2080 *Organometallics* **2010,** *29,* 2080–2084
DOI: 10.1021/om100042t

ORGANOMETALLICS
Article

Silicon-Bridged Tetramethylcyclopentadienyl–Phenoxy Complexes of Tantalum: Preparation and Alkylation of $Et_2Si(\eta^5\text{-}C_5Me_4)$-(3-^{t}Bu-5-Me-2-$C_6H_2O$)$TaCl_3$ and Generation of Its Cationic Complex

Taichi Senda,[†] Hidenori Hanaoka,[†] Yoshiaki Oda,*[,†] Hayato Tsurugi,[‡] and Kazushi Mashima*[,‡]

[†]*Organic Synthesis Research Laboratory, Sumitomo Chemical Co., Ltd., 1-98, Kasugadenaka 3-chome, Konohana-ku, Osaka 554-8558, Japan, and* [‡]*Department of Chemistry, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*

Received January 19, 2010

A tantalum complex of a silicon-bridged tetramethylcyclopentadienyl–phenoxy ligand, $Et_2Si(\eta^5\text{-}C_5Me_4)$(3-^{t}Bu-5-Me-2-$C_6H_2O$)$TaCl_3$ (**2**), was prepared by treating $TaCl_5$ with the dilithium salt generated by reaction of the corresponding ligand **1** with ^{n}BuLi in the presence of Et_3N in heptane. The molecular structure of **2**, as confirmed by X-ray analysis, showed a four-legged piano-stool geometry around the tantalum atom and slightly twisted ligand architecture with a bridging diethylsilylene unit. The tantalum complex **2** exhibited moderate catalytic activities for copolymerization of ethylene and 1-hexene in the presence of ^{i}Bu$_3$Al/Ph$_3$C[B(C$_6$F$_5$)$_4$]. The methylation reaction of the trichlorotantalum complex **2** afforded the corresponding trimethyltantalum complex **4**. Cationic dimethyltantalum species were generated by treating **4** with an equimolar amount of Ph$_3$C[B(C$_6$F$_5$)$_4$] or B(C$_6$F$_5$)$_3$ and found to be thermally stable in *o*-dichlorobenzene-*d*$_4$, even at elevated temperature.

Introduction

Metallocene complexes of early transition metals have attracted great interest due to their potential applicability as catalysts of various organic transformations and polymerizations.[1] In particular, the combination of metallocenes of group 4 metals with aluminoxane produced highly active homogeneous catalysts for α-olefin polymerization, and modification of ligand architecture, including an ansa-type bridge skeleton, in these metallocene systems produced stereoregular polymerization.[2] Half-metallocene complexes of group 4 metals, in which one of two cyclopentadienyl ligands on the metallocenes was replaced by different kinds of ancillary anionic ligands, have been anticipated as another attractive system because of their greater flexibility and feasibility in design together with high incorporation of α-olefin into polyethylene.[3] In addition, the isolation and structural characterization of cationic alkyl species of metallocene of group 4 metals fundamentally provide insight into the polymerization mechanism and would enable us to precisely design catalysts suitable for the desired catalytic performance.[4] It has already been demonstrated that the metallocene and half-metallocene complexes of group 3 metals also became polymerization catalysts for not only polymerization of ethylene but also the polymerization of polar monomers such as methyl methacrylate (MMA) and ε-caprolactone.[5] For niobium and tantalum, we have investigated half-metallocene complexes having 1,3-dienes as ancillary ligands as unique catalyst precursors for the living polymerization of ethylene[6] and MMA,[7] and several half-metallocene

---

*To whom correspondence should be addressed. E-mail: oday2@sc.sumitomo-chem.co.jp (Y.O.); mashima@chem.es.osaka-u.ac.jp (K.M.).

[1] (a) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907–3945. (b) Mashima, K.; Nakayama, Y.; Nakamura, A. *Adv. Polym. Sci.* **1997**, *133*, 1–51.

[2] (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223–1252. (c) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253–1345. (d) Razavi, A.; Thewalt, U. *Coord. Chem. Rev.* **2006**, *250*, 155–169. (e) Wang, B. *Coord. Chem. Rev.* **2006**, *250*, 242–258.

[3] (a) Okuda, J.; Eberle, T. In *Metallocenes: Synthesis Reactivity Applications*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. *1*, pp 415–453. (b) Siemeling, U. *Chem. Rev.* **2000**, *100*, 1495–1526. (c) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587–2598. (d) Qian, Y.; Huang, J.; Bala, M. D.; Lian, B.; Zhang, H.; Zhang, H. *Chem. Rev.* **2003**, *103*, 2633–2690. (e) Braunschweig, H.; Breitling, F. M. *Coord. Chem. Rev.* **2006**, *250*, 2691–2720. (f) Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A: Chem.* **2007**, *267*, 1–29.

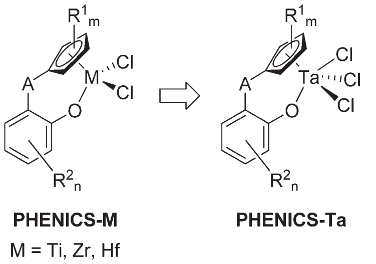
[4] (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325–387. (b) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255–270.

[5] (a) Watson, P. L.; Parshall, G. W. *Acc. Chem. Res.* **1985**, *18*, 51–56. (b) Yasuda, H.; Ihara, E. *Macromol. Chem. Phys.* **1995**, *196*, 2417–2441. (c) Yasuda, H.; Ihara, E. *Bull. Chem. Soc., Jpn.* **1997**, *70*, 1745–1767. (d) Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *133*, 53–101. (e) Hou, Z.; Wakatsuki, Y. *Coord. Chem. Rev.* **2002**, *231*, 1–22. (f) Arndt, S.; Okuda, J. *Chem. Rev.* **2002**, *102*, 1953–1976. (g) Nakayama, Y.; Yasuda, H. *J. Organomet. Chem.* **2004**, *689*, 4489–4498. (h) Zeimentz, P. M.; Arndt, S.; Elvidge, B. R.; Okuda, J. *Chem. Rev.* **2006**, *106*, 2404–2433.

[6] (a) Mashima, K.; Fujikawa, S.; Nakamura, A. *J. Am. Chem. Soc.* **1993**, *115*, 10990–10991. (b) Mashima, K.; Fujikawa, S.; Urata, H.; Tanaka, E.; Nakamura, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1623–1624. (c) Mashima, K.; Fujikawa, S.; Tanaka, Y.; Urata, H.; Oshiki, T.; Tanaka, E.; Nakamura, A. *Organometallics* **1995**, *14*, 2633–2640. (d) Mashima, K.; Nakayama, Y.; Ikushima, N.; Kaidzu, M.; Nakamura, A. *J. Organomet. Chem.* **1998**, *566*, 111–116. (e) Mashima, K. *Macromol. Symp.* **2000**, *159*, 69–76. (f) Mashima, K. *J. Synth. Org. Chem., Jpn.* **2004**, *62*, 1166–1171. (g) Nakamura, A.; Mashima, K. *J. Organomet. Chem.* **2004**, *689*, 4552–4563.

[7] Matsuo, Y.; Mashima, K.; Tani, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 960–962.

Chart 1



complexes of tantalum have been studied for the polymerization of nonpolar[8] and polar monomers.[9]

Bridged cyclopentadienyl−phenoxy complexes (PHENICS: phenoxy-induced complex of Sumitomo) of group 4 metals are industrially important half-metallocene catalyst systems that produce high-molecular-weight copolymers of ethylene and α-olefin with high comonomer content (Chart 1).[10] As an extension of our continuous synthesis of PHENICS of group 4 metals, we have synthesized the silicon-bridged PHENICS of tantalum (PHENICS-Ta), although there are some representative examples of tantalum-based nonmetallocene polymerization catalysts.[11] Thus, we report herein the structural features along with catalytic capability of these PHENICS−Ta complexes in comparison with the precedented silicon-bridged PHENICS of titanium (PHENICS-Ti). The isolation and characterization of a trialkyl complex and cationic dialkyl compounds of silicon-bridged PHENICS−Ta are also provided.

Results and Discussion

Synthesis and Characterization of Silicon-Bridged PHENICS of Tantalum. The silicon-bridged cyclopentadienyl−phenoxy ligand **1** was prepared by following modified procedures for the corresponding titanium and zirconium complexes.[10a] Treatment of **1** with ^{n}BuLi (2.1 equiv) in the presence of Et$_3$N (4.5 equiv) followed by reaction with TaCl$_5$ (1.2 equiv) gave the corresponding tantalum complex Et$_2$Si(η^5-C$_5$Me$_4$)(3-^{t}Bu-5-Me-2-C$_6$H$_2$O)TaCl$_3$ (**2**) in very low yield (2%). We thus chose a stepwise synthetic route, in which the dilithium salt **3** generated in heptane was collected by filtration and washed with hexane. When a toluene slurry of **3** was treated with 1 equiv of TaCl$_5$, the color of the mixture immediately changed to brown and the orange complex **2** was isolated in moderate yield (16%) (Scheme 1).

Scheme 1

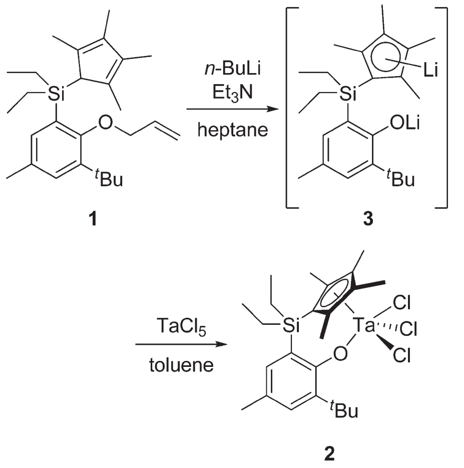


Table 1. Selected Bond Distances (Å) and Angles (deg) for Complex 2

Bond Distances			
Ta−Cl(1)	2.3696(12)	Ta−Cl(2)	2.3877(11)
Ta−Cl(3)	2.4033(11)	Ta−C(1)	2.319(4)
Ta−C(2)	2.423(4)	Ta−C(3)	2.509(5)
Ta−C(4)	2.485(4)	Ta−C(5)	2.363(4)
Ta−Cp$_{cent}$	2.094	Ta−O	1.875(3)
Si−C(1)	1.898(5)	Si−C(10)	1.882(5)
Bond Angles			
O−Ta−C(1)	87.15(14)	Ta−O−C(11)	150.5(3)
Cl(1)−Ta−Cl(2)	82.91(4)	Cl(2)−Ta−Cl(3)	81.56(4)
Cl(1)−Ta−Cl(3)	142.34(4)	Cp$_{cent}$−Ta−O	113.08
C(1)−Cp$_{cent}$−Ta	84.21	Cp$_{cent}$−C(1)−Ta	63.91
Torsion Angles			
C(1)−Si−C(10)−C(11)	10.9(5)		
Ta−O−C(11)−C(10)	20.7(8)		
Dihedral Angle			
θ^a	63.41		

[a] θ denotes the dihedral angle between the best plane of cyclopentadienyl ring and that of phenyl ring carbons.

The formulation and structure of **2** was revealed by elemental analysis and NMR spectroscopy along with a single-crystal X-ray analysis. Single crystals suitable for X-ray analysis were grown by slow evaporation of a toluene solution at room temperature. Selected bond distances and angles of **2** are summarized in Table 1. The crystal data and data collection parameters are provided in Table S1 (Supporting Information). Figure 1 shows the crystal structure of **2**, which adopts a four-legged piano-stool geometry. The torsion angles C(1)−Si−C(10)−C(11) (10.9(4)°) and Ta−O−C(11)−C(10) (20.7(8)°) and dihedral angle (θ) between the cyclopentadienyl ring and the phenyl ring of **2** (θ = 63.41°) indicate that **2** has a slightly twisted ligand backbone. Different from the case for the parent titanium complex Et$_2$Si(η^5-C$_5$Me$_4$)(3-^{t}Bu-5-Me-2-C$_6$H$_2$O)TiCl$_2$,[10e] both ethyl groups on the silicon atom are located on the upper side

---

(8) (a) Antonelli, D. M.; Leins, A.; Stryker, J. M. *Organometallics* **1997**, *16*, 2500–2502. (b) Decker, J. M.; Geib, S. J.; Meyer, T. Y. *Organometallcs* **1999**, *18*, 4417–4420. (c) Coles, M. P.; Dalby, C. I.; Gibson, V. C.; Little, I. R.; Marshall, E. L.; da Costa, M. H. R.; Mastroianni, S. *J. Organomet. Chem.* **1999**, *591*, 78–87. (d) Feng, S.; Roof, G. R.; Chen, E. Y.-X. *Organometallics* **2002**, *21*, 832–839. (e) Sánchez-Nieves, J.; Royo, P.; Mosquera, M. E. G. *Organometallics* **2006**, *25*, 2331–2336.

(9) (a) Mariott, W. R.; Gustafson, L. O.; Chen, E. Y.-X. *Organometallics* **2006**, *25*, 3721–3729. (b) Sánchez-Nieves, J.; Royo, P. *Organometallics* **2007**, *26*, 2880–2884.

(10) (a) Hanaoka, H.; Hino, T.; Souda, H.; Yanagi, K.; Oda, Y.; Imai, A. *J. Organomet. Chem.* **2007**, *692*, 4059–4066. (b) Hanaoka, H.; Hino, T.; Nabika, M.; Kohno, T.; Yanagi, K.; Oda, Y.; Imai, A.; Mashima, K. *J. Organomet. Chem.* **2007**, *692*, 4717–4724. (c) Nabika, M.; Katayama, H.; Watanabe, T.; Kawamura-Kuribayashi, H.; Yanagi, K.; Imai, A. *Organometallics* **2009**, *28*, 3785–3792. (d) Senda, T.; Hanaoka, H.; Hino, T.; Oda, Y.; Tsurugi, H.; Mashima, K. *Macromolecules* **2009**, *42*, 8006–8009. (e) Senda, T.; Hanaoka, H.; Okado, Y.; Oda, Y.; Tsurugi, H.; Mashima, K. *Organometallics* **2009**, *28*, 6915–6926. (f) Senda, T.; Hanaoka, H.; Nakahara, S.; Oda, Y.; Tsurugi, H.; Mashima, K. *Macromolecules* **2010**, *43*, 2299–2306.

(11) (a) Rodriguez, G.; Bazan, G. C. *J. Am. Chem. Soc.* **1995**, *117*, 10155–10156. (b) Hakala, K.; Löfgren, B. *Macromol. Rapid Commun.* **1997**, *18*, 635–638. (c) Murtuza, S.; Harkins, S. B.; Long, G. S.; Sen, A. *J. Am. Chem. Soc.* **2000**, *122*, 1867–1872. (d) Redshaw, C.; Rowan, M.; Homden, D. M.; Elsegood, M. R. J.; Yamato, T.; Pérez-Casas, C. *Chem. Eur. J.* **2007**, *13*, 10129–10139. (e) Yinghuai, Z.; Nong, L. C.; Zhao, L. C.; Widjaja, E.; Hwei, C. S.; Cun, W.; Tan, J.; Meurs, M. V.; Hosmane, N. S.; Maguire, J. A. *Organometallics* **2009**, *28*, 60–64. (f) Michiue, K.; Oshiki, T.; Takai, K.; Mitani, M.; Fujita, T. *Organometallics* **2009**, *28*, 6450–6457.

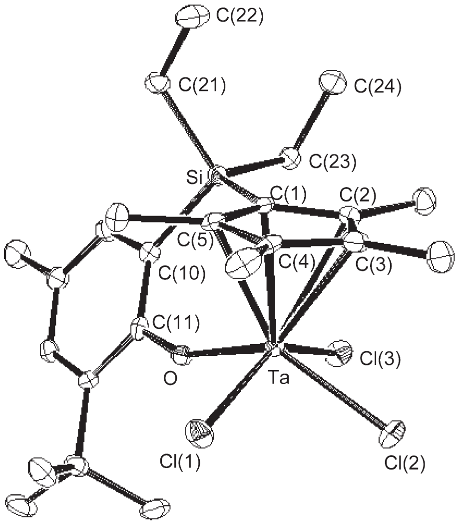
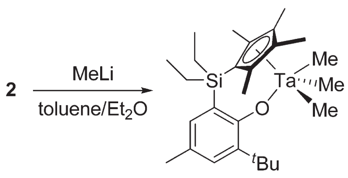


Figure 1. Molecular structure of the tantalum complex **2**. All hydrogen atoms are omitted for clarity. Key atoms are labeled.

of the cyclopentadienyl plane due to the steric repulsion between Cl(3) and C(24). The observed bond distance Ta−O (1.875(3) Å) is shorter than those of the nonbridged cyclopentadienyl−phenoxy tantalum complex $(\eta^5\text{-Cp*})(2,6\text{-Ph}_2\text{-}3,5\text{-}^t\text{Bu}_2\text{-C}_6\text{HO})\text{TaCl}_3$ (1.902(3) Å)[12] and the directly bridged indenyl−phenoxy tantalum complex with 4-phenylpyridine donor ligand $[2\text{-}(\eta^5\text{-C}_9\text{H}_6)\text{-}4,6\text{-}^t\text{Bu}_2\text{-C}_6\text{H}_2\text{O}]\text{TaCl}_3\text{(4-Ph-C}_5\text{H}_4\text{N)}$ (1.963(3) Å).[13] An almost identical Ta−O bond distance was reported for the bis(phenoxy) tantalum complexes $\text{Ta(OC}_6\text{H}_3\text{-}^t\text{Bu}_2\text{-}2,6)_2\text{Cl}_3$,[14] $\text{TaCl}_3[(\text{OC}_6\text{H}_3\text{-Ph})_2\text{-CH}_2](\text{C}_5\text{H}_5\text{N})$,[15] and $\text{TaCl}_2(\text{CH}_3)[(\text{OC}_6\text{H}_2\text{-}^t\text{Bu}_2)_2\text{C}_6\text{H}_4]$.[16] The bond angle Ta−O−C(11) (150.5(3)°) of **2** is nearly identical with those of $\text{Et}_2\text{Si}(\eta^5\text{-C}_5\text{Me}_4)(3\text{-}^t\text{Bu-5-Me-2-C}_6\text{H}_2\text{O})\text{TiCl}_2$ (151.29(13)°)[10e] and $(\eta^5\text{-Cp*})(2,6\text{-Ph}_2\text{-}3,5\text{-}^t\text{Bu}_2\text{-C}_6\text{HO})\text{TaCl}_3$ (149.9(3)°)[12] and is larger than that of $[2\text{-}(\eta^5\text{-C}_9\text{H}_6)\text{-}4,6\text{-}^t\text{Bu}_2\text{-C}_6\text{H}_2\text{O}]\text{TaCl}_3(4\text{-Ph-C}_5\text{H}_4\text{N})$ (129.0(3)°).[13]

Copolymerization of Ethylene and 1-Hexene Catalyzed by PHENICS-Ta. The tantalum complex **2** was used as a catalyst precursor for the copolymerization of ethylene and 1-hexene.[17] The tantalum complex **2** showed moderate activity (1.02 kg (mmol of Ta)$^{-1}$ h^{-1}) upon activation with $^i\text{Bu}_3\text{Al}$ (TIBA) and $\text{Ph}_3\text{C}[\text{B}(\text{C}_6\text{F}_5)_4]$ (TB) (Al/B/Ta = 400/3/1) in toluene at 40 °C to afford ethylene/1-hexene copolymer (M_w = 154 000; M_w/M_n = 1.4) with moderate 1-hexene content (6 short chain branches per 1000 carbon atoms).[18]

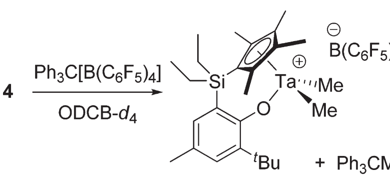
Alkylation of the Trichlorotantalum Complex. To gain insight into the active species of the polymerization catalyzed by the tantalum complex **2**, a methylation reaction of **2** was conducted. Thus, treatment of a toluene solution of **2** with 3 equiv of a diethyl ether solution of MeLi resulted in the formation of the corresponding trimethyltantalum complex **4** (eq 1). Recrystallization from pentane at −20 °C gave **4** as a yellow solid in moderate isolated yield (48%). The ^{1}H NMR spectrum of **4** in CDCl_3 exhibited one singlet signal at δ 0.28 assignable to three methyl protons bound to the tantalum atom, suggesting fluxional behavior of the three Ta methyl groups. Equivalent protons of Ta−Me$_3$ were also observed for trimethyltantalum complexes with a diamine[8d] or linked bis(phenoxy)[16] ligand.



(1)

4

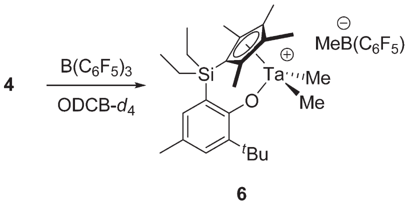
Formation of a Cationic Dimethyltantalum Compound. One equivalent of TB mixed with the neutral trimethyltantalum complex **4** in *o*-dichlorobenzene-*d*$_4$ (ODCB-*d*$_4$) at room temperature afforded clean conversion to the corresponding cationic dimethyltantalum species **5** (eq 2). Although some cationic complexes of group 4 metals were reported to react with aryl halides,[19] the cationic compound **5** was thermally stable under an inert atmosphere for long periods, even in halogenated solvent. The ^{1}H NMR spectrum of compound **5** showed one narrow signal due to the two equivalent Ta−Me groups (Figure S1b), indicating that the structure of **5** has a three-legged piano-stool geometry.



(2)

5

The methyl abstraction of **4** also proceeded cleanly using an equimolar amount of $\text{B}(\text{C}_6\text{F}_5)_3$ in ODCB-*d*$_4$ at room temperature to give the corresponding cationic species with the counteranion $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**6**) (Figure S1c). The ^{19}F NMR spectrum of the mixture showed a small $\Delta\delta(\text{F}_\text{meta}-\text{F}_\text{para})$ value of 2.45 ppm, indicating the presence of the solvent-separated, noncoordinated anion $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (Figure S6).[20]



(3)

6

Treatment of **4** with 3 equiv of TB also gave **5**, and no further methyl abstraction reaction occurred even at 150 °C (Figure S7).[21]

---

[12] Vilardo, J. S.; Salberg, M. M.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chim. Acta* **2000**, *299*, 135–141.

[13] Thorn, M. G.; Parker, J. R.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **2003**, *22*, 4658–4664.

[14] Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575–2578.

[15] Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **2000**, *19*, 35–42.

[16] Agapie, T.; Day, M. W.; Bercaw, J. E. *Organometallics* **2008**, *27*, 6123–6142.

[17] Preliminary polymerization of ethylene using **2** was conducted using various cocatalysts at 40 °C. The polymerization activities were as follows: MMAO (Al/Ta = 1000/1), 0.24 kg (mmol of Ta)$^{-1}$ h^{-1}; TIBA/$\text{B}(\text{C}_6\text{F}_5)_3$ (Al/B/Ta = 400/3/1), 0.09 kg (mmol of Ta)$^{-1}$ h^{-1}; TIBA/TB (Al/B/Ta = 400/3/1), 2.55 kg (mmol of Ta)$^{-1}$ h^{-1}; TIBA/$[\text{Me}_2\text{NHPh}][\text{B}(\text{C}_6\text{F}_5)_4]$ (Al/B/Ta = 400/3/1), 1.92 kg (mmol of Ta)$^{-1}$ h^{-1}.

[18] For copolymerization results of related titanium complexes, see ref 10a.

[19] (a) Wu, F.; Dash, A. K.; Jordan, R. F. *J. Am. Chem. Soc.* **2004**, *126*, 15360–15361. (b) Ma, K.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2006**, *128*, 3303–3313.

[20] (a) Horton, A. D.; de With, J.; van der Linden, A. J.; van de Weg, H. *Organometallics* **1996**, *15*, 2672–2674. (b) Klosin, J.; Roof, G. R.; Chen, E. Y.-X.; Abboud, K. A. *Organometallics* **2000**, *19*, 4684–4686. For related arguments, also see ref 8d, 8e, and 9a.

[21] For a reaction of Cp_2TaMe_3 with 2 equiv of TB, see ref 8d.

The result indicates that coordination of ODCB-d_4 to the tantalum metal center is strong enough to separate Ta−Me bonds of cationic species from an excess amount of TB.[22] The mixture of **4** and 3 equiv of TB in ODCB-d_4 was added to 500 equiv of 1-hexene at room temperature, giving low-molecular-weight poly(1-hexene) (M_w = 1430; M_w/M_n = 1.2) in 65.9% yield after 5 days. The low activity toward 1-hexene polymerization suggested that coordination of ODCB-d_4 to vacant site hampered the 1-hexene approach.[23]

Although cationic alkyl complexes of early transition metals are generally thermally unstable, the cationic dimethyltantalum complex derived from **4** is very stable in ODCB-d_4 even at elevated temperature.[24] The high temperature stability is attributable to the coordination of ODCB-d_4 and the bridged cyclopentadienyl−phenoxy framework, for which the characteristic ligand effects have been demonstrated by high-temperature ethylene/1-hexene copolymerization catalyzed by titanium derivatives.[10] The relatively low catalytic activity of PHENICS-Ta toward olefin polymerization is ascribed to the larger atom radius of tantalum as compared to that of titanium, which causes coordination of the aromatic solvent.[25,26]

Conclusion

In summary, we demonstrated the preparation of a trichlorotantalum complex bearing a bridged tetramethylcyclopentadienyl−phenoxy ligand, $Et_2Si(\eta^5\text{-}C_5Me_4)(3\text{-}^tBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_2O)TaCl_3$ (**2**), and the molecular structure of **2** was revealed by X-ray analysis. The alkylation reaction of **2** with MeLi afforded the corresponding trimethyltantalum complex **4**. The reaction of **4** with an equimolar amount of $Ph_3C[B(C_6F_5)_4]$ or $B(C_6F_5)_3$ led to the quantitative formation of the cationic dimethyltantalum complexes **5** and **6**, respectively, which were fully characterized by ^1H and ^{13}C NMR analyses. The ^{19}F NMR spectrum of **6** showed a small $\Delta\delta(F_{meta}-F_{para})$ value of $[MeB(C_6F_5)_3]^-$ and indicated the presence of a separated ion pair in *o*-dichlorobenzene-d_4. The cationic dimethyltantalum species was found to be thermally stable in *o*-dichlorobenzene-d_4 even at 150 °C in the presence of an excess amount of $Ph_3C[B(C_6F_5)_4]$, giving no further methyl abstraction. The observed ion separation and high temperature stability suggested a strong coordination of *o*-dichlorobenzene-d_4 to the vacant coordination site of the cationic tantalum metal center. The relatively lower polymerization activity of PHENICS-Ta is attributable to the lower Lewis acidity of the cationic species and the larger atom radius of tantalum as compared to that of the corresponding titanium-based PHENICS.

Experimental Section

General Procedures. All manipulations of air- and moisture-sensitive materials were performed under dry nitrogen using a glovebox or standard Schlenk line techniques. Solvents (heptane, pentane, and toluene) were purchased from Kanto Chemical Co., Inc. (anhydrous grade) and used as received. ^nBuLi was purchased from Kanto Chemical Co., Inc. $TaCl_5$ was purchased from Sigma-Aldrich. Et_3N was purchased from Nacalai Tesque Co., Inc. $C_6D_4Cl_2$ (*o*-dichlorobenzene-d_4) was purchased from Wako Pure Chemical Industries, Ltd. $^iBu_3Al$ (TIBA) was purchased from Tosoh Finechem. Co., Ltd. Ph_3C-$[B(C_6F_5)_4]$ (TB) was purchased from Asahi Glass Co., Ltd. The bridged cyclopentadienyl−phenoxy ligand **1** was prepared by the reported method.[10d] ^1H NMR (270 MHz) and ^{13}C NMR (68 MHz) were measured on a JEOL EX270 spectrometer. ^{19}F NMR spectra (282 MHz) were measured on a Bruker DPX-300 spectrometer. Chemical shifts for ^1H and ^{13}C NMR spectra were referenced using internal solvent resonances and are reported relative to TMS. ^{19}F NMR spectra were referenced to external $CFCl_3$. When $C_6D_4Cl_2$ was used as the solvent, the spectra were referenced to the resonance of the 3,6-positions of the residual solvent protons at δ 7.40 or that of the 4,5-positions at δ 7.14 in the ^1H NMR spectra. Elemental analyses were performed using an Elementar element analyzer at Sumika Chemical Analysis Service, Ltd. All melting points were measured in sealed aluminum pans under a nitrogen atmosphere by differential scanning calorimetry (DSC) on a TA Instruments Q2000 at a heating rate of 10 °C/min. Molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) were determined by high-temperature gel permeation chromatography (GPC). GPC analyses were carried out at 160 °C using a Symyx Rapid GPC^{TM}, equipped with three Plgel 10 μm mixed-B columns, and a Tosoh HLC-8121GPC/HT gel permeation chromatograph, equipped with TSKgel GMHHR-H(S)HT mixed bed columns. GPC columns were calibrated using commercially available polystyrene standards (Polymer Laboratories). FT-IR measurements were performed on a Bruker Equinox 55 + PIKE Mapp IR spectrometer to determine 1-hexene content in the copolymer.[27]

Preparation of $Et_2Si(\eta^5\text{-}C_5Me_4)(3\text{-}^tBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_2O)TaCl_3$ (2). To a heptane (40 mL) solution of Et_3N (2.44 g, 24.15 mmol) and **1** (1.98 g, 4.83 mmol) at −78 °C was added a hexane solution of ^nBuLi (1.55 M, 7.79 mL, 12.07 mmol). The mixture was warmed to room temperature and then stirred for 3 h. The solvent was evaporated, and the resulting solids were collected by filtration and washed with hexane. The dilithium salt **3** was obtained as a pale yellow powder (1.23 g). To a toluene (10 mL) slurry of $TaCl_5$ (0.94 g, 2.61 mmol) at −30 °C was added a toluene (10 mL) slurry of **3** (1.00 g, 2.61 mmol). The resulting mixture was warmed to room temperature and then stirred overnight. Insoluble materials were removed by filtration. Removal of the solvent followed by washing with pentane gave **2** as orange solids (0.42 g, 16% yield). Mp: 229−232 °C dec. ^1H NMR ($CDCl_3$): δ 1.00−1.32 (m, 10H, Si-*Et_2*), 1.40 (s, 9H, Ar-*^tBu*), 2.38 (s, 3H, Ar-*Me*), 2.53 (s, 6H, Cp-*Me_2*), 2.57 (s, 6H, Cp-*Me_2*), 7.08 (s, 1H, Ar-*H*), 7.29 (s, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 5.1 (Si-CH_2CH_3), 7.6 (Si-CH_2CH_3), 13.4 (Cp-*Me_2*), 15.5 (Cp-*Me_2*), 21.2 (Ar-*Me*), 31.0 (Ar-C*Me_3*), 34.9 (Ar-*C*Me_3), 110.3, 126.0, 130.1, 133.5, 133.6, 135.4, 139.5, 140.9, 164.0. Anal. Calcd for $C_{24}H_{36}Cl_3OSiTa$: C, 43.95; H, 5.53. Found: C, 44.04; H, 5.70.

Preparation of $Et_2Si(\eta^5\text{-}C_5Me_4)(3\text{-}^tBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_2O)TaMe_3$ (4). To a toluene (11 mL) solution of **2** (210 mg, 0.32 mmol)

---

[22] For coordination of a halogenated solvent to a cationic early-transition-metal center, see: (a) Bochmann, M.; Jaggar, A. J.; Nicholls, J. C. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780–782. (b) Bouwkamp, M. W.; de Wolf, J.; del Hierro Morales, I.; Gercama, J.; Meetsma, A.; Troyanov, S. I.; Hessen, B.; Teuben, J. H. *J. Am. Chem. Soc.* **2002**, *124*, 12956–12957. (c) Hayes, P. G.; Piers, W. E.; Parvez, M. *J. Am. Chem. Soc.* **2003**, *125*, 5622–5623. (d) Bouwkamp, M. W.; Budzelaar, P. H. M.; Gercama, J.; Morales, I. D. H.; de Wolf, J.; Meetsma, A.; Troyanov, S. I.; Teuben, J. H.; Hessen, B. *J. Am. Chem. Soc.* **2005**, *127*, 14310–14319.

[23] The cationic species **5** was insoluble in toluene. Generation of the cationic species **5** and the following polymerization of 1-hexene was attempted in toluene under more dilute conditions; however, no polymer was obtained.

[24] For a review, see: Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391–1434.

[25] For decreased polymerization activities by the coordination of toluene, see: Scollard, J. D.; McConville, D. H. *J. Am. Chem. Soc.* **1996**, *118*, 10008–10009.

[26] For cyclopentadienyl tantalum complexes with a pendant η^6-arene ligand, see: Otten, E.; Meetsma, A.; Hessen, B. *J. Am. Chem. Soc.* **2007**, *129*, 10100–10101.

[27] Blitz, J. P.; McFaddin, D. C. *J. Appl. Polym. Sci.* **1994**, *51*, 13–20.

at −78 °C was added dropwise an Et_2O solution of MeLi (1.12 M, 0.90 mL, 1.01 mmol). The mixture was warmed to room temperature and then stirred for 1 h. After evaporation of the solvent, hexane was added and insoluble materials were removed by filtration. The solvent was evaporated, and recrystallization from pentane at −20 °C gave **4** as yellow solids (91.3 mg, 48% yield). Mp: 175−177 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.28 (s, 9H, Ta-Me_3), 0.84−1.09 (m, 10H, Si-Et_2), 1.39 (s, 9H, Ar-^{t}*Bu*), 2.00 (s, 6H, Cp-Me_2), 2.03 (s, 6H, Cp-Me_2), 2.28 (s, 3H, Ar-*Me*), 6.95 (d, J = 2.1 Hz, 1H, Ar-*H*), 7.18 (d, J = 2.1 Hz, 1H, Ar-*H*). ^{13}C NMR ($CDCl_3$): δ 5.2 (Si-$\mathit{C}H_2CH_3$), 7.5 (Si-$CH_2\mathit{C}H_3$), 11.5 (Cp-Me_2), 13.8 (Cp-Me_2), 21.1 (Ar-*Me*), 30.6 (Ar-CMe_3), 34.8 (Ar-*C*$\mathrm{Me_3}$), 57.2 (Ta-Me_3), 101.0, 124.6, 125.6, 126.2, 129.8, 130.0, 133.5, 138.3, 162.9. Anal. Calcd for $C_{27}H_{45}OSiTa$: C, 54.53; H, 7.63. Found: C, 54.79; H, 7.73.

Preparation of $[Et_2Si(\eta^5\text{-}C_5Me_4)(3\text{-}^tBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_2O)TaMe_2]^+[B(C_6F_5)_4]^-$ (5). In a glovebox, $C_6D_4Cl_2$ (0.5 mL) was added to a mixture of **4** (7.7 mg, 12.9 μmol) and $Ph_3C[B(C_6F_5)_4]$ (11.9 mg, 12.9 μmol) at room temperature, and then the NMR spectrum was obtained. The ^{1}H NMR spectrum indicated the quantitative formation of the title compound. ^{1}H NMR ($C_6D_4Cl_2$): δ 0.92−1.05 (m, 10H, Si-Et_2), 1.20 (s, 6H, Ta-Me_2), 1.60 (s, 9H, Ar-^{t}*Bu*), 2.14 (s, 6H, Cp-Me_2), 2.25 (s, 6H, Cp-Me_2), 2.51 (s, 3H, Ar-*Me*), 7.48 (d, J = 1.5 Hz, 1H, Ar-*H*); one aryl proton signal was overlapped with Ph_3CMe resonances. ^{13}C NMR ($C_6D_4Cl_2$): δ 5.2 (Si-$\mathit{C}H_2CH_3$), 7.4 (Si-$CH_2\mathit{C}H_3$), 11.8 (Cp-Me_2), 13.1 (Cp-Me_2), 21.5 (Ar-*Me*), 30.4 (Ar-CMe_3), 35.1 (Ar-*C*$\mathrm{Me_3}$), 71.1 (Ta-Me_2), 105.6, 126.8, 131.3, 133.5, 134.0, 134.6, 137.1 (br d, J_{CF} = 247.5 Hz, C_6F_5), 137.6, 137.9, 139.0 (br d, J_{CF} = 245.4 Hz, C_6F_5), 149.2 (br d, J_{CF} = 243.4 Hz, C_6F_5), 160.6. The ipso carbon of the C_6F_5 group could not be assigned with confidence due to overlapping with the NMR solvent peaks. ^{19}F NMR ($C_6D_4Cl_2$): δ −131.28 (*o*-C_6F_5), −161.74 (*p*-C_6F_5), −165.57 (*m*-C_6F_5).

Preparation of $[Et_2Si(\eta^5\text{-}C_5Me_4)(3\text{-}^tBu\text{-}5\text{-}Me\text{-}2\text{-}C_6H_2O)TaMe_2]^+[MeB(C_6F_5)_3]^-$ (6). In a glovebox, $C_6D_4Cl_2$ (0.5 mL) was added to a mixture of **4** (19.9 mg, 33.5 μmol) and $B(C_6F_5)_3$ (17.1 mg, 33.5 μmol) at room temperature, and then the NMR spectrum was obtained. The ^{1}H NMR spectrum indicated the quantitative formation of the title compound. ^{1}H NMR ($C_6D_4Cl_2$): δ 0.92−1.05 (m, 10H, Si-Et_2), 1.19 (s, 6H, Ta-Me_2), 1.25 (s, 3H, B-*Me*), 1.58 (s, 9H, Ar-^{t}*Bu*), 2.13 (s, 6H, Cp-Me_2), 2.24 (s, 6H, Cp-Me_2), 2.50 (s, 3H, Ar-*Me*), 7.22 (d, J = 1.5 Hz, 1H, Ar-*H*), 7.47 (d, J = 1.5 Hz, 1H, Ar-*H*). ^{13}C NMR ($C_6D_4Cl_2$): δ 5.1 (Si-$\mathit{C}H_2CH_3$), 7.4 (Si-$CH_2\mathit{C}H_3$), 11.8 (Cp-Me_2), 13.1 (Cp-Me_2), 21.5 (Ar-*Me*), 30.4 (Ar−CMe_3), 35.1 (Ar-*C*$\mathrm{Me_3}$), 71.1 (Ta-Me_2), 105.6, 126.8, 131.2, 133.5, 134.0, 134.6, 137.2 (br d, J_{CF} = 249.5 Hz, C_6F_5), 137.5, 137.9, 138.2 (br d, J_{CF} = 243.4 Hz, C_6F_5), 149.4 (br d, J_{CF} = 235.3 Hz, C_6F_5), 160.6. The ipso carbon of the C_6F_5 group could not be assigned with confidence due to overlapping with the NMR solvent peaks. ^{19}F NMR ($C_6D_4Cl_2$): δ −131.21 (*o*-C_6F_5), −163.57 (*p*-C_6F_5), −166.02 (*m*-C_6F_5).

Copolymerization of Ethylene and 1-Hexene Catalyzed by 2. A Symyx Parallel Pressure Reactor (PPR) system was used for polymerization experiments. A prewashed glass vial insert and disposable stirring paddle were fitted to each reaction vessel of the reactor. The reactor was then closed, and TIBA (40 μmol, 160 μL, 0.25 M toluene solution), 1-hexene (60 μL), and toluene were injected into each reaction vessel through a valve. The total volume of the reaction mixture was adjusted with toluene to 5 mL. The temperature was then set to 40 °C, the stirring speed was set to 800 rpm, and the mixture was pressurized with ethylene to 0.6 MPa. Polymerization was started by addition of a toluene solution of tantalum complex **2** (0.1 μmol, 1 mM toluene solution) followed by a toluene solution of TB (0.3 μmol, 1 mM toluene solution). Ethylene pressure in the cell and the temperature setting were maintained by computer control until the end of the polymerization experiment. After the polymerization reaction, the reaction mixture was cooled to room temperature and the ethylene pressure in the cell was slowly vented. The glass vial insert was then removed from the pressure cell, and the volatile components were removed using a centrifuge vacuum evaporator to give the polymeric product.

Polymerization of 1-Hexene Catalyzed by 5. In a glovebox, a mixture of **4** (8.5 mg, 14.3 μmol) with TB (39.6 mg, 42.9 μmol) in ODCB-d_4 (0.5 mL) was added to 1-hexene (606.5 mg, 7.21 mmol) at room temperature. The reaction mixture was stirred for 5 days at room temperature. The reaction was quenched by adding MeOH, and the mixture was dried. The polymer was extracted by hexane, and the hexane extract was purified by passing through silica gel. Polymer was obtained by evaporating hexane and drying at 60 °C. The result is provided in the main text.

Crystallographic Data Collection and Structure Determination of 2. The crystal was mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113(2) K. The measurement was made on a Rigaku AFC7R/Mercury CCD detector with graphite-monochromated Mo Kα (0.710 75 Å) radiation. Crystal data and structure refinement parameters are summarized in Table S1 (Supporting Information). The structure was solved by direct methods (SIR 92)[28] and refined on F^2 using full-matrix least-squares methods (SHELXL-97).[29] Non-hydrogen atoms were anisotropically refined. H atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\mathrm{Max}(F_o^{2,0}) + 2F_c^2)/3$ with $\sigma^2(F_o^2)$ from counting statistics. The functions R_1 and wR_2 were $(\sum||F_o| - |F_c||)/(\sum|F_o|)$ and $[\{\sum w(F_o^2 - F_c^2)^2\}/\{\sum(wF_o^4)\}]^{1/2}$, respectively. The ORTEP-3 program (for Windows, version 2.02)[30] was used to draw the molecule.

Acknowledgment. We thank Mr. Takahiro Hino (Sumitomo Chemical) and Mr. Takuto Nakayama (Sumitomo Chemical) for polymerization experiments.

Supporting Information Available: Figures showing NMR spectra of **5** and **6** and a table and CIF file giving crystal data for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

---

[28] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[29] Sheldrick, G. M.; Schneider, T. R. *Methods Enzymol.* **1997**, *277*, 319–343.

[30] Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.