



# Generation of low-valent alkoxy niobium from Nb(OEt)<sub>5</sub> and Grignard reagents and their use as catalysts in the cyclotrimerization of isocyanates



Makoto Ozaki, Yasushi Obora\*, Yusuke Tada, Yasutaka Ishii

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

## ARTICLE INFO

### Article history:

Received 12 April 2013

Received in revised form

21 May 2013

Accepted 25 May 2013

### Keywords:

Low-valent niobium

Alkoxy niobium

Catalytic reaction

Cyclotrimerization

Isocyanate

## ABSTRACT

A new highly active low-valent alkoxy niobium species has been developed following the reaction of Nb(OEt)<sub>5</sub> with Grignard reagent such as *i*-PrMgCl or EtMgCl, with the material behaving as an efficient catalyst for cyclotrimerization reaction of isocyanates. In this reagent system, the existence of a low-valent niobium species was confirmed by the formation of the niobium–alkyne complex prepared from the Nb(OEt)<sub>5</sub>/Grignard reagent system and an alkyne. Furthermore, the hydrolysis and diallylation reactions of the niobium–alkyne complex provided further confirmation of its existence, with corresponding (*Z*)-alkene and diallylated products being isolated in good yields.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Low-valent transition metals have recently been the subject of considerable levels of interest as reagents for use in organic synthesis. Low-valent early transition metals in particular, such as Ti (II) [1], Zr (II) [2], Ta(III) [3], and Nb(III) [4] have been reported to behave as reducing reagents in the reactions of unsaturated compounds such as alkynes with electrophiles. Furthermore, low-valent niobium complexes, such as NbCl<sub>3</sub>(DME) have been used as thermally stable early-low-valent metal reagents for a variety of other transformations as well as catalysis.

We recently reported several low-valent niobium complex mediated reactions, including the NbCl<sub>3</sub>(DME)-mediated synthesis of 1*H*-indenes from aliphatic ketones and aryl-substituted alkynes [5a], and the NbCl<sub>3</sub>(DME)-catalyzed [2 + 2 + 2] cycloaddition reactions of terminal alkyne compounds to a variety of different olefinic compounds, including simple alkenes [5b],  $\alpha,\omega$ -dienes [5c], and internal alkynes [5d]. In the latter case, the active niobium species generated from the NbCl<sub>3</sub>/H–Si system catalyzed the cycloaddition reactions [5e].

We have also reported the development of the nickel-catalyzed cross-coupling reaction of niobium(III)–alkyne complexes with

aryl iodides [5g]. In this particular cross-coupling reaction, the use of a low-valent niobium–alkyne (i.e. NbCl<sub>3</sub>–alkyne) was found to be inefficient as a reagent for the purposes of the desired reaction, and the cross-coupling reaction was found to proceed with a greater degree of efficiency following the addition of 3 equiv of *i*-PrOLi to the NbCl<sub>3</sub>–alkyne complex, which led to the formation of a Nb(*i*-OPr)<sub>3</sub>–alkyne complex as a coupling partner. This result indicated that a low-valent niobium complex bearing an alkoxy substituent could be used as an efficient alternative to the standard catalysts and reagents used in this particular field of organic synthesis. The development of an efficient method for the preparation of low-valent alkoxy niobium compounds from the corresponding and readily available penta-alkoxy niobium compounds would therefore be highly desirable for further research toward the use of low-valent metals in organic synthesis. It is noteworthy that the penta-alkoxy niobium compounds are widely used as precursor materials for preparation of thin films using the metal-organic chemical vapor deposition (MOCVD) technique [6]. In addition, several examples of low-valent aryloxy niobium complexes such as aryloxy niobium–olefin [7a,b], aryloxy niobium–diene [7c], and aryloxy niobium–imine [7d] are known.

Isocyanurates are a group of versatile compounds that can be used to enhance the physical properties of a wide variety of polyurethanes and coating materials [8]. Polymers bearing isocyanurate groups show increased levels of thermal resistance, flame retardation, and chemical resistance, as well as film-forming characteristics [9]. For

\* Corresponding author. Tel.: +81 6 6368 0876; fax: +81 6 6339 4026.

E-mail address: [obora@kansai-u.ac.jp](mailto:obora@kansai-u.ac.jp) (Y. Obora).

example, triaryl isocyanurates are often used as activators for the polymerization and postpolymerization of  $\epsilon$ -caprolactam in the production of nylons with high melt viscosities [10]. Triallyl isocyanurate has been used in the preparation of flame-retardant laminating materials for electrical devices as well as in the preparation of copolymer resins that are water-resistant, transparent, and impact-resistant [11].

Traditionally, isocyanurates have been synthesized via the cyclotrimerization of the corresponding isocyanates. A number of reports have been published concerning this particular method of construction using a variety of different Lewis-basic catalysts, including *N*-heterocyclic carbenes [12], carbamate anions [13], amines [14], fluoride anions [15], *p*-toluenesulfonate [16], cyanates [17], alkoxyalkenes [18], and phosphines [19]. Several other reports have also been published concerning the transition metal catalyzed cyclotrimerization reactions of isocyanates, including the use of copper and nickel halides [20], palladium (0) [21], organozinc halides [22], and zirconium compounds [23] as the catalytic species.

Herein, we wish to disclose the development of an Nb(OEt)<sub>5</sub>/EtMgCl and *i*-PrMgCl reagent system for the generation of a low-valent alkoxy niobium species, and the subsequent evaluation of its high level of activity in the catalytic cyclotrimerization of isocyanates.

## 2. Results and discussion

To begin with, we conducted the cyclotrimerization reaction of an isocyanate in the presence a Nb(OEt)<sub>5</sub>/Grignard reagent catalytic system. To develop a deeper understanding of the reaction system, and ultimately to optimize the reaction conditions, *n*-hexyl isocyanate (**1a**) was selected as a model substrate for the transformation. The results of our initial investigation are shown in Table 1. When the cyclotrimerization reaction of the isocyanate was performed in the presence of Nb(OEt)<sub>5</sub> (10 mol%) and EtMgCl (10 mol%) in THF (2 mL) at 60 °C for 2 h under an atmosphere of Ar, trihexyl isocyanurate (**2a**) was produced in 83% yield (Table 1, entry 1). The yield of the product was considerably reduced when either the niobium(V) ethoxide or Grignard reagent was removed (Table 1, entries 2 and 3), demonstrating the importance of both materials to the success of the reaction.

We then proceeded to investigate a variety of different catalysts. When Nb(OPh)<sub>5</sub>, NbCl<sub>5</sub> and Ta(OEt)<sub>5</sub> (Table 1, entries 4, 5, and 6) were used as the catalysts, the desired product **2a** was obtained in low yields. It is noteworthy that the conventional low-valent niobium complex NbCl<sub>3</sub>(DME), which generally exhibits good levels of catalytic activity in related transformations, did not show any catalytic activity toward the present reaction (Table 1, entries 7–8).

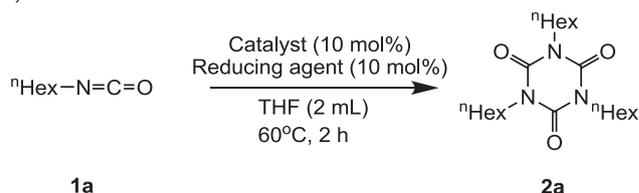
The introduction of a variety of different additives was also investigated, with EtMgCl being identified as the most effective. Several other reducing agents, however, such as *i*-PrMgCl, *n*-BuLi, and LiAlH<sub>4</sub>, provided similar levels of activity (Table 1, entry 1 and entries 9–11).

Different solvents were also investigated for the reaction, with THF provided comparable yield of **2a** to toluene (Table 1, entries 1 and 12). This reaction was also found to provide the desired product at ambient temperature, albeit in relatively low yield (Table 1, entry 13). A reduction in the amount of the catalyst present in the reaction from 10 to 5 mol% was found to be well tolerated, with the product **2a** being isolated in a reduced yield of 73% (Table 1, entry 14).

With the optimized conditions in hand, we proceeded to investigate the substrate scope of the reaction. The results are shown in Table 2. Under the optimized reaction conditions, a variety of different isocyanates (**1**) were converted to the corresponding cyclotrimerization products in moderate to high yields.

**Table 1**

Optimization of the Nb-catalyzed cyclotrimerization reaction of *n*-hexyl isocyanate (**1a**).<sup>a</sup>



Entry	Catalyst precursor	Reducing agent	Conv. (%)	Yield of <b>2a</b> (%) <sup>b</sup>
1	Nb(OEt) <sub>5</sub>	EtMgCl	> 99	89(83)
2	Nb(OEt) <sub>5</sub>	None	77	Trace
3	None	EtMgCl	> 99	21
4	Nb(OPh) <sub>5</sub>	EtMgCl	> 99	63.
5	NbCl <sub>5</sub>	EtMgCl	< 1	Trace
6	Ta(OEt) <sub>5</sub>	EtMgCl	> 99	36
7	NbCl <sub>3</sub> (DME)	None	10	n.d. <sup>c</sup>
8	NbCl <sub>3</sub> (DME)	LiOEt <sup>d</sup>	87	Trace
9	Nb(OEt) <sub>5</sub>	<i>i</i> -PrMgCl	> 99	65
10	Nb(OEt) <sub>5</sub>	<i>n</i> -BuLi	> 99	92
11	Nb(OEt) <sub>5</sub>	LiAlH <sub>4</sub>	> 99	88
12 <sup>e</sup>	Nb(OEt) <sub>5</sub>	EtMgCl	> 99	89
13 <sup>f</sup>	Nb(OEt) <sub>5</sub>	EtMgCl	> 99	46
14 <sup>g</sup>	Nb(OEt) <sub>5</sub>	EtMgCl	> 99	73

<sup>a</sup> Conditions: **1a** (2 mmol) was stirred with the catalyst in solvent (2 mL) at 60 °C for 2 h.

<sup>b</sup> Determined by GC. The number in the parentheses indicates the isolated yield. Ethyl hexylcarbamate was detected in <5% yield by GC as by-product.

<sup>c</sup> Not detected by GC.

<sup>d</sup> LiOEt (0.6 mmol) was used.

<sup>e</sup> Solvent was Toluene (2 mL).

<sup>f</sup> Reaction was conducted at room temperature.

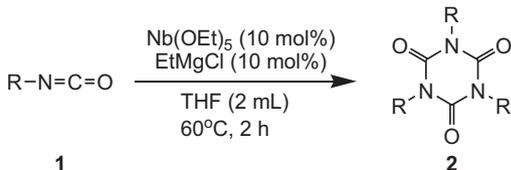
<sup>g</sup> Reaction was performed in the presence of Nb(OEt)<sub>5</sub> (5 mol%) and EtMgCl (5 mol%).

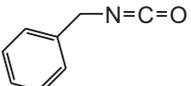
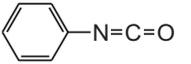
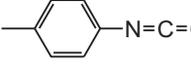
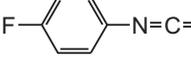
Isocyanates bearing alkyl substituents such as the *n*-hexyl (**1a**) and benzyl (**1b**) groups reacted well to afford the corresponding cyclotrimerization compounds in 83% (**2a**) and 62% (**2b**) yields, respectively (Table 2, entries 1 and 2). Aromatic isocyanates were also well tolerated as substrates under the optimized reaction conditions. For example, when phenyl isocyanate (**1c**) was used as the substrate, triphenyl isocyanurate (**2c**) was obtained in good yield (Table 2, entry 3). When other aromatic isocyanate bearing methyl and fluoro substituents at the para-position of their phenyl ring were subjected to the optimized conditions, they gave the corresponding isocyanurates in moderate yields (Table 2, entries 4 and 5). Unfortunately, however, when *t*-butyl isocyanate (**1f**) was used as the substrate, the corresponding isocyanurate (**2f**) was not detected by gas chromatographic (GC) analysis of the reaction mixture (Table 2, entry 6).

Urabe and Sato et al. [1j,k] previously reported that the use of Ti(O*i*Pr)<sub>4</sub> in conjunction with *i*-PrMgCl led to the formation of the corresponding low-valent alkoxytitanium species. Based on these results, we hypothesized that the low-valent niobium species generated from the Nb(OEt)<sub>5</sub>/Grignard reagent system was the catalytically active species in this reaction. To obtain some experimental evidence to support the existence of a low-valent niobium species as the active catalytic species in this cyclotrimerization reaction of isocyanates, we conducted a complexation reaction with an alkyne and carried out a subsequent experiment to verify the formation of the hypothesized low-valent metal species in this system (Scheme 1).

The hydrolysis of 4-octyne (**3**) (0.7 mmol) was conducted in the presence of Nb(OEt)<sub>5</sub> (2.5 mmol) and *i*-PrMgCl (2.5 mmol) in THF (2 mL) at 60 °C for 2 h, and subsequently quenched via the addition

**Table 2**  
Nb-catalyzed cyclotrimerization reactions of a variety of different isocyanates.<sup>a</sup>



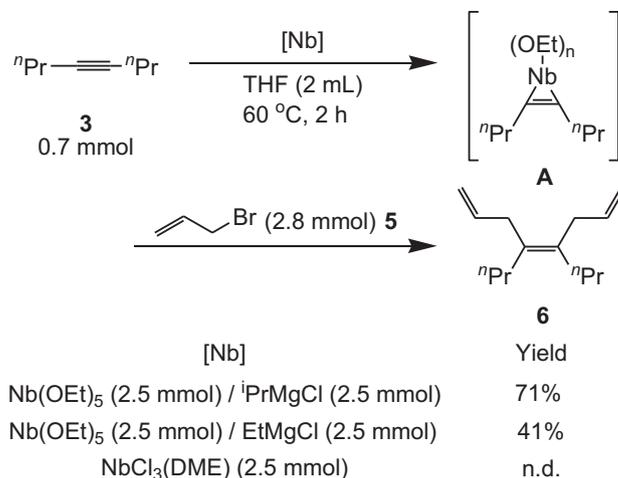
Entry	R–NCO	Product (2)	yield (%) <sup>b</sup>
1	<sup>n</sup> Hex–N=C=O	<b>1a</b>	83
2		<b>1b</b>	62
3		<b>1c</b>	71
4		<b>1d</b>	63
5		<b>1e</b>	50
6	<sup>t</sup> Bu–N=C=O	<b>1f</b>	n.d. <sup>c</sup>

<sup>a</sup> Conditions: **1a** (2 mmol) was stirred with the catalyst in solvent (2 mL) at 60 °C for 2 h.

<sup>b</sup> Isolated yields.

<sup>c</sup> Not detected by GC.

of water to provide (*Z*)-4-octene (or D<sub>2</sub>-4-octene) (**4**) in 91% yield by GC analysis. This result indicated that the alkoxy-niobium–alkyne complex **A** was formed in this reaction from the low-valent niobium species, which was derived itself from the reaction of Nb(OEt)<sub>5</sub> with *i*-PrMgCl. In addition, the <sup>13</sup>C NMR spectrum of the low-valent niobium–alkyne complex **A** revealed the presence of alkyne carbon peaks assignable to the Nb–alkyne (4-octyne) compound at 216.9 ppm (Fig. S1 in the Supplementary materials), which was comparable to the <sup>13</sup>C NMR peak reported for the related alkyne carbon of the NbCl<sub>3</sub>–alkyne (4-octyne) complex at 250.9 ppm (Fig. S2 in Supplementary materials) [5f]. In contrast, the

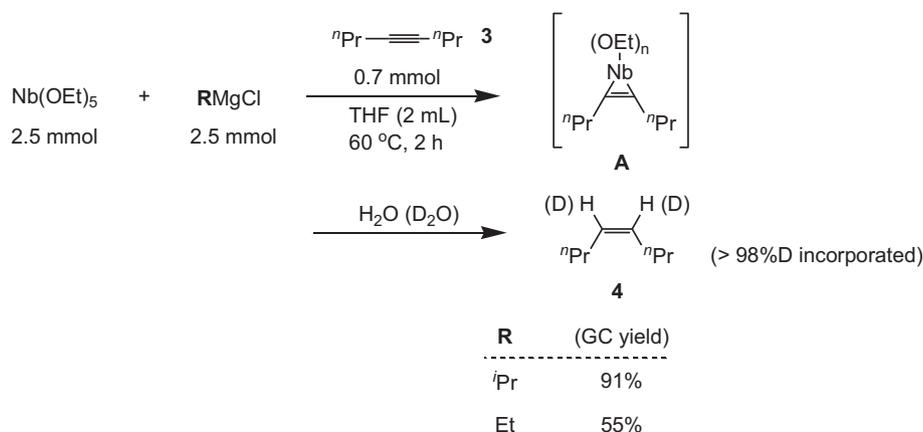


**Scheme 2.** Alkylation of 4-octyne.

use of EtMgCl which showed a higher level of catalytic activity in the cyclotrimerization of isocyanates, gave lower yield of **4**. Although a detailed reason and experimental evidence of this outcome is not confirmed, this might be due to the formation of unstable niobium species such as niobium hydride during the reaction course [24].

For the generation of the low-valent alkoxytitanium compounds described above, the addition of 2 equiv of a reducing agent such as a Grignard reagent to Ti(O<sup>*i*</sup>Pr)<sub>4</sub> was required to allow the reaction to proceed [1j,k]. Interestingly, the current method only required the addition of 1 equiv of Grignard reagent to react with the Nb(OEt)<sub>5</sub> to maintain the low-valent metal species. In addition, to evaluate the reactivity of the niobium–alkyne complex, a reaction was conducted between the alkyne and a suitable electrophile in the presence of the Nb(OEt)<sub>5</sub>/Grignard reagent system (Scheme 2).

The alkylation reaction of 4-octyne (**3**) with allyl bromide proceeded smoothly in the presence of the Nb(OEt)<sub>5</sub>/Grignard reagent to afford the diallyl product **5** in 71% yield. The use of EtMgCl afforded **5** in 41% yield. In contrast, the alkylation compound was not obtained when NbCl<sub>3</sub>(DME) was used under these conditions. This result indicated that the Nb–alkyne species generated from the reaction of Nb(OEt)<sub>5</sub> and the Grignard reagent with the alkyne showed a higher level of activity than the conventional Nb–alkyne species generated from the reaction of NbCl<sub>3</sub>(DME) with an alkyne.



**Scheme 1.** Hydrolysis of 4-octyne.

### 3. Conclusions

In conclusion, we have developed a Nb(OEt)<sub>5</sub>/Grignard reagent system as a new highly active low-valent alkoxy-niobium species. This material behaved as an efficient catalyst for the cyclo-trimerization of a variety of different isocyanates as well as a good reagent for the allylation reaction of alkynes.

### 4. Experimental section

#### 4.1. General

GLC analysis was performed with a flame ionization detector using a 0.22 × 25 m capillary column (BP-5). <sup>1</sup>H and <sup>13</sup>C NMR were measured at 400 and 100 MHz, respectively, in CDCl<sub>3</sub> and C<sub>2</sub>D<sub>5</sub>OD with Me<sub>4</sub>Si as the internal standard. The products were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR. All reagents were commercially available and used without further purification.

Compound **2a** [25], **2b** [26], **2c** [27], **2d** [28] and **2e** [29] is known compound and reported previously.

#### 4.2. Typical reaction procedure for the preparation of **2a**

A 2 M solution of EtMgCl in THF (0.1 mL, 0.2 mmol) was added to Nb(OEt)<sub>5</sub> (64 mg, 0.2 mmol) in THF (2 mL), and the resulting mixture was stirred at room temperature for 0.5 h under an atmosphere of Ar. *n*-Hexyl isocyanate (**1a**) (2 mmol) was then added and the resulting mixture was stirred for 2 h at 60 °C under an atmosphere of Ar. Product yields were estimated from their GC peak areas based on an internal standard (tridecane), with the product **2a** being obtained in 89% yield. The product **2a** was isolated by silica gel column chromatography (ethyl acetate/*n*-hexane = 4/1) in 83% yield (211.1 mg).

#### 4.3. Hydrolysis of 4-octyne

A 2 M solution of *i*-PrMgCl in THF (1.25 mL, 2.5 mmol) was added to Nb(OEt)<sub>5</sub> (800 mg, 2.5 mmol) in THF (2 mL), and the resulting mixture was stirred at room temperature for 0.5 h under an atmosphere of Ar. 4-Octyne (**3**) (77.1 mg, 0.7 mmol) was then added and the resulting mixture was stirred for 24 h at 60 °C under an atmosphere of Ar. The mixture was then quenched by the addition of H<sub>2</sub>O. The conversion and yield of the product was estimated from its peak area by GC based on an internal standard (tridecane), with the product **4** being obtained in 91% yield.

#### 4.4. Typical reaction procedure for the allylation of 4-octyne

A 2 M solution of *i*-PrMgCl in THF (1.25 mL, 2.5 mmol) was added to a mixture of Nb(OEt)<sub>5</sub> (800 mg, 2.5 mmol) and THF (2 mL), and the resulting mixture was stirred at room temperature for 0.5 h under an atmosphere of Ar. 4-Octyne **3** (77.1 mg, 0.7 mmol) was then added to the reaction mixture and the resulting mixture was stirred for 24 h at 60 °C under an atmosphere of Ar. Allyl bromide (**5**) (339 mg, 2.8 mmol) was then added to the reaction mixture and the resulting mixture was stirred for 24 h at 60 °C under an atmosphere of Ar. The mixture was then quenched via the addition of a 10% (v/v) HCl solution. The solvent was then removed *in vacuo* to give the crude product, which was purified by silica gel column chromatography using *n*-hexane as the eluent to give compound **6** (95 mg) in 71% yield.

### Acknowledgments

This work was supported by MEXT-Supported Program for the Strategic Research Foundation at Private Universities (2010–2014),

the Kansai University Research Grants (Grant-in Aid for Encouragement of Scientists, 2012), and METI.

### Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2013.05.035>.

### References

- [1] (a) R.D. Broene, S.L. Buchwald, *Science* 261 (1993) 1696; (b) T. Kawaji, N. Shohji, K. Miyashita, S. Okamoto, *Chem. Commun.* 47 (2011) 7857; (c) U. Rosenthal, V.V. Burlakov, M.A. Bach, T. Beweries, *Chem. Soc. Rev.* 36 (2007) 719; (d) K. Fukuhara, S. Okamoto, F. Sato, *Org. Lett.* 5 (2003) 2145; (e) I.L. Lysenko, K.K. Hyung, G. Lee, J.K. Cha, *J. Am. Chem. Soc.* 130 (2008) 15997; (f) M.A. Tarselli, G.C. Micalizio, *Org. Lett.* 11 (2009) 4596; (g) T. Hanamoto, K. Yamada, *J. Org. Chem.* 74 (2009) 7559; (h) G.J. Balaich, I.P. Rothwell, *J. Am. Chem. Soc.* 115 (1993) 1581; (i) E.S. Johnson, G.J. Balaich, I.P. Rothwell, *J. Am. Chem. Soc.* 119 (1997) 7685; (j) K. Harada, H. Urabe, F. Sato, *Tetrahedron Lett.* 36 (1995) 3203; (k) F. Sato, H. Urabe, S. Okamoto, *Chem. Rev.* 100 (2000) 2835.
- [2] (a) T. Takahashi, F.-Y. Tsai, Y. Li, K. Nakajima, M. Kotori, *J. Am. Chem. Soc.* 121 (1999) 11093; (b) K. Kanno, E. Igarashi, L. Zhou, K. Nakajima, T. Takahashi, *J. Am. Chem. Soc.* 130 (2008) 5624; (c) G. Wang, E. Negishi, *Eur. J. Org. Chem.* (2009) 1679; (d) Y. Nishihara, M. Miyasaka, M. Okamoto, H. Takahashi, E. Inoue, K. Tanemura, K. Takagi, *J. Am. Chem. Soc.* 129 (2007) 12634; (e) A. Ohff, S. Pulst, C. Lefeber, N. Peulecke, P. Arndt, V.V. Burlakov, U. Rosenthal, *Synlett* (1996) 111.
- [3] (a) H. Shimizu, S. Kobayashi, *Tetrahedron Lett.* 46 (2005) 7593; (b) T. Oshiki, K. Tanaka, J. Yamada, T. Ishiyama, Y. Kataoka, K. Mashima, K. Tani, K. Takai, *Organometallics* 22 (2003) 464; (c) K. Takai, M. Yamada, K. Utimoto, *Chem. Lett.* (1995) 851; (d) I. Shibata, T. Kano, N. Kanazawa, S. Fukuoka, A. Baba, *Angew. Chem. Int. Ed.* 41 (2002) 1389; (e) W.W. Brennessel, J.E. Ellis, M.K. Pomije, V.J. Sussman, E. Urnezis, V.G. Young Jr., *J. Am. Chem. Soc.* 124 (2002) 10258; (f) T. Oshiki, H. Nomoto, K. Tanaka, K. Takai, *Bull. Chem. Soc. Jpn.* 77 (2004) 1009.
- [4] (a) E.J. Roskamp, S.F. Pedersen, *J. Am. Chem. Soc.* 109 (1987) 6551; (b) E.J. Roskamp, P.S. Dragovich, J.B. Hartung, S.F. Pedersen, *J. Org. Chem.* 54 (1989) 4736; (c) Y. Kataoka, J. Miyai, K. Oshima, K. Takai, K. Utimoto, *J. Org. Chem.* 57 (1992) 1973; (d) K. Fuchibe, T. Akiyama, *J. Am. Chem. Soc.* 128 (2006) 1434; (e) S. Arai, S. Takita, A. Nishida, *Eur. J. Org. Chem.* (2005) 5262; (f) Y. Kataoka, K. Takai, K. Oshima, K. Utimoto, *Tetrahedron Lett.* 31 (1990) 365; (g) Y. Kataoka, J. Miyai, M. Tezuka, K. Takai, *Tetrahedron Lett.* 31 (1990) 369.
- [5] (a) Y. Obora, M. Kimura, M. Tokunaga, Y. Tsuji, *Chem. Commun.* 7 (2005) 901; (b) Y. Obora, K. Takeshita, Y. Ishii, *Org. Biomol. Chem.* 7 (2009) 428; (c) Y. Obora, Y. Satoh, Y. Ishii, *J. Org. Chem.* 75 (2010) 6046; (d) Y. Satoh, Y. Obora, *Org. Lett.* 13 (2011) 2568; (e) Y. Satoh, Y. Obora, *J. Org. Chem.* 76 (2011) 8569; (f) Y. Satoh, K. Yasuda, Y. Obora, *Organometallics* 31 (2012) 5235; (g) Y. Obora, M. Kimura, T. Ohtake, M. Tokunaga, Y. Tsuji, *Organometallics* 25 (2006) 2097.
- [6] (a) Y. Akiyama, K. Shitanaka, H. Murakami, Y. Shin, M. Yoshida, N. Imaishi, *Thin Solid Films* 515 (2007) 4975; (b) M. Iwai, M. Ohmori, T. Yoshino, S. Yamaguchi, M. Imaeda, *Jpn. J. Appl. Phys.* 43 (2004) 8195; (c) T. Matsuzaki, H. Funakubo, *J. Appl. Phys.* 86 (1999) 4559; (d) K. Chikuma, A. Onoe, A. Yoshida, *Jpn. J. Appl. Phys.* 37 (1998) 5582; (e) M.J. Nystrom, B.W. Wessels, D.B. Studebaker, T.J. Marks, W.P. Lin, G.K. Wong, *Appl. Phys. Lett.* 67 (1995) 365; (f) D. Monsma, J. Becker, *Mater. Matt.* 1 (2006) 5.
- [7] (a) J.S. Yu, P.E. Fanwick, I.P. Rothwell, *J. Am. Chem. Soc.* 112 (1990) 8171; (b) J.S. Yu, L. Felter, M.C. Potyten, J.R. Clark, V.M. Visciglio, P.E. Fanwick, I.P. Rothwell, *Organometallics* 15 (1996) 4443; (c) V.M. Visciglio, M.T. Nguyen, J.R. Clark, P.E. Fanwick, I.P. Rothwell, *Polyhedron* 15 (1996) 551; (d) A. Caselli, E. Solari, R. Scopelliti, C. Floriani, *J. Am. Chem. Soc.* 121 (1999) 8296.
- [8] I.S. Lin, J.E. Kresta, K.C. Frisch, *Reaction Injection Molding and Fast Polymerization Reactions*, Plenum Publishing, New York, 1982, p. 147.
- [9] (a) Z. Wirpsza, *Polyurethanes: Chemistry, Technology and Application*, Ellis Horwood, London, 1993;

- (b) T. Nawata, J.E. Kresta, K.C. Frisch, *J. Cell. Plast.* (1975) 267;  
(c) L. Nicholas, G.R. Gmitter, *J. Cell. Plast.* (1965) 85.
- [10] (a) Z. Bukac, J. Sebenda, *Chem. Prum.* 35 (1985) 361;  
(b) J. Horsky, V. Kubanek, J. Marilk, J. Kralicek, *Chem. Prum.* 32 (1982) 599.
- [11] (a) G. Xiao, S. Gao, X. Xie, M. Xu, *Polym. Adv. Technol.* 20 (2009) 1157;  
(b) W. Sun, X. Yan, X. Zhu, *J. Appl. Polym. Sci.* 122 (2011) 2359;  
(c) T.S. Leu, *J. Appl. Polym. Sci.* 102 (2006) 2470;  
(d) A. Matsumoto, T. Kubo, T. Yamakawa, H. Aota, Y. Takayama, A. Kameyama, T. Nakanishi, *Angew. Makromol. Chem.* 268 (1999) 36.
- [12] H.A. Duong, M.J. Cross, J. Louie, *Org. Lett.* 6 (2004) 4679.
- [13] M.S. Khajavi, M. Dakamin, H. Hazarkhani, *J. Chem. Res. Synop.* (2000) 145.
- [14] (a) Y. Taguchi, I. Shibuya, M. Yasumoto, T. Tsuchiya, K. Yonemoto, *Bull. Chem. Soc. Jpn.* 63 (1990) 3486;  
(b) R. Richter, H. Ulrich, *Synthesis* (1975) 463;  
(c) S.W. Wong, K.C. Frisch, *J. Polym. Sci. Polym. Chem. Ed.* 24 (1986) 2877;  
(d) I.C. Kogon, *J. Am. Chem. Soc.* 78 (1956) 4911;  
(e) A.F.A. Wallis, R.H. Wearne, *Eur. Polym. J.* 26 (1990) 1217.
- [15] Y. Nambu, T. Endo, *J. Org. Chem.* 58 (1993) 1932.
- [16] F.M. Moghaddam, M.G. Dekamin, M.S. Khajavi, S. Jalili, *Bull. Chem. Soc. Jpn.* 75 (2002) 851.
- [17] F. Tanimoto, T. Tanka, H. Kitano, K. Fukui, *Bull. Chem. Soc. Jpn.* 39 (1966) 1922.
- [18] J. Mizura, T. Yokozawa, T. Endo, *J. Polym. Sci. Polym. Chem.* 29 (1991) 1544.
- [19] J. Tang, T. Mohan, J.G. Verkade, *J. Org. Chem.* 59 (1994) 4931.
- [20] J.F. Villa, H.B. Powell, *Synth. React. Metal-Org. Chem.* 6 (1976) 59.
- [21] F. Paul, S. Moulin, O. Piechaczyk, P. Le Floch, J.A. Osborn, *J. Am. Chem. Soc.* 129 (2007) 7294.
- [22] J.G. Noltes, J. Boersma, *J. Organomet. Chem.* 7 (1966) 6.
- [23] Y. Li, H. Matsumura, M. Yamanaka, T. Takahashi, *Tetrahedron* 60 (2004) 1393.
- [24] R.M. Sultanov, U.M. Dzhemiev, E.V. Samoilo, R.R. Ismagilov, L.M. Khalilov, N.R. Popod'ko, *J. Organomet. Chem.* 715 (2012) 5.
- [25] E.V. Ganin, L.Ya. Glinskaya, *Ukr. Khim. Zhurnal (Russ. Ed.)* 56 (1990) 323.
- [26] Y. Wu, S. Wang, X. Zhu, G. Yang, Y. Wei, L. Zhang, H. Song, *Inorg. Chem.* 47 (2008) 5503.
- [27] K.A. Krasukii, M. Movsum-Zade, *Zh. Obshch. Khim* 6 (1936) 1203.
- [28] J. Shi, Z. Guo, X. Wei, D. Liu, M.F. Lappert, *Synlett* 13 (2011) 1937.
- [29] B. Bantu, G.M. Pawar, U. Decker, K. Wurst, A.M. Schmidt, M.R. Buchmeiser, *Chem. Eur. J.* 15 (2009) 3103.