cocatalysts. The activities for copolymerization of ethylene and 1-hexene were higher than those for ethylene homopolymerization. This phenomenon, so-called "comonomer effect", is often observed in metallocene catalysts.[10]

**Table 3. Ethylene Homopolymerization Catalyzed by Heterobimetallic Dinitrogen Complex 1d[a]**

| entry | catalyst | cocatalyst[b] | activity[c] | $M_w$ × $10^{-4}$ | $M_w/M_n$ |
|---|---|---|---|---|---|
| 14 | **1d** | B | 61 | 45 | 4.8 |
| 15 | **1d** | A | 56 | 121 | 15.2 |
| 16 | CGC | B | 21 | 31 | 4.1 |
| 17 | CGC | A | 0.8 | 50 | 5.4 |

[a] Conditions: toluene 200 mL, ethylene 0.6 MPa, 60 °C, 1 h, catalyst 0.1 $\mu$mol. [b] B: $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ (0.25 mmol/1.0 $\mu$mol); A: MMAO (0.5 mmol). [c] kg mmol(cat)$^{-1}$ h$^{-1}$.



**2d**: Ti-C1 2.126(4), Ti-C2 2.124(4), Ti-N2 1.842(3), N1-N2 1.237(4), W-N1 1.818(3), W-CL 2.5157(8)

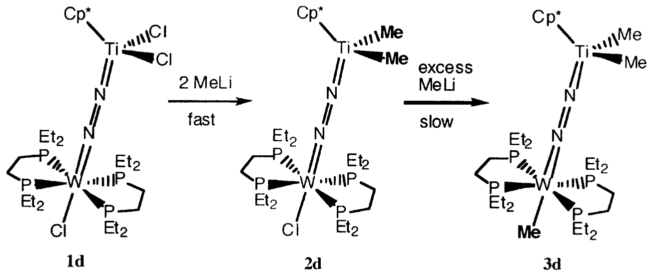
**3d**: Ti-C1 2.140(6), Ti-C2 2.155(5), Ti-N2 1.836(4), N1-N2 1.239(6), W-N1 1.839(4), W-C3 2.381(4)

C1-Ti-C2 98.7(2), Ti-N2-N1 177.2(3), N2-N1-W 176.7(3), N1-W-CL 178.6(1)

C1-Ti-C2 98.7(2), Ti-N2-N1 178.2(4), N2-N1-W 176.7(4), N1-W-C3 178.8(2)

**Figure 2.** Molecular structures of **2d** (left) and **3d** (right). One of the two crystallographically independent molecules is shown. Drawn with 50% probability ellipsoids. Hydrogen atoms are partly omitted for clarity.

**Scheme 1. Methylation of the Heterobimetallic Dinitrogen Complex 1d**



Treatment of **1d** with MeLi gave the dimethylated derivative **2d** in good yield. The $^1H$ NMR analysis of the reaction with an excess (5 equiv) of MeLi revealed that the Ti−Cl bond was initially methylated at room temperature after 1 h, while the formation of the W-$CH_3$ group was substantiated as a quintet signal at −2.1 ppm after 24 h. This shows that the methylation of the W-Cl group is much slower than that of the Ti-Cl group. The trimethylated complex **3d** was isolated in moderate yield. Both the di- and trimethylated complexes **2d** and **3d** were structurally characterized by X-ray analysis (Figure 2). The molecular structures of these complexes were fundamentally the same as that of **1d**.

Both **2d** and **3d** showed high catalytic activity for olefin polymerization in combination with $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ or MMAO (Table 4). The activities of

---

(8) MMAO is modified methylaluminoxane containing 50% isobutyl groups.

(9) The polymer yield increased straightforwardly with an increase in the reaction time at least for 60 min.

**Table 4. Copolymerization of Ethylene and 1-Hexene Catalyzed by the Dimethyl- and Trimethyl Complexes 2d and 3d**[a]

| entry | catalyst | cocatalyst[b] | activity[c] | $M_w \times 10^{-4}$ | $M_w/M_n$ | 1-hexene content |
|---|---|---|---|---|---|---|
| 18 | **2d** | B | 132 | 81 | 2.3 | 1.62 |
| 19 | **3d** | B | 180 | 105 | 3.3 | 1.54 |
| 20 | **2d** | A | 45 | 108 | 2.5 | 1.50 |
| 21 | **3d** | A | 112 | 77 | 4.2 | 1.24 |

[a] Conditions: toluene 198 mL, 1-hexene 2 mL, ethylene 0.6 MPa, 60 °C, 1 h, catalyst 0.025 $\mu$mol. [b] B: $Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$ (0.25 mmol/1.0 $\mu$mol); A: MMAO (1.0 mmol). [c] kg mmol(cat)$^{-1}$ h$^{-1}$.

**2d** and **3d** were, however, apparently lower than that observed for **1d**, presumably because the methyl derivatives are extremely sensitive toward air, moisture, and light.[11] Our attempts to isolate the cationic species from **2d** and $[Ph_3C][B(C_6F_5)_4]$ have been unsuccessful so far.

Since the niobium−tungsten complex $[CpNbCl_3(\mu\text{-}N_2)\text{-}WCl(dppe)_2]$[7] produced only negligible amounts of copolymers under the same reaction conditions, we presume that the polymerization proceeds on the titanium atom in complexes **1**−**3**. The monometallic complex $[CpTiCl_3]$ also showed very low activity. This suggests that the high catalytic activity of **1** is realized by the coordination of the $[(\mu\text{-}N_2)WX(L)_4]$ (X = Cl, alkyl) moiety, as an ancillary ligand, to the titanium center. It is to be emphasized that the tungsten dinitrogen moiety in the heterobimetallic complexes might be regarded as a unique nitrogen ligand containing a metal, which is quite different from conventional organonitrogen ligands.

**Acknowledgment.** This work was supported by the Japan Society for the Promotion of Science (JSPS) FY2000 and FS2001 “Research for the Future Program”.

**Supporting Information Available:** Synthetic procedures and spectroscopic data of **1c**−**g**, **2d**, and **3d**, crystallographic data of **1d**, **2d**, and **3d** (PDF and CIF), and experimental details of polymerization reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049447X

---

[10] For example: (a) Kaminsky, W. *Stud. Surf. Sci. Catal.* **1986**, *25*, 293−304. (b) Koivumäki, J.; Seppälä, J. V. *Macromolecules* **1993**, *26*, 5535−5538. (c) Cruz, V. L.; Muñoz-Escalona, A.; Martinez-Salazar, J. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1157−1167. (d) Kaminsky, W. *Adv. Catal.* **2001**, *46*, 89−159. (e) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 1143−1170, and references therein.

[11] Irradiation of **2d** in $C_6D_6$ with a mercury lamp (100 W) at room temperature resulted in its degradation (conv. 80% after 1 h), while 75% of **2d** remained in the dark.