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# **Trialkylaluminum N-Heterocyclic Olefin (NHO) Adducts as Catalysts for the Polymerization of Michael-Type Monomers**

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Dedicated to Prof. Dr. Manfred Scheer on the Occasion of his 65th Birthday

Abstract. The synthesis of new trialkylaluminum adducts with N-heterocyclic olefin (NHO) ligands is described. These well-defined complexes can catalyze the polymerization of various Michael-type monomers, such as 2-vinylpyridine, methylacrylate, and dimethylacrylamide.

## Introduction

N-Heterocyclic olefins (NHOs), first reported by *Kuhn* in the mid 1990s,<sup>[1]</sup> are an emerging class of ylidic carbon-based donors that have attracted recent attention due to their ability to stabilize various reactive main group species.<sup>[2]</sup> Related to *N*-heterocyclic carbenes (NHCs), NHOs feature an exocyclic alkylidene unit (=CR<sub>2</sub>) attached to a heterocyclic imidazole ring, and are good  $\sigma$ -donating ligands but lack the ability to act as  $\pi$  acceptors.<sup>[3]</sup>

NHOs have also been explored as organocatalysts/initiators within the realms or synthetic organic and polymer chemistry.<sup>[4]</sup> For example, *Naumann* and co-workers showed that NHOs can be used as initiators in the polymerization of dimethylacrylamide (DMAA).<sup>[4c]</sup> Furthermore, *Chen* and coworkers demonstrated that NHO·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> Lewis pairs are capable of polymerizing lactones and challenging Michael-type monomers, such as crotonates;<sup>[5]</sup> in addition, the *Lu* group showed that methylmethacrylate (MMA) can be polymerized with NHO·Al(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> complexes as initiators.<sup>[6]</sup> In related work, *Chen* and co-workers used NHC·AlR<sub>3</sub> adducts to polymerize methylmethacrylate.<sup>[7]</sup>

In this communication we report the preparation of NHO·AIR<sub>3</sub> adducts, such as <sup>Me</sup>IPrCH<sub>2</sub>·AIMe<sub>3</sub> (Figure 1)  $[^{Me}IPrCH_2 = (MeCNDipp)_2C=CH_2; Dipp = 2,6-$ *i* $Pr_2C_6H_3]$ . These complexes are structurally related to the NHC or N-heterocyclic imine (NHI) adducts made previously by *Robin*-

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*son* and *Masuda*, respectively (Figure 1).<sup>[8]</sup> We also found that one of our newly prepared NHO·AlR<sub>3</sub> complexes is a competent catalyst for the polymerization of Michael-type monomers at room temperature.



Figure 1. Examples of trimethylaluminum adducts with N-heterocyclic donors.

### **Results and Discussion**

The first NHO·AIR3 adduct in our series, MeIPrCH2·AlMe3 (1), was obtained by allowing <sup>Me</sup>IPrCH<sub>2</sub> to combine with one equivalent of AlMe<sub>3</sub> in toluene at room temperature (Scheme 1). Encouraged by these results, we performed a similar reaction between MeIPrCH2 and AlEt3, leading to the formation of the monoadduct MeIPrCH<sub>2</sub>·AlEt<sub>3</sub> (2). Upon binding of MeIPrCH<sub>2</sub> to either AlMe<sub>3</sub> or AlEt<sub>3</sub>, an upfield shift in the <sup>1</sup>H NMR signals (in  $C_6D_6$ ) is observed relative to the free NHO. Specifically, the exocyclic  $CH_2$  resonance shifts from 2.33 ppm in free MeIPrCH<sub>2</sub> to values of 2.01 ppm and 1.89 ppm in adducts 1 and 2, respectively. The <sup>1</sup>H NMR resonances belonging to the  $AIR_3$  moieties in 1 and 2 are also upfield-shifted in comparison to the uncomplexed alanes AlMe<sub>3</sub> and AlEt<sub>3</sub>; for example, the methyl resonance for the AlMe<sub>3</sub> group in **1** is found at  $\delta = -0.52$  ppm in C<sub>6</sub>D<sub>6</sub>, while the corresponding resonance for AlMe<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> is -0.37 ppm.<sup>[9]</sup>

Figure 2 shows the structure of <sup>Me</sup>IPrCH<sub>2</sub>·AlMe<sub>3</sub> (1), as determined by X-ray crystallography, while the structure of <sup>Me</sup>IPrCH<sub>2</sub>·AlEt<sub>3</sub> (2) is found in Figure S3 (Supporting Information).<sup>[9]</sup> The coordinative  $C_{NHO}$ -Al bond in 1 is 2.1198(13) Å, and is similar in length as the  $C_{NHC}$ -Al distance

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Scheme 1. Preparation of MeIPrCH2·AlMe3 (1) and MeIPrCH2·AlEt3 (2).

found in Robinson's NHC·AlMe<sub>3</sub> adduct [2.124(6) Å] in Figure 1,<sup>[8a]</sup> whereas longer than the coordinative N<sub>NHI</sub>–Al interaction in Masuda's NHI·AlMe<sub>3</sub> complex [1.9648(19) Å] (Figure 1).<sup>[8b]</sup> The latter observation follows a general trend of shorter ligand-element bonds with N-heterocyclic imine (NHI) adducts in comparison to NHO-element bonds.<sup>[10]</sup> While the carbene adduct IPr·AlEt<sub>3</sub> (IPr = [(HCNDipp)<sub>2</sub>C:]) has been previously synthesized by *Dagorne* in 2017,<sup>[11]</sup> a crystal structure has not been reported, obviating the chance to directly compare its structure with <sup>Me</sup>IPrCH<sub>2</sub>·AlEt<sub>3</sub> (**2**).



**Figure 2.** Molecular structure of <sup>Me</sup>IPrCH<sub>2</sub>·AlMe<sub>3</sub> (1) with thermal ellipsoids shown at a 30% probability level. All hydrogen atoms except those on C6 are omitted for clarity. Selected bond lengths /Å and angles /°: C1–C6 1.4439(17), C6–Al1 2.1198(13), Al1–C8 1.9925(16), C1–C6–Al1 130.01(9), C7–Al1–C8 109.59(7).

<sup>Me</sup>IPr=CH–CH=CH<sub>2</sub>, an allyl-appended NHO with two potential sites to accommodate a Lewis acid, has been reported by our group (Scheme 2).<sup>[12]</sup> In our previously described palladium complexes with this ligand, only evidence of coordination via the terminal exocyclic carbon atom was found, presumably due to the steric crowding imparted by the flanking Dipp groups in <sup>Me</sup>IPr=CH–CH=CH<sub>2</sub>.<sup>[12]</sup> Thus we wondered if



Scheme 2. Important resonance forms associated with <sup>Me</sup>IPr=CH– CH=CH<sub>2</sub>, illustrating two potential sites of coordination.

an alternate coordination mode would be possible when complexes were formed with less hindered Lewis acids, such as AlMe<sub>3</sub>. Upon combining <sup>Me</sup>IPr=CH–CH=CH<sub>2</sub> with AlMe<sub>3</sub> in a 1:1 ratio, the corresponding adduct <sup>Me</sup>IPrCHCHCH<sub>2</sub>·AlMe<sub>3</sub> (**3**) was obtained [Equation (1)].



X-ray crystallography (Figure 3) revealed a similar terminal NHO-AlMe<sub>3</sub> binding mode was present as in our Pd complexes.<sup>[12]</sup> As with <sup>Me</sup>IPrCH<sub>2</sub>•AlMe<sub>3</sub> (1), a diagnostic upfield shift in the methyl resonance for the AlMe<sub>3</sub> group in 3 was found (to a value of -0.42 ppm in C<sub>6</sub>D<sub>6</sub>). The formally dative Al- $C_{NHO}$  distance of 2.1135(13) Å in 3 (Al-C4; Figure 3) is similar to the corresponding Al-C<sub>NHO</sub> interaction in <sup>Me</sup>IPrCH<sub>2</sub>·AlMe<sub>3</sub> (1) [2.1198(13) Å]. We believe that the terminal olefin coordination mode in 3 is adopted for two reasons: (1) the steric bulk close to the heterocycle makes binding to the proximal exocyclic carbon (C2 in Figure 3) difficult, and (2) Natural Population Analysis (NPA)<sup>[12]</sup> of <sup>Me</sup>IPr=CH-CH=CH<sub>2</sub> showed a more negative charge at the terminal carbon compared to the one adjacent to the MeIPr unit  $(-0.53 \text{ e}^- \text{ vs.} -0.46 \text{ e}^-)$ , making the terminal site slightly more Lewis basic.



**Figure 3.** Molecular structure of  $^{Me}$ IPrCHCHCH<sub>2</sub>·AlMe<sub>3</sub> (**3**) with thermal ellipsoids shown at a 30% probability level. Co-crystallized toluene solvate and all hydrogen atoms besides those on C2, C3 and C4 are omitted for clarity. Selected bond lengths /Å and angles /°: C1–C2 1.4205(16), C2–C3 1.3665(17), C3–C4 1.4203(17), Al1–C4 2.1135(13); C1–C2–C3 128.34(11), C3–C4–Al1 116.12(9).

The new NHO·AlR<sub>3</sub> adducts **1–3** are only sparingly soluble in C<sub>6</sub>D<sub>6</sub>, which made the acquisition of <sup>13</sup>C{<sup>1</sup>H} NMR spectra a challenge. When **1–3** were dissolved in [D<sub>8</sub>]THF (to possibly obtain more intense <sup>13</sup>C{<sup>1</sup>H} NMR resonances), the dissociation of these adducts into free NHO and AlR<sub>3</sub> was found.<sup>[9,13]</sup> Motivated by prior work<sup>[4c,6,7,14]</sup> involving the use of Frustrated Lewis pairs (FLPs) as initiators, we decided to investiZeitschrift für and

gate if **1** could act as a viable polymerization catalyst for Michael-type monomers (Scheme 3).

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Scheme 3. (top) The Michael-type monomers investigated in this study; (bottom) polymerization conditions.

We began our polymerization trials by combining dimethylacrylamide (DMAA) with 0.5 mol-% of 1 in THF. Upon adding 0.5 mol-% of 1 to a stirring solution of DMAA in THF, we noted a rapid increase in temperature, as is typical for this type of polymerization. After stirring for 1 h, the solution was quenched by the addition of ethanol, and the resulting polymer was isolated and purified via precipitation from a concentrated solution of the polymer in CH<sub>2</sub>Cl<sub>2</sub> into cold (-30 °C) pentane. According to gel permeation chromatography (GPC) on the isolated sample in THF/H<sub>2</sub>O (with 9 g·L<sup>-1</sup> [*n*Bu<sub>4</sub>N]Br added to increase the ionic strength), a number average molecular weight  $(M_{\rm p})$  of 150 kDa and a polydispersity index (PDI) of 1.18 was found (Table 1). For comparison, the use of 1 as a catalyst afforded higher molecular weight polymer vs. Naumann's NHO-only polymerization, with (MeCNMe)<sub>2</sub>C=CMe<sub>2</sub> as an initiator (67% conversion, 2 h, 0.5 mol-% NHO).<sup>[4c]</sup> Of note, the expected molecular weight if 1 fully instigated the living polymerization of DMAA would be ca. 20 kDa (i.e. a degree of polymerization, DP, of 200); however the higher molecular weight obtained (150 kDa), while keeping a low PDI, is consistent with a low effective initiator efficiency  $(I^*)$ .<sup>[15]</sup> Another notable system is the polymerization of DMAA by the NHO-alane adduct  $[(DippNC(H)C(H)NiPr)C] \cdot Al(C_6F_5)_3$ , which transpired in only 4 min, significantly faster than 1, with a low PDI (ca. 1.05) and an M<sub>n</sub> of 170 kDa.<sup>[7]</sup> This is consistent with the observation that the polymerization of Michaeltype monomers occurs quickly in the presence of strong Lewis acids.[16]

**Table 1.** Polymerization of various Michael-type monomers using  $^{Me}$ IPrCH<sub>2</sub>·AlMe<sub>3</sub> 0.5 mol-% as an initiator in THF (1 h).

Monomer	Isolated yield /%	$M_{\rm n}$ /10 <sup>3</sup> kDa	$M_{\rm w}/M_{\rm n}$
DMAA	> 99	150	1.18
2VP	98	840	1.35
MA DEVP	5 no polymerization	10	2.08

Knowing that DMAA is polymerized by **1**, we then attempted the polymerization of several other monomers (Scheme 3). Methyl acrylate (MA), 2-vinylpyridine (2VP), and diethylvinylphosphonate (DEVP) were each combined with **1** under the same conditions used for DMAA (vide supra). While the polymerizations MA and 2VP were successful (Table 1), diethylvinylphosphonate (DEVP) failed to yield any polymer.<sup>[17]</sup>

The polymerization of 2-vinylpyridine (2VP) with catalytic 1 affords very high molecular weight polymer, with  $M_n$  values exceeding 800 kDa (Table 1). 2VP has also been polymerized with NHC/Al( $C_6F_5$ )<sub>3</sub> systems (excess Lewis acid) to yield polymer with molecular weights ( $M_n$ ) in the 10–80 kDa range.<sup>[18]</sup>

Chen has demonstrated that an NHO-AlMe<sub>3</sub> Lewis pair can promote the slow polymerization of methylmethacrylate (MMA) (38% yield over 12 h),<sup>[16]</sup> however no reactions were tried with the less hindered monomer methyl acrylate (MA).<sup>[16]</sup> Combining 0.5 mol% of 1 with MA in THF only gave a small amount of isolated poly(methylacrylate) (ca. 5% yield) with a low  $M_n$  value of 10 kDa (PDI = 2.08; Table 1). To the best of our knowledge, Lewis pair polymerization has not been used to polymerize MA prior to our work. Notably, poly(methyacylate) with a narrow PDI (1.03) and high I\* (ca. 80%) was obtained from MA via group transfer polymerization with 1-triisopropylsiloxy-1-methoxy-2-methyl-1-propene (MTS<sup>iPr</sup>) as an initiator and  $C_6F_5CHTf_2$  as a catalyst (Tf = SO<sub>2</sub>CF<sub>3</sub>).<sup>[19]</sup> Industrially, the polymerization of acrylic monomers is typically achieved using radical initiators,<sup>[20]</sup> however these methods often yield high PDI values, [20c] making Frustrated Lewis pair catalysis attractive when smaller PDI values are desired.

We also attempted polymerization trials with MA and 2VP monomer using <sup>Me</sup>IPrCHCHCH<sub>2</sub>·AlMe<sub>3</sub> (**3**) as a catalyst. However these trials gave disappointingly low yields of polymer (3 and 15% for pMA and p2VP, respectively); thus we did not explore this catalyst further. The ability of <sup>Me</sup>IPrCH<sub>2</sub>·AlEt<sub>3</sub> (**2**) to act as a catalyst was not investigated due to the constant presence of a minor amount of unidentified NHO-containing impurity (according to <sup>1</sup>H NMR analysis<sup>[9]</sup>), which we were unable to remove via washing or recrystallization.

To verify that the FLP pair of 1 in THF was performing the polymerizations, we re-examined the interaction of 2-vinylpyridine (2VP) with both MeIPrCH<sub>2</sub> and AlMe<sub>3</sub> individually. When MeIPrCH2 was combined with 2VP under the same conditions outlined in Table 1, no polymerization was detected in situ by <sup>1</sup>H NMR spectroscopy. Likewise treatment of 2VP with AlMe<sub>3</sub> gave no evidence of polymerization by in situ <sup>1</sup>H NMR analysis of the mixture in  $[D_8]$ THF. Interestingly, when the mixture of AlMe<sub>3</sub> and 2VP was quenched with methanol, we observed a violent exothermic reaction, as expected upon the reaction of AlMe<sub>3</sub> with alcohol; however somewhat to our surprise, a small amount of poly(2-vinylpyridine) was observed (6% isolated yield). Knowing that unstabilized 2VP can autopolymerize at -20 °C over the course of a week,<sup>[20b]</sup> we hypothesize that the reflux induced by quenching the mixture with MeOH is responsible for some polymerization of 2VP.

#### Conclusions

We have described the synthesis of the new NHO-trialkylaluminum complexes (1–3) and found that <sup>Me</sup>IPrCH<sub>2</sub>·AlMe<sub>3</sub> (1) showed FLP-type behavior in THF, leading to the polymerizaZeitschrift für anorganische und allgemeine Chemie

tion of several Michael-type monomers under very mild conditions. Future work will involve targeting the synthesis of more electron deficient and lower coordinate NHO-aluminum species bearing anionic NHOs<sup>[21]</sup> as supporting ligands.

# **Experimental Section**

Materials and Instrumentation: All reactions were performed using standard Schlenk line techniques in an atmosphere of nitrogen or in an inert atmosphere glovebox (Innovative Technology Inc.). Solvents were dried using a Grubbs-type solvent purification system manufactured by Innovative Technology Inc., and stored under an atmosphere of nitrogen over 4 Å molecular sieves prior to use. MeIPrCH<sub>2</sub><sup>[3]</sup> and  $^{Me}IPr = CH-CH=CH_2^{[12]}$  were prepared according to literature procedures. Trimethylaluminum (2.0 M solution in toluene) and triethvlaluminum (1.0 M solution in hexanes) were purchased from Sigma-Aldrich and used as received. Dimethylacrylamide (DMMA) and 2vinylpyridine (2VP) were purchased from Sigma-Aldrich, distilled over calcium hydride and freeze-thaw degassed before use. Methyl acrylate (MA) was purchased from Sigma-Aldrich, washed with a saturated NaOH solution, distilled over calcium hydride, and freeze-thaw degassed before use. [D<sub>8</sub>]THF was purchased from Sigma-Aldrich and distilled from sodium benzophenone, then stored over Na/K before use. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on 400 MHz, 500 MHz, and 700 MHz Varian Inova spectrometers and referenced externally to SiMe<sub>4</sub> ( ${}^{1}H$ ,  ${}^{13}C{}^{1}H$ ). Elemental analyses were performed by the Analytical and Instrumentation Laboratory at the University of Alberta. Melting points were measured in sealed glass capillaries under nitrogen using a MelTemp melting point apparatus and are uncorrected. GPC measurements for p2VP and pMA were performed at 40 °C using THF as the eluent at a flow rate of 0.5 mL per minute. A Viscotek VE 2001 autosampler, one Viscotek T6000M column, GPC 270 Max dual detector, and Viscotek VE 3580 refractive index detector were used for sample analysis and data collection. Multidetector calibration was done using refractive index (RI) detection in conjunction with low angle light scattering (LALS) and right angle light scattering (RALS), using 99 kDa polystyrene to create the calibration method and 235 kDa polystyrene to verify the calibration. GPC measurements for pDMAA were performed using two PL Polargel columns in THF:H2O [1:1; v:v] [with 272 mg·L<sup>-1</sup> 3,5-di-tert-butyl-4-hydroxytoluene (BHT) and 9 g·L<sup>-1</sup> tetrabutylammonium bromide (TBAB)] as the eluent. The determination of the absolute molecular weights was performed with multi-angle light scattering on a Wyatt Dawn Heleos II instrument equipped with an Wyatt Optilab rEX 536 RI detector for concentration determination. The dn/dc value for the absolute molecular weight measurements was determined to be 0.1282 mL·g<sup>-1</sup>.

**X-ray Crystallography:** Crystals of appropriate quality for X-ray diffraction studies<sup>[9]</sup> were removed from either a Schlenk tube under a stream of nitrogen, or from a vial (glove box) and immediately covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fiber, and quickly placed in a low-temperature stream of nitrogen. All data were collected using a Bruker APEX II CCD detector/D8 diffractometer using Mo- $K_a$  or Cu- $K_a$  radiation, with the crystal cooled to -100 °C or -80 °C, respectively. The data were corrected for absorption through Gaussian integration from indexing of the crystal faces. Structures were solved using the direct methods programs SHELXT-2014,<sup>[22]</sup> and refinements were completed using the program SHELXL-2014.<sup>[23]</sup> Hydrogen atoms were assigned positions based on the sp<sup>2</sup>- or sp<sup>3</sup>-hybridization geometries of their attached carbon atoms, and were given thermal parameters 20% greater than those of their parent atoms.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1968013, CCDC-1968014, and CCDC-1968015 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

Synthesis of MeIPrCH<sub>2</sub>·AlMe<sub>3</sub> (1): A solution of AlMe<sub>3</sub> (0.210 mL, 2.0 M solution in toluene, 0.42 mmol) was gently layered atop of a solution of MeIPrCH<sub>2</sub> (0.1810 g, 0.420 mmol) in 1.5 mL of toluene. After allowing the mixture to remain undisturbed for 4 h, colorless X-ray quality crystals formed. The supernatant was decanted away and the crystals of <sup>Me</sup>IPrCH<sub>2</sub>·AlMe<sub>3</sub> (1) were washed with  $3 \times 2$  mL of cold (-30 °C) toluene, and dried in vacuo. (0.1428 g, 68 %). <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ ):  $\delta = 7.21$  (t, 2 H,  ${}^3J_{HH} = 7.6$  Hz, ArH), 7.17 (d, 4 H,  ${}^{3}J_{\text{HH}} = 7.6 \text{ Hz}$ , ArH), 2.80 [m, 4 H, CH(CH<sub>3</sub>)<sub>2</sub>], 2.01 (s, 2 H,  $CCH_2AIMe_3$ ), 1.38 (s, 6 H, CN- $CH_3$ ), 1.38 [d, 12 H,  ${}^{3}J_{HH}$  = 6.8 Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 0.98 [d, 12 H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>], -0.52 [s, 9 H, -Al(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -4.4$  [-Al(CH<sub>3</sub>)<sub>3</sub>], 9.6 (H<sub>3</sub>CCN), 24.5 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.6 [CH(CH<sub>3</sub>)<sub>2</sub>], 28.8 [CH(CH<sub>3</sub>)<sub>2</sub>], 125.3 (ArC), 128.0 (ArC), 128.2 (ArC), 128.4 (ArC), 131.0 (ArC), 145.5 (NCN), 146.9 (CCH2-AlEt3); one of the ArC resonances could not be observed. C33H55AlN2: calcd. C, 78.84; H, 10.23; N, 5.57%; found: C, 78.69; H, 10.23; N, 5.46%. Mp (°C): 229 (dec.).

Synthesis of MeIPrCH<sub>2</sub>·AlEt<sub>3</sub> (2): A solution of AlEt<sub>3</sub> (1.0 M solution in hexanes, 1.476 mL, 1.5 mmol) was carefully layered atop of a solution of MeIPrCH<sub>2</sub> (0.6357 g, 1.476 mmol) in 1.5 mL of toluene. After allowing the mixture to remain undisturbed for 4 h, colorless crystals of MeIPrCH<sub>2</sub>·AlEt<sub>3</sub> (2) were deposited. The supernatant was then decanted away, the remaining crystals washed with  $3 \times 2$  mL of cold (-30 °C) hexanes and dried in vacuo (0.6115 g, 75%). <sup>1</sup>H NMR (700 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 7.22 (t, 2 H, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, ArH), 7.12 (d, 4 H,  ${}^{3}J_{\text{HH}} = 7.8$  Hz, ArH), 2.70 [sept, 4 H,  ${}^{3}J_{\text{HH}} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 1.89 (s, 2 H, CCH<sub>2</sub>-AlEt<sub>3</sub>), 1.37 [d, 12 H,  ${}^{3}J_{HH} = 6.8$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 1.34 (t, 9 H,  ${}^{3}J_{\text{HH}} = 8.1$  Hz, AlCH<sub>2</sub>CH<sub>3</sub>), 1.33 (s, 6 H, H<sub>3</sub>CCN), 0.95 [d, 12 H,  ${}^{3}J_{HH} = 6.9$  Hz, CH(CH<sub>3</sub>)<sub>2</sub>], 0.01 (q, 6 H,  ${}^{3}J_{HH} = 8.1$  Hz, AlCH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 3.0$ [-Al(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>], 9.5 (H<sub>3</sub>CCN), 11.4 [Al(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>], 24.3 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.4 [CH(CH<sub>3</sub>)<sub>2</sub>], 28.8 [CH(CH<sub>3</sub>)<sub>2</sub>], 125.3 (ArC), 125.7 (ArC), 128.3 (ArC), 128.4 (ArC), 131.0 (ArC), 131.8 (ArC), 145.8 (NCN), 146.6 (CCH<sub>2</sub>-AlEt<sub>3</sub>). C<sub>36</sub>H<sub>57</sub>AlN<sub>2</sub>: calcd. C, 79.36; H, 10.55; N, 5.14%; found: C, 78.82; H, 10.47; N, 4.99%. Mp (°C): 132 (dec).

Synthesis of MeIPrCHCHCH2·AIMe3 (3): A solution of AlMe3 (2.0 M solution in toluene, 0.193 mL, 0.39 mmol) was gently layered atop of a solution of MeIPr=CH-CH=CH<sub>2</sub> (0.1760 g, 0.3854 mmol) in 1.5 mL of toluene. The mixture was then left undisturbed for 16 h, resulting in the formation of colorless crystals of <sup>Me</sup>IPrCHCHCH<sub>2</sub>·AlMe<sub>3</sub> (3). The supernatant was decanted away, and the remaining crystals were washed with 3 mL of cold (-30 °C) toluene and dried in vacuo (0.1271 g, 62 %). <sup>1</sup>H NMR (700 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.22$  (t, 2 H,  ${}^{3}J_{HH} = 7.7$  Hz, ArH), 7.08 (d, 4 H,  ${}^{3}J_{HH} = 7.8$  Hz, ArH), 6.57 (dt, 1 H,  ${}^{3}J_{HH} = 14.3$ ,  ${}^{3}J_{HH} = 10.7$  Hz, CHCHCH<sub>2</sub>-AlMe<sub>3</sub>), 4.67 (d, 1 H,  ${}^{3}J_{HH} = 14.3$  Hz, CHCHCH<sub>2</sub>-AlMe<sub>3</sub>), 2.79 (d, 2 H,  ${}^{3}J_{HH}$ = 10.7 Hz, CHCHCH<sub>2</sub>-AlMe<sub>3</sub>), 2.60 [sept, 4 H,  ${}^{3}J_{HH}$  = 6.9 Hz,  $CH(CH_3)_2$ ], 1.30 (s, 6 H,  $H_3C$ -CN), 1.29 [d, 12 H,  ${}^3J_{HH}$  = 7.4 Hz,  $CH(CH_3)_2$ ], 1.01 [d, 12 H,  ${}^{3}J_{HH} = 6.9$  Hz,  $CH(CH_3)_2$ ], -0.42 [s, 9 H, -Al(CH<sub>3</sub>)<sub>3</sub>]. <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -6.1$  [-Al(CH<sub>3</sub>)<sub>3</sub>], 8.7 (H<sub>3</sub>CCN), 23.6 [CH(CH<sub>3</sub>)<sub>2</sub>], 24.2 [CH(CH<sub>3</sub>)<sub>2</sub>], 29.1 [CH(CH<sub>3</sub>)<sub>2</sub>], 58.6 (CH-CHCH2-AlMe3), 85.3 (CHCHCH2-AlMe3), 121.4 (ArC), 125.3 (ArC), 127.9 (ArC), 128.4 (ArC), 130.4 (ArC), 131.4 (ArC), (H<sub>3</sub>CCN), 147.5 (NCN), 162.2 (CHCHCH<sub>2</sub>-AlMe<sub>3</sub>). 146.7

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 $C_{35}H_{53}AlN_2:$  calcd. C, 79.50; H, 10.10; N, 5.30%; found: C, 79.39; H, 9.91; N, 5.12%. Mp (°C): 218 (dec).

**Polymerization of Michael-type Monomers (General Procedure):**  $^{Me}$ IPrCH<sub>2</sub>·AlMe<sub>3</sub> (0.025 g, 0.050 mmol) was added to a solution of monomer (10 mmol) in 5 mL of THF. After 1 h of stirring the reaction mixture was quenched with ca. 0.5 mL of ethanol, and the volatiles were removed in vacuo. The resulting solid was dissolved in ca. 5 mL of dichloromethane and precipitated into 100 mL of pentane at –30 °C. The resulting polymer was dried under high vacuum while heated at 50 °C.

**Supporting Information** (see footnote on the first page of this article): NMR spectra of NHO-AlR<sub>3</sub> complexes and AlR<sub>3</sub> starting materials, molecular structure of **2**, full X-ray crystallographic details, and GPC traces of p2VP, pMA, and pDMAA.

## Acknowledgements

This work was supported by the Canadian Foundation for Innovation, the Faculty of Science at the University of Alberta, and the Natural Sciences and Engineering Research Council (NSERC) of Canada (Discovery and Accelerator Supplement grants to E.R.; CREATE fellowship to I.W.). B.R. and E.R. acknowledge funding from DFG IRTG (2022) and NSERC CREATE (CREATE 4639900–2015) program for the Alberta/TU München International Graduate School. I.W. thanks B.R. for hosting him as a researcher at TUM. I.W. thanks *Bruno Luppi* for his assistance with GPC measurements. E.R. is also grateful to the Alexander von Humboldt Foundation for support, and to *Prof. Dr. Manfred Scheer* for his friendship and hospitality during E.R.'s excellent stays in Regensburg.

**Keywords:** N-Heterocyclic olefins; Aluminum; Polymerization; Michael-type monomers; Frustrated Lewis pairs

## References

- a) N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser, R. Boese, *J. Chem. Soc., Chem. Commun.* **1993**, 1136–1137; b) N. Kuhn, H. Bohnen, D. Bläser, R. Boese, *Chem. Ber.* **1994**, *127*, 1405–1407.
- [2] a) M. M. D. Roy, E. Rivard, Acc. Chem. Res. 2017, 50, 2017–2025;
  b) S. M. I. Al-Rafia, A. C. Malcolm, S. K. Liew, M. J. Ferguson, R. McDonald, E. Rivard, Chem. Commun. 2011, 47, 6987–6989; c)
  Y. W. Wang, M. Y. Abraham, R. J. Gilliard Jr., D. R. Sexton, P. Wei, G. H. Robinson, Organometallics 2013, 32, 6639–6642; d) S. M. I. Al-Rafia, M. R. Momeni, M. J. Ferguson, R. McDonald, A. Brown, E. Rivard, Organometallics 2013, 32, 6658–6665; e) R. S. Ghadwal, C. J. Schürmann, D. M. Andrada, G. Frenking, Dalton Trans. 2015, 44, 14359–14367; f) R. S. Ghadwal, Dalton Trans. 2016, 45, 16081–16095; g) W.-H. Lee, Y.-F. Lin, G.-H. Lee, S.-M. Peng, C.-W. Chiu, Dalton Trans. 2016, 45, 5937–5940; h) L. Y. M. Eymann, P. Varava, A. M. Shved, B. F. E. Curchod, Y. Liu, O. M. Planes, A. Sienkiewicz, R. Scopelliti, F. F. Tirani, K. Severin, J. Am. Chem. Soc. 2019, 141, 17112–17116.
- [3] K. Powers, C. Hering-Junghans, R. McDonald, M. J. Ferguson, E. Rivard, *Polyhedron* 2016, 108, 8–14.
- [4] For selected reviews and articles, see: a) S. Naumann, *Chem. Commun.* 2019, 55, 11658–11670; b) R. D. Crocker, T. V. Nguyen, *Chem. Eur. J.* 2016, 22, 2208–2213; c) S. Naumann, K. Mundsinger, L. Cavallo, L. Falivene, *Polym. Chem.* 2017, 8, 5803–5812; d) C. Hering-Junghans, I. C. Watson, M. J. Ferguson, R. McDonald, E. Rivard, *Dalton Trans.* 2017, 46, 7150–7153; e) P. Walther, A. Krauß, S. Naumann, *Angew. Chem. Int. Ed.* 2019, 58, 10737–10741.

- [5] M. McGraw, E. Y.-X. Chen, ACS Catal. 2018, 8, 9877–9887.
- [6] Y.-B. Jia, Y.-B. Wang, W.-M. Ren, T. Xu, J. Wang, X.-B. Lu, *Macromolecules* 2014, 47,1966–1972.
- [7] Y. Zhang, G. M. Miyake, E. Y.-X. Chen, Angew. Chem. Int. Ed. 2010, 49, 10158–10162.
- [8] a) X.-W. Li, J. Su, G. Robinson, *Chem. Commun.* 1996, 2683–2684;
   b) A. D. K. Todd, W. L. McClennan, J. D. Masuda, *RSC Adv.* 2016, 6, 69270–69276.
- [9] For full crystallographic details and copies of the NMR and GPC data for this study, see the Supporting Information.
- [10] a) C. Hering-Junghans, P. Andreiuk, M. J. Ferguson, R. McDonald, E. Rivard, *Angew. Chem. Int. Ed.* **2017**, *56*, 6272–6275; b) M. Lui, C. Merten, M. J. Ferguson, R. McDonald, Y. Xu, E. Rivard, *Inorg. Chem.* **2015**, *54*, 2040–2049; for a review on NHI complexes, see:
  c) T. Ochiai, D. Franz, S. Inoue, *Chem. Soc. Rev.* **2016**, *45*, 6327–6344.
- [11] G. Schnee, A. Bolley, F. Hild, D. Specklin, S. Dagorne, *Catal. Today* 2017, 289, 204–210.
- [12] I. C. Watson, A. Schumann, H. Yu, E. C. Davy, R. McDonald, M. J. Ferguson, C. Hering-Junghans, E. Rivard, *Chem. Eur. J.* 2019, 25, 9678–9690.
- [13] Variable temperature <sup>1</sup>H NMR analysis of 1:1 mixtures of <sup>Me</sup>IPrCH<sub>2</sub>/AlMe<sub>3</sub>, <sup>Me</sup>IPrCH<sub>2</sub>/AlEt<sub>3</sub>, and <sup>Me</sup>IPrCH<sub>2</sub>CHCH<sub>2</sub>/AlMe<sub>3</sub> in [D<sub>8</sub>]toluene were conducted in the temperature range of -60 to +80 °C. None of these Lewis pair adducts (1-3) showed any evidence of separating into their respective free Lewis acid and base. See Figures S18, S19, and S20 (Supporting Information) for the spectra.
- [14] M. Weger, R. K. Grötsch, M. G. Knaus, M. M. Giuman, D. C. Mayer, P. J. Altmann, E. Mossou, B. Dittrich, A. Pöthig, B. Rieger, *Angew. Chem. Int. Ed.* **2019**, 58, 9797–9801.
- [15] a) Z. Zhao, Q. Wang, J. He, Y. Zhang, *Polym. Chem.* 2019, 10, 4328–4335; b) T. Xu, E. Y.-X. Chen, J. Am. Chem. Soc. 2014, 136, 1774–1777.
- [16] Q. Wang, W. Zhao, S. Zhang, J. He, Y. Zhang, E. Y.-X. Chen, ACS Catal. 2018, 8, 3571–3578.
- [17] For the polymerization of DEVP, see: M. Weger, P. Pahl, F. Schmidt, B. S. Soller, P. J. Altmann, A. Pöthig, G. Gemmecker, W. Eisenreich, B. Rieger, *Macromolecules* 2019, 52, 7073–7080 and references cited therein.
- [18] J. He, Y. Zhang, E. Y.-X. Chen, Synlett 2014, 25, 1534–1538.
- [19] K. Takada, K. Fuchise, Y. Chen, T. Satoh, T. Kakuchi, J. Polym. Sci. Part A: Polym. Chem. 2012, 50, 3560–3566.
- [20] a) R. Goseki, T. Ishizone, in: *Encyclopedia of Polymeric Nanomaterials* (Eds.: S. Kobayashi, K. Müllen), Springer, Heidelberg, **2015**, p. 1703; b) J. G. Kennemur, *Macromolecules* **2019**, *52*, 1354–1370; c) A. Rudin, P. Choi, *The Element of Polymer Science & Engineering*, 3rd ed., Academic Press, Waltham, MA, USA, **2013**, p. 380.
- [21] For work on complexes with anionic NHO ligands, see: a) S. M. I. Al-Rafia, M. J. Ferguson, E. Rivard, *Inorg. Chem.* 2011, *50*, 10543–10545; b) R. S. Ghadwal, S. O. Reichmann, F. Engelhardt, D. M. Andrada, G. Frenking, *Chem. Commun.* 2013, *49*, 9440–9442; c) N. R. Paisley, M. W. Lui, R. McDonald, M. J. Ferguson, E. Rivard, *Dalton Trans.* 2016, *45*, 9860–9870; d) C. C. Chong, B. Rao, R. Ganguly, Y. Li, R. Kinjo, *Inorg. Chem.* 2017, *56*, 8608–8614; e) M. M. D. Roy, M. J. Ferguson, R. McDonald, Y. Zhou, E. Rivard, *Chem. Sci.* 2019, *10*, 6476–6481; f) M. K. Sharma, S. Blomeyer, B. Neumann, H.-G. Stammler, M. van Gastel, A. Hinz, R. S. Ghadwal, *Angew. Chem. Int. Ed.* 2019, *58*, 17599–17603; g) E. Hupf, F. Kaiser, P. A. Lummis, M. M. D. Roy, R. McDonald, M. J. Ferguson, F. Kühn, E. Rivard, *Inorg. Chem.* 2020, *59*, 1592–1601; h) M. K. Sharma, B. Neumann, H.-G. Stammler, D. M. Andrada, R. S. Ghadwal, *Chem. Commun.* 2019, *55*, 14669–14672.
- [22] G. M. Sheldrick, Acta Crystallogr., Sect. A 2015, 71, 3-8.
- [23] G. M. Sheldrick, Acta Crystallogr., Sect. C 2015, 71, 3-8.

Received: December 11, 2019 Published Online: ■ Journal of Inorganic and General Chemistry

Zeitschrift für anorganische und allgemeine Chemie



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Trialkylaluminum N-Heterocyclic Olefin (NHO) Adducts as Catalysts for the Polymerization of Michael-Type Monomers

