Syntheses and Structures of Bulky Monophosphine-Ligated Methylpalladium Complexes: Application to Homo- and Copolymerization of Norbornene and/or Methoxycarbonylnorbornene

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Several new bulky monophosphine-ligated methylpalladium complexes were synthesized. Treatment of Pd(cod)MeCl (cod = cyclooctadiene) with bulky phosphines, P^tBu_3, or P(*o*-tol)$_3$ afforded monophosphine-ligated methylpalladium chloride complexes **1a** and **1b**, which were isolated as crystalline solids in excellent yields. The structures depended on the shape of the ligand: a mononuclear three-coordinate structure for **1a** and a chloride-bridged dinuclear structure for **1b**. Absorption of chloride from methylpalladium chloride complexes **1a** and **1b** afforded the corresponding methylpalladium triflate complexes **2a** and **2b**, which were structurally characterized by NMR spectroscopy and X-ray crystallography. In the presence of NaB[3,5-$(CF_3)_2C_6H_3]_4$, **1a** and **1b** catalyzed the addition homopolymerization of norbornene or methoxycarbonylnorbornene. The activity of the catalyst was found to be dependent on the structure of the complexes and the counteranions. The catalyst system **1a**-NaB[3,5-$(CF_3)_2C_6H_3]_4$ was also active for the copolymerization of norbornene and methoxycarbonylnorbornene to form a block-type copolymer. The obtained copolymer has the highest ester content probably due to the two vacant sites on the palladium. The molecular weight distribution reached the narrowest value, indicating the long lifetime of the catalyst.

Introduction

Late transition metal catalysts, such as nickel and palladium, are active for the addition polymerization of norbornenes.[1] Recently, the less oxophilic character of the late transition metal has been considered to be effective for the polymerization of heteroatom-functionalized monomers.[2] However, the rate of polymerization of functionalized norbornene[3−11] is apparently slower than that of the unsubstituted norbornene. This deceleration may be due to the coordination of functional group to the metal center to form a strong chelate.[8,11] The examples of nickel and palladium catalysts that can polymerize methoxycarbonylnorbornene are classified into the following types of complexes: (1) solvent-coordinated dicationic palladium, [Pd(NCMe)$_4$]X$_2$ (X = BF_4, SbF_6),[3] (2) cationic allylpalladium [(η^3-allyl)Pd]X$_2$ (X = counteranion),[4,5] (3) olefin-coordinated cationic norbornylpalladium,[6,7] (4) PPh_3-ligated cationic methylpalladium complex, where the active catalyst was assumed to be "[(Ph_3P)PdMe]B[3,5-$(CF_3)_2C_6H_3]_4$",[8,11] (5) phosphine-ligated cationic allylpalladium complex [(η^3-allyl)Pd(PR_3)]B$(C_6F_5)_4$ (R = alkyl, aryl),[9] and (6) cationic cyclooctadiene methylpalladium complex [(cod)PdMe]B[3,5-$(CF_3)_2C_6H_3]_4$.[10]

Over the past few years, bulky monophosphines are widely known as the ligands that develop active catalyst systems in palladium-catalyzed reactions.[12−50] For example, the palladium-

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(1) Janiak, C.; Lassahn, P. G. *J. Mol. Catal. A Chem.* **2001**, *166*, 193−209.

(2) Younkin, T. R.; Conner, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460−462.

(3) Breunig, S.; Risse, W. *Makromol. Chem.* **1992**, *193*, 2915−2927.

(4) Reinmuth, A.; Mathew, J. P.; Melia, J.; Risse, W. *Macromol. Rapid Commun.* **1996**, *17*, 173−180.

(5) Mathew, J. P.; Reinmuth, A.; Melia, J.; Swords, N.; Risse, W. *Macromolecules* **1996**, *29*, 2755−2763.

(6) Heinz, B. S.; Heitz, W.; Krugel, S. A.; Raubacher, F.; Wendorff, J. H. *Acta Polym.* **1997**, *48*, 385−391.

(7) Heinz, B. S.; Alt, F. P.; Heitz, W. *Macromol. Rapid Commun.* **1998**, *19*, 251−256.

(8) Hennis, A. D.; Polley, J. D.; Long, G. S.; Sen, A.; Yandulov, D.; Lipian, J.; Benedikt, G. M.; Rhodes, L. F.; Huffman, J. *Organometallics* **2001**, *20*, 2802−2812.

(9) Lipian, J.; Mimna, R. A.; Fondran, J. C.; Yandulov, D.; Shick, R. A.; Goodall, B. L.; Rhodes, L. F.; Huffman, J. C. *Macromolecules* **2002**, *35*, 8969−8977.

(10) Kang, M.; Sen, A. *Organometallics* **2004**, *23*, 5396−5398.

(11) Funk, J. K.; Andes, C. E.; Sen, A. *Organometallics* **2004**, *23*, 1680−1683.

(12) Nishiyama, M.; Yamamoto, T.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 617−620.

(13) Yamamoto, T.; Nishiyama, M.; Koie, Y. *Tetrahedron Lett.* **1998**, *39*, 2367−2370.

(14) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 2411−2413.

(15) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020−4028.

(16) Littke, A. F.; Schwarz, L.; Fu, G. C. *J. Am. Chem. Soc.* **2002**, *124*, 6343−6348.

(17) Littke, A. F.; Fu, G. C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4176−4121.

(18) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722−9723.

(19) Yang, B. H.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125−146.

(20) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1999**, *38*, 2413−2416.

(21) Muci, A. R.; Buchwald, S. L. *Top. Curr. Chem.* **2001**, *219*, 131−209.

(22) Torraca, K. E.; Huang, X. H.; Parrish, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 10770−10771.

(23) Kuwabe, S.; Torraca, K. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2001**, *123*, 12202−12206.

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catalyzed coupling reactions of aryl halides with organometallic species or amines were accelerated using bulky monophosphines as ligands.[24,30,34,51–53] Various bulky monophosphine-ligated palladium complexes, LPd(R)X [L = monophosphine, R = aryl, allyl, X = halogen or heteroatom], were isolated as reaction intermediates.[37,51–53] In contrast to the intensive studies of aryl or allyl complexes, corresponding alkyl complexes have never been isolated[54] until we have recently reported the syntheses of methylpalladium complexes bearing a monodentate phosphine ligand.[55] Thus, we became interested in the structures and catalytic properties of monophosphine-ligated alkylpalladium complexes for the polymerization of functionalized norbornene.

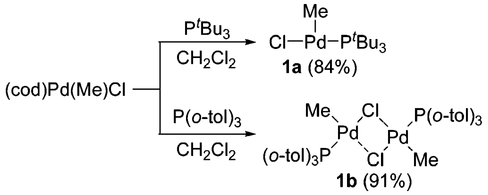
Bulky monophosphine-ligated arylpalladium complexes, $(R_3P)Pd(Ar)X$,[51–53] were reported to have a formal vacant site to form a T-shape, three-coordinate structure around the palladium atom. The vacant site may be useful for the polymerization of methoxycarbonylnorbornene in the following two points. (1) A large monomer, norbornene, can coordinate to the vacant site to lead to a high catalytic activity. (2) The monomer can approach the metal center even in the presence of an intramolecularly coordinated functional group, such as an ester group.

Here we report the syntheses and full structural characterizations of bulky monophosphine-ligated methylpalladium complexes and their applications to homo- and copolymerization of norbornene and/or methoxycarbonylnorbornene.

Results and Discussion

Syntheses of Monophosphine-Ligated Methylpalladium Chloride Complexes 1a and 1b. The syntheses of monophosphine-ligated methylpalladium chloride complexes are shown in Scheme 1. Simple ligand exchange reactions of Pd(cod)MeCl (cod = cyclooctadiene)[56,57] with bulky phosphines $^{t}Bu_3P$ or (*o*-tol)$_3$P gave the corresponding methylpalladium chloride complexes **1a** and **1b**, which were isolated as crystalline solids in excellent yields.

Scheme 1. Syntheses of Methylpalladium Chloride Complexes (1a and 1b)



Single crystals of **1a** and **1b** suitable for X-ray crystallographic analysis were obtained from a CCl_4 solution of **1a** or a $CHCl_3$ solution of **1b** diffused by hexane at 0 °C. The crystal structures of the complexes **1a** and **1b** are presented in Figures 1 and 2, respectively. Selected bond lengths and angles are shown in Table 1. The X-ray crystallography revealed that complex **1a** has a three-coordinate T-shape structure stabilized by a weak C–H agostic interaction between the palladium atom and a C–H bond of the *tert*-butyl group. This is the first example of a three-coordinate alkylpalladium complex. An electron-donating methyl ligand was located trans to the formal vacant site. These structural features are similar to those of the recently reported aryl palladium complex $Pd(P^{t}Bu_3)PhBr$.[52] In the ^{1}H NMR spectrum at room temperature, the *tert*-butyl groups of **1a** were all equivalent, indicating free rotation of both the Pd–P and P–C bond on the NMR time scale. In contrast to **1a**, complex **1b** has a Cl-bridged dinuclear structure where half of the molecule is in the unit cell. Despite the bulkiness of the ligands, bond lengths and angles around the central palladium atom in **1b** are similar to those of usual Cl-bridged dinuclear complexes.[58–62] One of the two Pd–Cl bonds, Pd(1)–Cl(1), is shorter than Pd(1)–Cl(1*). Thus, one can expect the longer Pd(1)–Cl(1)* bond cleavage in **1b** to lead to the equilibrium

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(24) Yin, J.; Rainka, M. P.; Zhang, X.-X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 1162–1163.

(25) Strieter, E. R.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 13978–13980.

(26) Nguyen, H. N.; Huang, X.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 11818–11819.

(27) Huang, X.; Anderson, K. W.; Zim, D.; Jiang, L.; Klapars, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **2003**, *125*, 6653–6655.

(28) Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2004**, *6*, 2649–2652.

(29) Milne, J. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **2004**, *126*, 13028–13032.

(30) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2004**, *43*, 1871–1876.

(31) Anderson, K. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6173–6177.

(32) Charles, M. D.; Schultz, P.; Buchwald, S. L. *Org. Lett.* **2005**, *7*, 3965–3968.

(33) Vorogushin, A. V.; Huang, X. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 8146–8149.

(34) Barder, T. E.; Walker, S. D.; Martinelli, J. R.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696.

(35) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887–9888.

(36) Uozumi, Y.; Tanahashi, A.; Lee, S. Y.; Hayashi, T. *J. Org. Chem.* **1993**, *58*, 1945–1948.

(37) Hayashi, T.; Iwamura, H.; Naito, M.; Matsumoto, Y.; Uozumi, Y.; Miki, M.; Yanagi, K. *J. Am. Chem. Soc.* **1994**, *116*, 775–776.

(38) Uozumi, Y.; Kitayama, K.; Hayashi, T.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713–722.

(39) Hayashi, T. *J. Organomet. Chem.* **1999**, *576*, 195–202.

(40) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354–362.

(41) Kawatsura, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1473–1478.

(42) Mann, G.; Incarvito, C.; Rheingold, A. L.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 3224–3225.

(43) Hartwig, J. F.; Kawatsura, M.; Hauck, S. I.; Shaughnessy, K. H.; Alcazar-Roman, L. M. *J. Org. Chem.* **1999**, *64*, 5575–5580.

(44) Hartwig, J. F. *Pure Appl. Chem.* **1999**, *71*, 1417–1423.

(45) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 10718–10719.

(46) Lee, S.; Jorgensen, M.; Hartwig, J. F. *Org. Lett.* **2001**, *3*, 2729–2732.

(47) Lee, S.; Beare, N. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 8410–8411.

(48) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553–5566.

(49) Beare, N. A.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 541–555.

(50) Kawashima, Y.; Okano, K.; Nozaki, K.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 347–355.

(51) Stambuli, J. P.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2002**, *124*, 9346–9347.

(52) Stambuli, J. P.; Incarvito, C. D.; Buhl, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 1184–1194.

(53) Yamashita, M.; Hartwig, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 5344–5345.

(54) Propargyl derivatives have been reported, see: Tsutsumi, K.; Ogoshi, S.; Nishiguchi, S.; Kurosawa, H. *J. Am. Chem. Soc.* **1998**, *120*, 1938–1939.

(55) Yamashita, M.; Takamiya, I.; Jin, K.; Nozaki, K. *J. Organomet. Chem.* **2006**, *691*, 3189–3195.

(56) Rulke, R. E.; Ernsting, J. M.; Spek, A. L.; Elsevier, C. J.; Vanleeuwen, P. W. N. M.; Vrieze, K. *Inorg. Chem.* **1993**, *32*, 5769–5778.

(57) Ladipo, F. T.; Anderson, G. K. *Organometallics* **1994**, *13*, 303–306.

(58) Oliver, J. D.; Mullica, D. F.; Milligan, W. O. *Inorg. Chem.* **1982**, *21*, 3284–3286.

(59) Youngs, W. J.; Mahood, J.; Simms, B. L.; Swepston, P. N.; Ibers, J. A.; Shang, M. Y.; Huang, J. L.; Lu, J. X. *Organometallics* **1983**, *2*, 917–921.

(60) Geib, S. J.; Rheingold, A. L. *Acta Crystallogr., Sect. C* **1987**, *43*, 1427–1428.

(61) Alyea, E. C.; Ferguson, G.; Malito, J.; Ruhl, B. L. *Organometallics* **1989**, *8*, 1188–1191.

(62) Kim, J. S.; Sen, A.; Guzei, I. A.; Siable-Sand, L. M.; Rheingold, A. L. *J. Chem. Soc., Dalton Trans.* **2002**, 4726–4731.

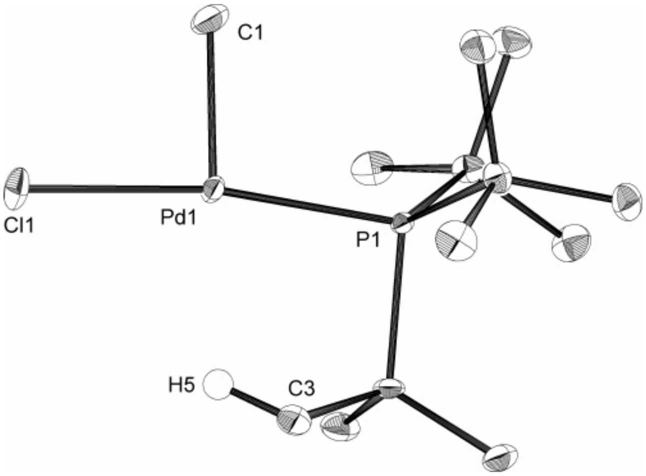


Figure 1. ORTEP drawing of **1a** (all hydrogen atoms except for H5 are omitted for clarity).

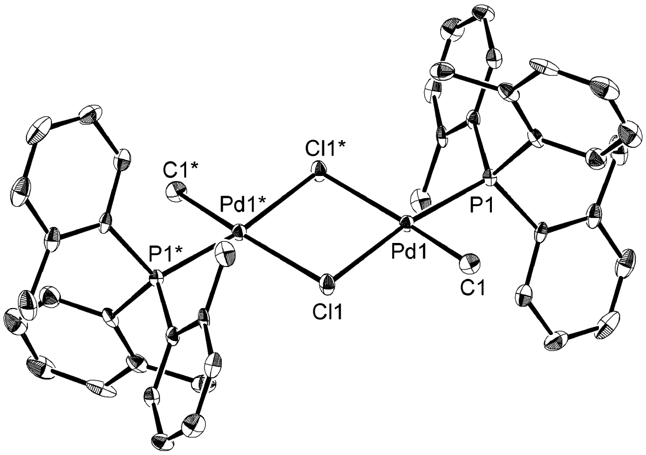


Figure 2. ORTEP drawing of **1b** (all hydrogen atoms are omitted for clarity).

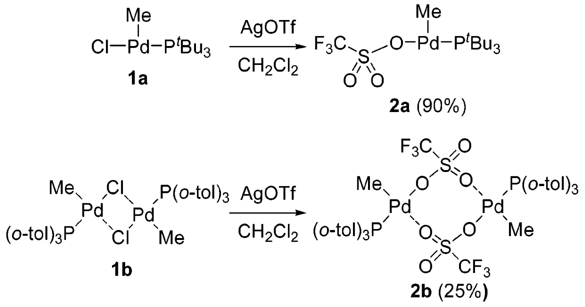
Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 1a and 1b

	1a	1b
Pd(1)−C(1)	1.985(5)	2.029(5)
Pd(1)−P(1)	2.245(3)	2.249(4)
Pd(1)−Cl(1)	2.336(3)	2.416(4)
Pd(1)−Cl(1)*		2.455(4)
C(1)−Pd(1)−Cl(1)	92.98(16)	87.70(19)
C(1)−Pd(1)−P(1)	97.50(16)	85.77(19)
P(1)−Pd(1)−Cl(1)	169.40(5)	172.27(4)

between the dinuclear complex and the corresponding mononuclear complex LPd(Me)Cl, which has a three-coordinate structure similar to that of **1a** as reported for the equilibrium in [(*o*-tol)$_3$PPd(*p*-tol)Br]$_2$.[63] In **1b**, it was indicated that free rotation of both the Pd−P and P−C bond is inhibited, because the three methyl signals of the ligand are inequivalent and broadened in its ^{1}H NMR spectrum, as was observed for [(*o*-tol)$_3$PPd(*p*-tol)Br]$_2$.[63] Lowering the temperature of the CD$_2$Cl$_2$ solution of **1b** to −80 °C resulted in three clearly separated peaks for the methyl group of the *o*-tol groups and two separated peaks for the methyl group on the palladium.

Synthesis of Monophosphine-Ligated Methylpalladium Triflate Complexes 2a and 2b. To compare the counteranion effect for the structure and reactivity, methylpalladium triflate complexes were also synthesized. Treatment of **1a** and **1b** with AgOTf in CH$_2$Cl$_2$ formed corresponding methylpalladium triflate complexes **2a** and **2b** in excellent to moderate yields (Scheme 2).

Scheme 2. Syntheses of Methylpalladium Triflate Complexes (2a and 2b)



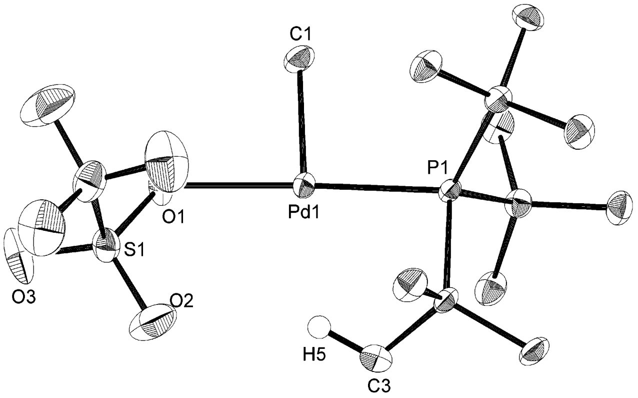


Figure 3. ORTEP drawing of **2a** (all hydrogen atoms except for H5 are omitted for clarity).

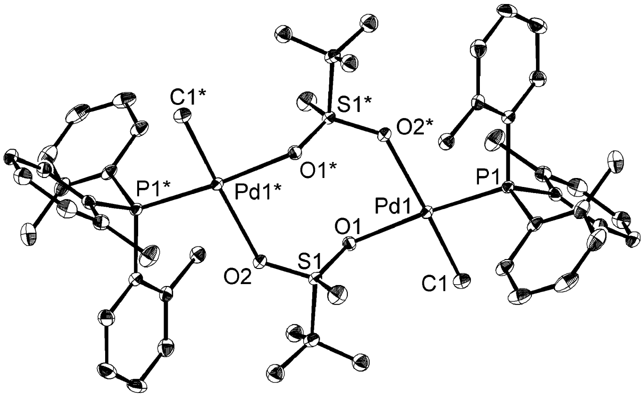


Figure 4. ORTEP drawing of **2b** (all hydrogen atoms are omitted for clarity).

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 2a and 2b

	2a	2b
Pd(1)−C(1)	2.002(2)	2.013(2)
Pd(1)−P(1)	2.2277(6)	2.2157(7)
Pd(1)−O(1)	2.1640(15)	2.1889(14)
Pd(1)−O(2)*		2.2391(14)
C(1)−Pd(1)−O(1)	86.07(9)	89.46(7)
C(1)−Pd(1)−P(1)	97.16(8)	86.09(7)
O(1)−Pd(1)−P(1)	175.33(4)	175.49(4)

The crystal structures of complexes **2a** and **2b** are presented in Figures 3 and 4, respectively. Selected bond lengths and angles are shown in Table 2. It was found that **2a** has a mononuclear structure stabilized by a C−H bond agostic interaction, like **1a**. There was no significant difference of the bond lengths and angles between **1a** and **2a**. From ^{1}H NMR

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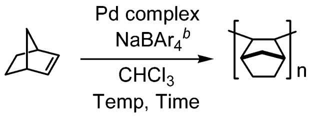
[63] Paul, F.; Joe, P.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030−3039.

Table 3. Polymerization of Norbornene by 1a, 1b, 2a, and 2b[a]



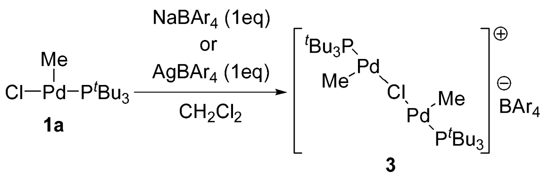
entry	Pd complex	Pd (mol %)	additive[b]	T (°C)	time (h)	yield (%)	TOF[c]
1	**1a**	1.7×10^{-1}	NaBAr$_4$	rt	2	95	280
2	**1a**	1.7×10^{-2}	NaBAr$_4$	rt	2	94	2800
3	**1a**	1.7×10^{-3}	NaBAr$_4$	rt	2	88	26000
4	**1a**	1.7×10^{-3}	NaBAr$_4$	0	6	95	9300
5	**1b**	1.7×10^{-1}	NaBAr$_4$	rt	2	90	270
6	**1b**	1.7×10^{-2}	NaBAr$_4$	rt	2	52	1500
7	**1b**	1.7×10^{-3}	NaBAr$_4$	rt	2	0	
8	**2a**	1.7×10^{-1}	none	rt	2	16	47
9	**2a**	1.7×10^{-1}	none	rt	6	21	21
10	**2a**	1.7×10^{-1}	none	40	2	43	130
11	**2b**	1.7×10^{-1}	none	rt	2	0	

[a] Norbornene (5.8 mmol) was used. Molecular weight was not determined due to the low solubility of most of the products in organic solvents. [b] Pd/NaBAr$_4$ = 1. [c] Calculated as (mol$_{\mathrm{NB}}$ in polymer) mol$_{\mathrm{Pd}}$$^{-1}$ h^{-1}.

spectrum, it was clear that the *tert*-butyl groups of **2a** were all equivalent, like **1a**, and the chemical shifts of both complexes were similar. Despite the very weak coordinating ability of the triflate anion, triflate anions existed as bridging ligands in **2b**, which is the first example of a triflate-bridged Pd dinuclear structure. The dinuclear structure is in contrast to the mononuclear structure of the only example of a (o-tol)$_3$P-ligated palladium triflate complex, [(o-tol)$_3$P]Pd(η^3-allyl)OTf.[9] Methyl groups on the phosphine in the ^{1}H NMR spectrum of **2b** showed a broad peak similar to the case of **1b**. One can also expect that there is an equilibrium between **2b** and its corresponding mononuclear structure; however, there was no proof from NMR.

Polymerization of Norbornene (NB). Complexes **1a**, **1b**, **2a**, and **2b** were examined as catalytst precursors for the homopolymerization of NB.[1] The results are summarized in Table 3. The polymerization did not take place using **1a** or **1b** in the absence of any additives. In the presence of NaB(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$ (NaBAr$_4$),[64] both **1a** and **1b** showed catalytic activity. Catalyst loading could be lowered to 1.7×10^{-3} mol % of **1a** to afford polyNB in excellent yields (entries 1−3). Longer reaction time and lower temperature improved the yield (entry 4). The complex **1b** displayed moderate catalytic activity when the catalyst loading was decreased (entries 5−7). In the case of triflate complexes **2a** and **2b**, only **2a** showed catalytic activity without NaBAr$_4$ (entry 8). Extension of the reaction time or elevation of the temperature slightly improved the yield (entries 9, 10). The result that catalytic activity of **2a** was lower than the **1a**−NaBAr$_4$ system indicated that one of the most weakly coordinating counteranions such as B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$$^-$ was necessary to afford active species. The obtained polymers were insoluble in common organic solvents except entries 1, 5, 8, 9, and 10. The ^{1}H NMR spectra of all soluble polymers were proven to have no olefinic protons, suggesting that the polymerization proceeded via addition-type chain propagation, not via ring-opening metathesis polymerization (ROMP).[65] Broadening of all aliphatic regions in the ^{1}H NMR spectra indicates that the obtained polymer is atactic.[66] The highest activity of 26 000 mol$_{\mathrm{NB}}$ mol$_{\mathrm{Pd}}$$^{-1}$ h^{-1} was achieved in entry 3.[1,67]

Scheme 3. Reaction of 1a with NaBAr$_4$ or AgBAr$_4$



Scheme 4. Possible Equilibrium Containing Cationic Complex 3a

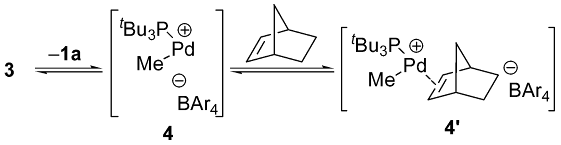
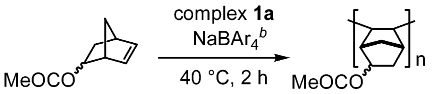


Table 4. Polymerization of the Methyl Ester of Norbornene Carboxylic Acid by 1a−NaBAr$_4$[a]



entry	solvent	Pd (mol %)	yield (%)	TOF[c]	M_n	M_w/M_n
1	CHCl$_3$	1.7×10^{-1}	13	38	9300	1.3
2	CHCl$_3$	8.5×10^{-1}	77	45	14 000	1.5
3	CH$_2$Cl$_2$	1.7×10^{-1}	20	59	14 000	2.1
4	CH$_2$Cl$_2$	8.5×10^{-1}	54	54	19 000	1.3

[a] NBE (5.8 mmol) was treated with **1a**. [b] Pd/NaBAr$_4$ = 1. [c] Calculated as (mol$_{\mathrm{NBE}}$ in polymer) mol$_{\mathrm{Pd}}$$^{-1}$ h^{-1}.

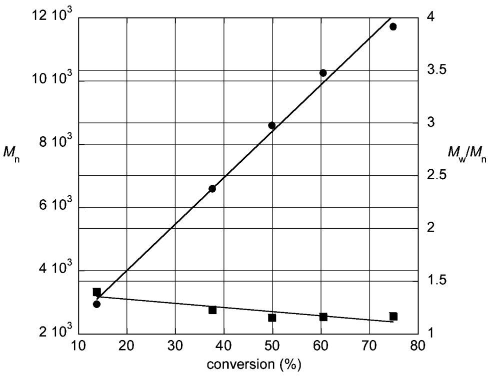


Figure 5. Plot of conversion vs M_n and M_w/M_n in the polymerization of NBE using **1a**−NaBAr$_4$ in CDCl$_3$ at room temperature (solid circle: M_n; solid square: M_w/M_n).

Reaction of 1a with NaBAr$_4$. To identify the active species in the polymerization of NB, **1a** was treated with 1 or 0.5 equiv of NaBAr$_4$ at room temperature, and the resulting mixture was analyzed by ^{1}H, ^{31}P, ^{13}C, ^{19}F, and ^{11}B NMR spectra.[68] All multinuclear NMR spectra of these two reaction mixtures were identical. The integration in the ^{1}H NMR spectra indicated the ratio of the methyl on the palladium to BAr$_4$ to be 1:2. These results are consistent with the formation of the Cl-bridged dinuclear complex **3** shown in Scheme 3. A similar Cl-bridged dinuclear structure of a palladium complex was reported in the literature.[69] An isolated green powder from the reaction of **1a** with AgBAr$_4$ afforded the same results, indicating the formation

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[64] Bahr, S. R.; Boudjouk, P. *J. Org. Chem.* **1992**, *57*, 5545−5547.

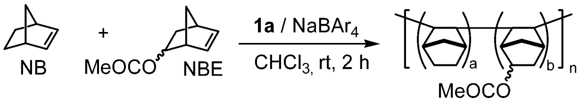
[65] Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18−29.

[66] Zhu, Y. Z.; Liu, J. Y.; Li, Y. S.; Tong, Y. J. *J. Organomet. Chem.* **2004**, *689*, 1295−1303.

[67] The best TOF of palladium catalyst ever reported for norbornene polymerization is 10 000 000 mol$_{\mathrm{NB}}$ mol$_{\mathrm{Pd}}$$^{-1}$ h^{-1}; see ref 6.

[68] The related multinuclear NMR studies were reported for the activation process of precatalyst, L$_2$PdCl$_2$, or polychlorinated anionic palladium complexes, using B(C$_6$F$_5$)$_3$ in the polymerization of norbornene. (a) Lassahn, P. G.; Lozan, V.; Wu, B.; Weller, A. S.; Janiak, C. *Dalton Trans.* **2003**, 4437−4450. (b) Lassahn, P. G.; Lozan, V.; Janiak, C. *Dalton Trans.* **2003**, 927−935.

Table 5. Copolymerization of Norbornene (NB) with the Methyl Ester of Norbornene Carboxylic Acid (NBE) by 1a−NaBAr$_4$



entry	Pd (mol %)	NB/NBE	NBE[a] content	yield[b] (NB)	yield[c] (NBE)	yield[d] (total)	TOF[e]	M_n[f]	M_w/M_n[f]
1	1.7×10^{-1}	50/50	0.29	96	39	68	200	53 000	1.3
2	1.7×10^{-1}	80/20	0.13	92	55	84	250	56 000	1.3
3	1.7×10^{-2}	50/50	0.11	78	10	44	1600	140 000	1.2
4	1.7×10^{-2}	80/20	0.09	95	38	84	2300	120 000[g]	1.1

[a] NBE content in the copolymer = $b/(a + b)$, determined by ^{1}H NMR. [b] Mol of NB in the copolymer/mol of starting NB. [c] Mol of NBE in the copolymer/mol of starting NBE. [d] Mol of NB + NBE in copolymer/mol of starting NB + NBE. [e] Calculated as (mol$_{NB+NBE}$ in copolymer) mol$_{Pd}$$^{-1}$ h^{-1}. [f] Polystyrene standard in THF. [g] Polystyrene standard in CHCl$_3$.

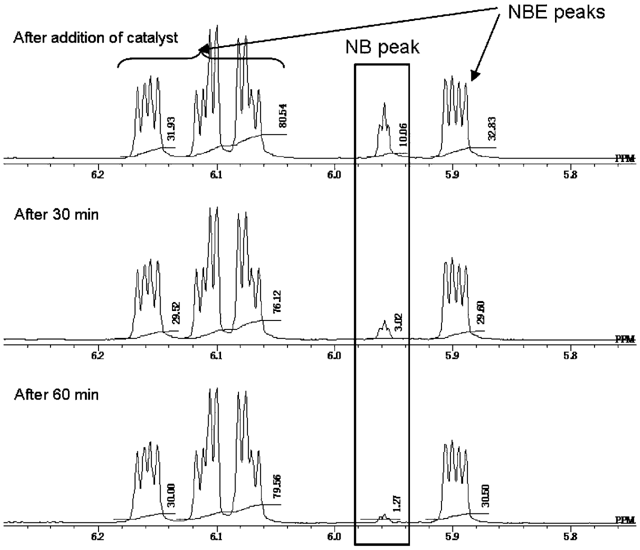


Figure 6. Change of vinylic protons in the ^{1}H NMR spectra during the copolymerization of NB and NBE with conditions for entry 1 in Table 5. Values of the integral were calculated from the ratio of each peak to an added ferrocene as internal standard.

of **3** even in the reaction with excess amounts of the silver salt. One can expect the dissociation equilibrium of **3** to produce cationic species **4** or olefin-coordinated cationic species **4′** as an active catalyst (Scheme 4). In the presence of an excess of NaBAr$_4$ and olefinic monomers, **1a** may be completely converted to **4** or **4′**.

Polymerization of the Methyl Ester of Norbornene Carboxylic Acid (NBE). The most active catalyst **1a**−NaBAr$_4$ for polymerization of NB also catalyzed the polymerization of NBE (*endo*/*exo* = 1.1/1.0). The results were summarized in Table 4. When CH$_2$Cl$_2$ was used as a solvent, the activity was slightly increased from that with CHCl$_3$. Higher catalyst loadings were required to obtain higher yields than that in the polymerization of norbornene (entries 2 and 4). All the obtained polymeric materials were analyzed by NMR spectroscopy. Most probably, the polymer is soluble in CHCl$_3$ and was atactic because the polymer has broadened peaks, as was observed in the previous examples.[4,5,7] The highest activity of 59 mol$_{NBE}$ mol$_{Pd}$$^{-1}$ h^{-1} was achieved in entry 3.[6,70] even in the presence of the formal vacant site on the central palladium. A plot of conversion versus molecular weight was confirmed to be linear when the polymerization was carried out at room temperature in CDCl$_3$, which is characteristic for living polymerization (Figure 5). The plot slightly deviates from the line at high conversion of >70% probably due to the high viscosity of the reaction solution. The higher molecular weight distribution in Table 4 than those in Figure 4 may be attributed to the decomposition of the catalyst at higher temperature under the conditions of Table 4.

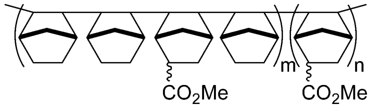


Figure 7. Estimated structure of the obtained NB/NBE copolymer.

Copolymerization of NB and NBE. The copolymerization[4,5,7,71] of NB with NBE was examined with the catalyst **1a**−NaBAr$_4$. Copolymerization reactions were carried out with a 50/50 or 80/20 molar ratio (NB/NBE) in CHCl$_3$ at room temperature for 2 h (Table 5). The NBE content was determined from the integral ratio of the methoxy group of the ester unit to all the aliphatic protons in ^{1}H NMR spectra. For quantitative discussion, we calculate a series of yields based on (1) mol of NB in copolymer/mol of starting NB, (2) mol of NBE in copolymer/mol of starting NBE, and (3) mol of NB + NBE in copolymer/mol of starting NB + NBE (Table 5).

The NBE content was 0.29, and 96% of starting NB and 39% of starting NBE were incorporated into the obtained copolymer when the reaction was started from NB/NBE = 50/50 (entry 1). Reducing NBE to a molar ratio of NB/NBE = 80/20 led to a decrease of the NBE content to 0.13 (entry 2). It should be noted that, although the NBE content was lowered, the incorporated starting NBE monomer was increased (55%, entry 2). Decreasing the amount of catalyst to 1.7×10^{-2} mol % with NB/NBE = 50/50 (entry 3) led to a higher TOF (1600) and M_w (140 000). These higher TOF and M_w come from the increased monomer/catalyst ratio and the fast polymerization of NB. The same catalyst loading with NB/NBE = 80/20 afforded the highest TOF and the lowest NBE content (entry 4). The highest TOF may come from the larger NB/catalyst ratio, and the lowest NBE content may come from decreasing the polymerization rate of NBE due to lower concentration of NBE, as was observed in the yield (NBE).

The copolymerization rate was comparable to those in the previous examples using palladium or nickel complexes without phosphine ligands.[4,5,7,71] In other words, the vacant site(s) of the metal center remained reactive, if only one phosphine ligand exists per metal center. As a result, the highest NBE content ever reported[4,72] was achieved in entry 1. It seems that the Pd complex was barely poisoned when one of the vacant coordination sites was occupied by the ester group. In addition, the narrowest molecular weight distributions of 1.1 could be achieved.[4,5,7,71]

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(69) Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004**, *23*, 600−609.

(70) The best TOF of a palladium catalyst ever reported for polymerization of NBE is 310 mol$_{NBE}$ mol$_{Pd}$$^{-1}$ h^{-1}; see ref 4.

(71) Suzuki, H.; Matsumura, S.-i.; Satoh, Y.; Sogoh, K.; Yasuda, H. *React. Funct. Polym.* **2004**, *58*, 77−91.

The NBE content of 0.29 in entry 1 was higher than 0.11 in entry 3. This corresponds to the higher reactivity of NB than that of NBE. If the copolymer had a random character to afford a similar consumption rate of each comonomer, the obtained copolymer would have similar composition and lead to similar NBE content.

Monitoring the Copolymerization by ^{1}H NMR Spectroscopy. To check the relative consumption rate of comonomers qualitatively, the copolymerization reaction was monitored by ^{1}H NMR spectroscopy. Under the conditions in entry 1 of Table 5, a faster consumption of the NB peak at δ 5.96 than that of the NBE peaks was observed in the ^{1}H NMR monitoring of the copolymerization (Figure 6). The consumption of NB was much faster than that of NBE. Additionally, the obtained copolymer showed a monomodal peak in each GPC analysis. These results suggest that poly(NB) grew up first with some incorporation of NBE until most of the NB monomer was consumed, and then the poly(NBE) chain propagated slowly. This means the obtained copolymer may have a diblock-type character, which consists of a polyNB part containing a little NBE and a polyNBE part (Figure 7).

Conclusion. Four new monophosphine-ligated methylpalladium complexes, **1a**,**b** [LPd(Me)Cl]$_n$ (n = 1 or 2), and **2a**,**b** [LPd(Me)OTf]$_n$ (n = 1 or 2) were synthesized and structurally characterized. X-ray crystallography revealed that **1a** and **2a** are the first examples of three-coordinate alkylpalladium complexes. **1b** was proven to have a chloride-bridged dinuclear structure. It was first shown that triflate anions were able to exist as bridging ligands to the palladium atom in **2b**. The combination of **1a** and NaBAr$_4$ is highly active for the homopolymerization of norbornene (NB). The system **1a**−NaBAr$_4$ also catalyzed the polymerization of methoxycarbonylnorbornene (NBE). The obtained copolymer was endowed with the highest ester content ever reported, possibly because the palladium center with a monodentate ligand was barely poisoned by the ester coordination. At the same time, the narrowest molecular weight distribution was achieved for the copolymer, possibly due to the long lifetime of the ligated metal complex.

Experimental Section

General Methods. Unless otherwise noted, all reactions and manipulations were conducted by using standard Schlenk or vacuum line techniques under argon except for the filtration procedures through filtering papers. ^{1}H (500 MHz), ^{11}B{^{1}H} (160 MHz), ^{13}C{^{1}H} (125 MHz), ^{19}F{^{1}H} (470 MHz), and ^{31}P{^{1}H} (202 MHz) NMR spectra were recorded on a JNM-ECP500 spectrometer with shifts relative to the residual protiated solvent, an external BF$_3$−OEt$_2$ standard, the deuterated solvent, CFCl$_3$, and an external 85% H$_3$PO$_4$ standard. High-resolution mass spectrometry was performed on a JEOL JMS-AX505H spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on an Applied Biosystems BioSpectrometry workstation model Voyager-DE STR spectrometer using dithranol as a matrix. Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, Graduate School of Science, The University of Tokyo. Melting points were determined by using a Yanaco MP-500D. X-ray crystallographic analyses were recorded on a Rigaku Mercury CCD diffractometer. Gel permeation chromatography (GPC) analyses were carried out using a GL Sciences instrument (HPLC pump PU610, LC columns oven Model556) equipped with a Shodex SE-61 RI detector, SIV GPC board, and two columns (Shodex KF-804L). The GPC columns were eluted with tetrahydrofuran at 40 °C at 1 mL/min. Chloroform, dichloromethane, hexane, and tetrahydrofuran were purchased as dehydrated solvents from Kanto Chemical. The other chemicals were used as received from the chemical company. Pd(cod)MeCl,[6] NaB(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$,[64] and AgB(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$[73] were prepared as previously reported.

Syntheses of Three-Coordinated Methylpalladium Chloride Complexes. Synthesis of ^{t}Bu$_3$PPd(Me)Cl (1a). In a globebox, to a mixture of ^{t}Bu$_3$P (0.411 g, 2.03 mmol) and (cod)Pd(Me)Cl (0.539 g, 2.03 mmol) was added CH$_2$Cl$_2$ (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 5 min and was poured into vigorously stirred hexane to precipitate a yellow solid. The resulting solid was isolated by filtration to give the desired product (0.560 g, 84%): ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.49 (d, J = 13 Hz, 27H), 1.75 (d, J = 0.8 Hz, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) δ −1.90 (CH$_3$), 31.8 (d, J = 3.8 Hz, CH$_3$), 39.8 (d, J = 11 Hz, 4°); ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz) δ 70.1 (s); mp 163.2−164.8 °C (dec). Anal. Calcd for C$_{13}$H$_{30}$ClPPd: C, 43.47; H, 8.42. Found: C, 43.47; H, 8.29.

Synthesis of {[(*o*-tol)$_3$P]Pd(Me)Cl}$_2$ (1b). To a mixture of (*o*-tol)$_3$P (0.660 g, 2.16 mmol) and (cod)Pd(Me)Cl (0.574 g, 2.17 mmol) was added CH$_2$Cl$_2$ (4 mL) at room temperature. The reaction mixture was stirred at room temperature for 4 h and was poured into vigorously stirred hexane to precipitate an off-white solid. The resulting solid was isolated by filtration through a filtering paper to give the desired product (0.907 g, 91%): ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.35−0.65 (br s, 3H), 1.45−3.55 (br, 9H), 6.95−7.65 (br, 12H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) δ 4.8−6.7 (br, CH$_3$), 22.8−25.3 (br, CH$_3$), 124.4−126.6 (CH), 128.1−129.7 (br, 4°), 131.0−133.0 (br, CH), 142.0−144.4 (br, 4°); ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz) δ 36.2 (s); mp 207.7−209.3 °C (dec). Anal. Calcd for C$_{22}$H$_{24}$ClPPd: C, 57.28; H, 5.24. Found: C, 57.00; H, 5.33.

Syntheses of Methylpalladium Triflate Complexes. Synthesis of ^{t}Bu$_3$PPd(Me)OTf [OTf = OSO$_2$CF$_3$] (2a). In a glovebox, to a mixture of AgOTf (0.411 g, 2.03 mmol) and **1a** (0.539 g, 0.138 mmol) was added CH$_2$Cl$_2$ (1 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h and was filtered through a Celite pad. Volatiles were removed from the filtrate under reduced pressure to obtain a dark green solid (0.560 g, 77%): ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.51 (d, $^3J_{\mathrm{PH}}$ = 13 Hz, 27H), 1.67 (s, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) δ 0.71 (s, CH$_3$), 31.7 (s, CH$_3$), 40.4 (d, J = 8.5 Hz, 4°), 120.1 (q, $^1J_{\mathrm{FC}}$ = 318 Hz, CF$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz) δ 76.9 (s); ^{19}F{^{1}H} NMR (CDCl$_3$, 470 MHz) δ −77.4 (s); mp 60.9−62.3 °C (dec); HRMS-FAB (m/z) [M − CF$_3$SO$_3$]$^+$ calcd for C$_{13}$H$_{30}$PPd, 321.1126, 322.1136, 323.1120, 325.1124, 327.1137; found, 321.1109, 322.1139, 323.1132, 325.1132, 327.1137.

Synthesis of {[(*o*-tol)$_3$P]Pd(Me)OTf}$_2$ (2b). To a mixture of AgOTf (0.232 g, 0.907 mmol) and **1b** (0.233 g, 0.507 mmol) was added CH$_2$Cl$_2$ (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 1 h, filtered with Celite, and poured into vigorously stirred hexane to precipitate an off-white solid. The resulting solid was washed with hexane three times to give the desired product (0.0715 g, 25%): ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.75 (s, 3H), 2.10−2.50 (br s, 9H), 7.17−7.25 (br, 6H), 7.40 (t, J = 7.5 Hz, 3H), 7.48−7.64 (br, 3H); ^{13}C{^{1}H} NMR (CDCl$_3$, 125 MHz) δ 6.07 (CH$_3$), 23.1 (d, J = 8.2 Hz, CH$_3$), 118.9 (q, $^1J_{\mathrm{FC}}$ = 317 Hz, CF$_3$), 125.4. (4°), 125.8 (d, J = 13 Hz, CH), 131.3 (CH), 132.2 (d, J = 8.2 Hz, CH), 135.2 (br, CH), 142.9 (d, J = 9.1 Hz, 4°); ^{31}P{^{1}H} NMR (CDCl$_3$, 202 MHz) δ 34.7 (s); ^{19}F{^{1}H} NMR (CDCl$_3$, 470 MHz) δ −77.7 (s); mp 173.2−174.1

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(72) In the abstract No. PB124 of the 52nd Symposium on Organometallic Chemistry, Japan 2005, Wakatsuki reported that a combination of CpNi(Me)(PPh$_3$) and B(C$_6$F$_5$)$_3$ could catalyze the copolymerization of NB and NBE with high NBE content and high molecular weight: $b/(a + b)$ = up to 0.57, M_n = up to 407 000, M_w/M_n = down to 1.57.

(73) Miller, K. J.; Kitagawa, T. T.; Abu-Omar, M. M. *Organometallics* **2001**, *20*, 4403−4412.

Table 6. Crystallographic Data and Structure Refinement Details for 1a, 1b, 2a, and 2b

	1a	**1b**	**2a**	**2b**
formula	$C_{13}H_{30}ClPPd$	$C_{23}H_{25}Cl_4PPd$	$C_{14}H_{30}F_3O_3PPdS$	$C_{23}H_{24}F_3O_3PPdS$
fw	359.19	580.60	472.81	574.85
T (K)	120(2)	120(2)	120(2)	120(2)
λ (Å)	0.71070	0.71070	0.71070	0.71070
cryst syst	triclinic	triclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a (Å)	8.551(9) Å	9.385(18)	8.0898(10)	9.727(2)
b (Å)	9.521(9) Å	10.88(2)	16.7280(13)	10.568(2)
c (Å)	9.873(11)	11.97(2)	14.8439(18)	13.079(3)
α (deg)	91.59(2)	81.62(9)	90	67.835(11)
β (deg)	91.034(20)	80.91(9)	104.9956(15)	74.702(12)
γ (deg)	94.29(2)	83.78(9)	90	72.953(11)
V (Å^3)	801.0(14)	1190(4)	1940.4(4)	1172.4(5)
Z	2	2	4	2
D_{calc} (g/cm^3)	1.489	1.620	1.619	1.628
μ (mm^{-1})	1.402	1.305	1.182	0.995
F(000)	372	584	968	580
cryst size (mm)	0.60 × 0.60 × 0.40	0.50 × 0.20 × 0.10	0.40 × 0.30 × 0.15	0.50 × 0.40 × 0.30
2θ range (deg)	3.02−25.00	3.00−25.00	3.09−24.99	3.03−25.00
no. of reflns collected	4948	7490	18 062	7303
no. of indep reflns/R_{int}	2707/0.0183	4068/0.0452	3408/0.0215	3986/0.0117
no. of params	155	266	329	293
GOF on F^2	1.212	0.961	1.078	1.055
R_1, wR_2 [$I > 2\sigma(I)$]	0.0315, 0.0916	0.0357, 0.0809	0.0219, 0.0522	0.0202, 0.0519
R_1, wR_2 (all data)	0.0322, 0.0918	0.0398, 0.0823	0.0230, 0.0528	0.0211, 0.0524

°C (dec); HRMS-FAB (m/z) [M − CF_3SO_3]$^+$ calcd for $C_{22}H_{24}PPd$, 423.0656, 424.0667, 425.0651, 427.0655, 429.0667; found, 423.0624, 424.0646, 425.0662, 427.0662, 429.0664.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **1a**, **1b**, **2a**, and **2b** are listed in Table 6. In each case a suitable crystal was mounted with mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractmeter with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) to $2\theta_{max} = 55°$. The structures were solved by direct methods with SIR-97[74] or SHELXS[75] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97[75]). The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions.

General Procedure for Norbornene Polymerization. A 20 mL Schlenk flask was charged with **1a** (3.6 mg, 0.010 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (8.9 mg, 0.010 mmol), and this mixture was dissolved in $CHCl_3$ (1.0 mL). The solution was degassed by three freeze−pump−thaw cycles. Another 20 mL Schlenk flask was charged with norbornene (546 mg, 5.80 mmol) and $CHCl_3$ (4.0 mL), and the solution was degassed by three freeze−pump−thaw cycles. To this flask was added the solution of palladium complex at room temperature. After being stirred for the indicated time, the reaction mixture was poured into acidified ethanol. The resulting solid was separated by filtration, washed with methanol several times, and dried under vacuum at 60 °C.

General Procedure for Norbornene Polymerization at Low Catalyst Loading. In a glovebox, **1a** (9.0 mg, 0.025 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (22.5 mg, 0.025 mmol) were placed into a screw-capped, 5 mL volumetric flask. After dissolution of the mixture in $CHCl_3$, the resulting solution was diluted to 5 mL to make a stock solution. A 20 mL Schlenk flask was charged with norbornene (546 mg, 5.80 mmol) and $CHCl_3$ (4.8 mL), and the solution was degassed by three freeze−pump−thaw cycles. A 200 μL portion of the stock solution was syringed into the flask. After being stirred for the indicated time, the reaction mixture was poured into acidified ethanol. The resulting solid was separated by filtration, washed with methanol several times, and dried under vacuum at 60 °C.

Reaction of 1a with $NaBAr_4$. A screw-capped NMR tube was charged with **1a** (10.0 mg, 0.0278 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (24.7 mg, 0.0278 mmol or 12.3 mg, 0.0139 mmol), and $CDCl_3$ was vacuum-transferred. After shaking the NMR tube, the NMR spectra were collected. Except for the integral ratio of the BAr_4 part to others, all the NMR spectra were identical to the product from the following reaction of **1a** with $NaBAr_4$.

Reaction of 1a with $AgBAr_4$. In a glovebox, to a mixture of $AgBAr_4$ (135 mg, 0.139 mmol) and **1a** (50.0 mg, 0.139 mmol) was added CH_2Cl_2 (4 mL) at room temperature. The reaction mixture was stirred at room temperature for 3 h and was filtered through a Celite pad. The filtrate was poured into vigorously stirred hexane to precipitate a green solid. The resulting solid was isolated by filtration to give the desired product (79.5 mg, 74%). A mass pattern in the MALDI-TOF-MS analysis of the product was identical to a calculated pattern for the cationic part of **3** (see Supporting Information): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.49 (d, $^3J_{PH} = 13$ Hz, 27H), 1.74 (s, 3H), 7.53 (s, 2H), 7.71 (s, 4H); ^{13}C-{^{1}H} NMR ($CDCl_3$, 125 MHz) δ 0.69 (s, CH_3), 31.9 (s, CH_3), 40.9 (d, $J = 12.5$ Hz, 4°), 117.7 (sp, $^3J_{FC} = 3.8$ Hz, CH), 124.8 (q, $^1J_{FC} = 273$ Hz, CF_3), 129.1 (qq, $^2J_{FC} = 16$ Hz, $^3J_{BC} = 2.9$ Hz, 4°), 135.0 (s, CH), 162.0 (q, $^1J_{BC} = 49.9$ Hz, 4°); ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) δ 74.6 (s); ^{19}F{^{1}H} NMR ($CDCl_3$, 470 MHz) δ −62.2 (s); ^{11}B{^{1}H} NMR ($CDCl_3$, 160 MHz) δ 6.95 (s); mp 111.4−113.3 °C (dec).

General Procedure for the Methyl Ester of Norbornene Carboxylic Acid Polymerization. A 20 mL Schlenk flask was charged with **1a** (3.6 mg, 0.010 mmol) and NaB(3,5-$(CF_3)_2C_6H_3)_4$ (8.9 mg, 0.010 mmol), and this mixture was dissolved in $CHCl_3$ (1.0 mL). The solution was degassed by three freeze−pump−thaw cycles. Another 20 mL Schlenk flask was charged with the methyl ester of norbornene carboxylic acid (0.89 mL, 5.8 mmol) and $CHCl_3$ (4.0 mL), and the solution was degassed by three freeze−pump−thaw cycles. To this flask was added the solution of palladium complex at room temperature. After being stirred for the indicated time, the reaction mixture was poured into acidified ethanol. The resulting polymer was separated by filtration, washed with methanol several times, and dried under vacuum at 60 °C: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82−3.07 (br, CH, CH_2), 3.38−4.00 (br, $COOCH_3$).

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(74) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

(75) Sheldrick, G. M. *SHELXL-97*, Program for the Refinement of Crystal Structures; University of Göttingen: Göttingen, Germany, 1997.

Procedure for Plot of Conversion versus Molecular Weight (Figure 5). A 20 mL Schlenk flask was charged with **1a** (18.0 mg, 0.050 mmol) and $NaB(3,5-(CF_3)_2C_6H_3)_4$ (44.5 mg, 0.050 mmol), and the mixture was dissolved in $CDCl_3$ (4.0 mL). The solution was degassed by three freeze−pump−thaw cycles. Another 20 mL Schlenk flask was charged with the methyl ester of norbornene carboxylic acid (0.89 mL, 5.8 mmol) and $CDCl_3$ (1.0 mL), and the solution was degassed by three freeze−pump−thaw cycles. To this flask was added the solution of palladium complex and phenanthrene (103.4 mg, 0.58 mmol) as internal standard at room temperature. After being stirred, a 0.1 mL aliquot of the reaction mixture was transferred to an NMR sample tube by use of syringe, and the solution was diluted by $CDCl_3$ up to 0.6 mL. After collection of the NMR spectrum, the solution in the NMR sample tube was immediately poured into methanol to stop polymerization, and volatiles were removed under reduced pressure to conduct GPC analysis.

General Procedure for Copolymerizaton of Norbornene with the Methyl Ester of Norbornene Carboxylic Acid. A 20 mL Schlenk flask was charged with **1a** (3.6 mg, 0.010 mmol) and $NaB(3,5-(CF_3)_2C_6H_3)_4$ (8.9 mg, 0.010 mmol), and this mixture was dissolved in $CHCl_3$ (1.0 mL). The solution was degassed by three freeze−pump−thaw cycles. Another 20 mL Schlenk flask was charged with norbornene (273 mg, 2.90 mmol), the methyl ester of norbornene carboxylic acid (0.45 mL, 2.9 mmol), and $CHCl_3$ (4.0 mL), and the solution was degassed by three freeze−pump−thaw cycles. To this flask was added the solution of palladium complex at room temperature. After being stirred for the indicated time, the reaction mixture was poured into acidified ethanol. The resulting solid was separated by filtration, washed with methanol several times, and dried under vacuum at 60 °C: ^1H NMR ($CDCl_3$, 500 MHz) δ 0.13−3.09 (br, CH, CH_2), 3.29−3.96 (br, $COOCH_3$).

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Supporting Information Available: Crystallographic data of **1a**, **1b**, **2a**, and **2b** are available free of charge via the Internet at http://pubs.acs.org.

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