# Organochromium complexes as catalysts for the carboalumination of unactivated terminal olefins

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The addition of aluminium alkyls to terminal olefins leads to branched organoaluminium compounds which can be converted into functionalised alkanes. This carboalumination reaction is efficiently catalysed by a donor functionalised Cp-chromium(III) complex. The active catalyst is obtained by activation of the chromium(III) dichloride precursor with MAO or with a mixture of trialkylaluminium and *N*,*N*-dimethylanilinium tetrakispentaflourphenylborate. Primary aminoalkenes deactivate the catalyst whereas secondary and tertiary aminoalkenes can also be carboaluminated.

# Introduction

The addition of metal organyls to alkenes or alkynes is an advantageous method for the synthesis of many organic compounds. Such carbometallations are known for a variety of metal organyls and have been studied thoroughly.1 As early as 1928 Ziegler and Bähr reported the carbometalation of olefins using alkaline metal alkyls.<sup>2</sup> In 1952 the same group described the carboalumination of terminal olefins with AlEt<sub>3</sub> at elevated temperature.<sup>3</sup> Since then catalytically controlled carboalumination reactions using e.g. titanium<sup>4</sup> or zirconocene systems<sup>5</sup> have been developed. Chiral zirconocenes enable enantio- and diastereoselective reactions<sup>6,7</sup> In 2005 Molander and Sommers employed donor functionalised cyclopentadienyl Cr-complexes for the synthesis of allenes via carboalumination of alkynes.8 We now report the carboalumination of unactivated, terminal olefins, mediated by chromium(III) half-sandwich complexes, which consist of rigid 8-quinolylcyclopentadienyl ligands that lead to a predefined geometry and increased stability. These are related to chromium complexes developed by Jolly and co-worker.9 and, upon activation with established co-catalysts (e.g. MAO), they show excellent properties in the polymerisation and co-polymerisation of olefins.9,10 Although the catalytically active species has not yet been isolated, all experimental and theoretical investigations are in accordance with an unsaturated cationic chromium(III) alkyl complex.<sup>10e,11</sup> In the presence of additional donors, related complexes have been structurally characterised by Theopold and others.<sup>12</sup> However, certain neutral chromium(III) complexes have also been reported to be active in olefin polymerisation without addition of any cocatalyst.13 In olefin polymerisation the chain transfer from the Crcatalyst to aluminium alkyls is an important chain termination reaction and therefore influences the molecular weight of the polyolefin. If this transfer becomes dominant, a carboalumination reaction results. For our system this is the case if higher  $\alpha$ -olefins are used and stoichiometric amounts of aluminium alkyls are present. The investigations described here were performed with compound 1 (Fig. 1) as catalyst precursor<sup>14</sup> and 1-dodecene as well as aminoalkenes as terminal olefins. Compared to other derivatives with the same ligand backbone, 1 has an increased air stability and solubility in organic solvents. In addition to that, the activated catalyst is stable for several days at room temperature in the absence of air.



Fig. 1 Complex 1 used as catalyst precursor.

# **Results and discussion**

For better comparison with published results<sup>6</sup> 1 mol% of **1**, and 1dodecene as substrate, was used in preparative scale. More detailed kinetic analysis then showed that for the carboalumination of 1-dodecene the catalytic system is able to achieve complete conversion after a few hours only (Table 1, entry 1). Thus, kinetic studies *via* NMR spectroscopy were accomplished using 0.1 mol% of **1**.

### Carboalumination of 1-dodecene

The catalyst precursor **1** was activated with different co-catalysts and various organoaluminium reagents ([Al]-R) were added in stoichiometric amounts (relative to the substrate).

Initially methylalumoxane (MAO) was used as both co-catalyst and [Al]-R reagent. The reaction progress was monitored by the decreasing olefinic <sup>1</sup>H-NMR signals. 1 combined with MAO leads to a nearly complete conversion after 30 h (Table 1, entry 2). A reaction mixture containing AlMe<sub>3</sub> and MAO in a 4 : 1 Alratio yielded over 80% of the methylated product after 30 h (Table 1, entry 4). To further clarify the role of AlMe<sub>3</sub> as methyltransmitter and MAO as the generator of the active species, we

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	Substrate	Methylation-reagent/co-catalyst	t/h	Conversion (%)	Cr : Al	mol% Cr	Al : Substrate
1	Dodecene	MAO/MAO <sup>a</sup>	4	98°	1:200	1	2:1
2	Dodecene	MAO/MAO <sup>a</sup>	30	99 <sup>c</sup>	1:1000	0.1	1:1
3	Dodecene	AlEt <sub>3</sub> /HNMe <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> $[B(C_6F_5)_4]^{-b}$	30	86 <sup>c</sup>	1:1000	0.1	1:1
4	Dodecene	$AlMe_3/MAO^a$ (4 : 1)	30	81 <sup>c</sup>	1:1000	0.1	1:1
5	Dodecene	$AlMe_3/[HNMe_2C_6H_5]^+ [B(C_6F_5)_4]^{-b}$	30	68 <sup>c</sup>	1:1000	0.1	1:1
6	Dodecene	AlMe <sub>3</sub> /—	30	$2^{c}$	1:1000	0.1	1:1
7	Dodecene	AlEt <sub>3</sub> /—	30	1 <sup>c</sup>	1:1000	0.1	1:1
8	$CH_2 = CHCH_2C(CH_3)_2CH_2NH_2$	MAO/MAO <sup>a</sup>	24	$0^d$	1:300	1	3:1
9	$CH_2 = CH(CH_2)_3N(H)CH_2Ph$	MAO/MAO <sup>a</sup>	24	9 <sup><i>d</i>,<i>e</i></sup>	1:300	1	3:1
10	$CH_2 = CH(CH_2)_3N(CH_3)CH_2Ph$	MAO/MAO <sup>a</sup>	24	22 <sup><i>d</i>,<i>e</i></sup>	1:300	1	3:1

 Table 1
 Results of the carboalumination of 1-dodecene and aminoalkenes mediated by 1

<sup>*a*</sup> MAO as 10 wt% solution in toluene. <sup>*b*</sup> Anilinium borate : Cr = 1 : 1. <sup>*c*</sup> NMR analysis. <sup>*d*</sup> GC-MS analysis. <sup>*e*</sup> Isolated yield.

used AlMe<sub>3</sub> together with [HNMe<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> ("anilinium borate") in catalytic amounts. Such anilinium salts are known to generate cationic alkyl complexes from metal dialkyls under elimination of alkane resulting in particularly active catalysts for olefin insertion and polymerisation.<sup>15-17</sup> With 1 and "anilinium borate" in combination with AlMe<sub>3</sub> 70% conversion after 30 h was obtained (Table 1, entry 5). This result is in accordance with a cationic complex as active species. Consequently, when using AlMe<sub>3</sub> alone (without MAO), hardly any reactivity was observed (Table 1, entry 6). Although AlMe<sub>3</sub> alkylates the catalyst precursor, it is not able to abstract an alkyl group from the chromium dialkyl species, which is a precondition for the formation of the cationic active catalyst.

To proof that the carboalumination reaction is indeed catalytically driven, several tests with only MAO as aluminium alkyl source, but without any chromium complex, have been performed. No reaction progress could be observed after one day.

Fig. 2 shows the reaction progress of the carboalumination monitored by NMR spectroscopy. The activity of the catalytic system depends on the activator and on the alkylaluminium reagent. AlEt<sub>3</sub> shows a higher reactivity compared to AlMe<sub>3</sub>. Although the reaction time for a complete conversion varies between 3 h and more than 70 h, the catalyst remains active until complete conversion is achieved.



Fig. 2 Reaction progress of the carboalumination of 1-dodecene with  $AlMe_3$ ,  $AlEt_3$  or MAO respectively, catalysed by 1 and various co-catalysts. The curves correspond to entries 1–6 in Table 1.

The structure of the intermediate organoaluminium species (Scheme 1) is supposed to be a dimeric tris-alkyl aluminium



**Scheme 1** Carboalumination of terminal olefins using different co-catalysts, terminal olefins and organoaluminium compounds.

compound where one or more alkyl groups originate from the applied terminal olefin. This proposed structure is in accordance with the hydrolysis products and with the observations of other carboalumination reactions studied earlier with and without catalysts.<sup>6,18</sup>

The most abundant side products after hydrolysis of the reaction mixture were alkylated dimers of the terminal olefins used. This is not surprising, since the catalyst is known to polymerise olefins. The amount of alkylated dimers, analysed by gas chromatography, is 30-40% when MAO was used, but only 10% for the catalyst activated with AlR<sub>3</sub>/aniliniumborate. The regioselectivity of the carboalumination mediated by 1 was investigated by treating the reaction mixture (conditions Table 1, entry 4) with D<sub>2</sub>O and the resulting product was analysed by  $^{13}$ C DEPT NMR and  $^{2}$ H NMR. The  $^{13}$ C NMR-spectrum showed the signal of the CDH<sub>2</sub> group which is split into a triplet due to coupling to deuterium. No deuterium coupled tertiary carbon signal was observed, which would have been the result of a 2,1-insertion. The  $^{2}$ H NMR-spectrum showed 2,1-insertion product in an amount of about 3%.

The capability of triethylaluminium (AlEt<sub>3</sub>) instead of AlMe<sub>3</sub> or MAO as aluminium alkyl source was also examined. Without any co-catalyst  $1/AlEt_3$ —analogous to  $1/AlMe_3$ —is almost inactive in the carboalumination reaction. By adding [HNMe<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> in catalytic amounts activities result, which are comparable to those achieved with MAO.

#### Carboalumination of aminoalkenes

Aminoalkenes are substrates for the intramolecular hydroamination catalysed by titanocene- or zirconocene-type complexes.<sup>19</sup> Under the conditions used in this work no hydroamination reaction could be observed. Thus, we investigated the carboalumination of aminoalkenes and the tolerance of activated chromium(III)species towards amine groups. A primary, secondary or tertiary amine was used, together with MAO as methylation reagent and co-catalyst, and 1 mol% of the catalyst precursor **1** (see Table 1). Primary amines completely deactivate the catalytic system, while the reaction with a secondary amine shows little conversion (9% isolated product after 24 h). With tertiary amines moderate conversion was observed (22% isolated product after 24 h).

## Conclusion

The potential of organochromium complexes like **1** as efficient catalyst precursors for the carboalumination of unactivated olefins with AlMe<sub>3</sub> or AlEt<sub>3</sub> respectively was demonstrated. For the formation of the active catalyst, a suitable activator like MAO or the aniliuniumborate [HNMe<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>3</sub>)<sub>4</sub>]<sup>-</sup> is indispensable. The high catalytic activity outranges those of established zirconocene systems, which makes this chromium system attractive for non-enantioselective functionalisation of olefins.

## Experimental

#### General procedure for carboalumination of olefins

In a schlenk tube  $10^{-4}$  equivalents (0.1 mol%) of **1** are dissolved in dry toluene. 1 equivalent of aluminium alkyl and an activator ( $10^{-4}$  equivalents if anilinium borate is used) is added followed by addition of the olefin. After stirring at room temperature the mixture is quenched with ice water/HCl, neutralised with NaOH and extracted with diethyl ether. The solvent is removed under vacuum and the isolated product is analysed by GC-MS and NMR-spectroscopy.

#### Procedures for entries in Table 1

*Entry 1*: 10.0 mg (23.30 µmol) of **1** was dissolved in 1 ml of dry  $C_6D_6$ . 4.66 mmol of aluminium (MAO, 10 wt% in toluene, supplier: Sigma-Aldrich) was added followed by addition of 0.39 g of 1-dodecene (2.33 mmol). Then 0.5 ml of the reaction mixture was transferred into a NMR-tube and the reaction progress was followed by <sup>1</sup>H-NMR spectroscopy.

*Entries 2, 4, 6 and 7*: 2.0 mg ( $4.66 \mu$ mol) of 1, 1000 equivalents ( $4.66 \mu$ mol) of aluminium (AlEt<sub>3</sub>, AlMe<sub>3</sub> and/or MAO) and 0,78 g of 1-dodecene ( $4.66 \mu$ mol) were used.

*Entries 3 and 5*: The procedure follows the procedure for entries 2, 4, 6 and 7. After adding the aluminium compound, 3.73 mg  $(4.66 \,\mu\text{mol})$  [HNMe<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup> was added.

*Entries* 8–10: 10.00 mg (23.30  $\mu$ mol) of **1** was dissolved in 2 ml of dry toluene. A total of 300 equivalents (6.99 mmol) of aluminium (MAO) was added followed by addition of 0.23 mmol of aminoalkene. The reaction mixture was stirred at room temperature overnight and quenched with ice–water/HCl. The crude product was extracted with diethyl ether, purified by column chromatography and analysed by GC-MS.

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#### Notes and references

- (a) A. G. Fallis and P. Forgione, *Tetrahedron*, 2001, **57**, 5899; (b) J. F. Normant and A. Alexakis, *Synthesis*, 1981, 841; (c) W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 38; (d) E. Negishi, *Pure Appl. Chem.*, 1981, **53**, 2333; (e) P. Knochel, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Able and F. G. A. Stone, G. Wilkinson; Pergamon: Oxford, 1995, **11**, 159; (f) P. Knochel, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming; Pergamon: Oxford, 1991, **4**, 865; (g) Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207; (h) E. Negishi and D. Y. Kondakov, *Chem. Rev.*, 1996, **96**, 417; (i) I. Marek, J. F. Normant, in *Carbometallation Reactions in Metal Catalyzed Cross-Coupling Reactions*, ed. F. Diederich and P. Stang, Wiley VCH, New York, 1998, 271.
- 2 K. Ziegler and K. Bähr, Chem. Ber., 1928, 61B, 253.
- 3 K. Ziegler, H. G. Gellert, H. Kühlhorn, H. Martin, K. Meyer, K. Nagel, H. Sauer and K. Zosel, *Angew. Chem.*, 1952, **64**, 323.
- 4 (a) E. Negishi, M. D. Jensen, D. Y. Kondakov and S. Wang, J. Am. Chem. Soc., 1994, 116, 8404; (b) D. B. Millward, A. P. Cole and R. M. Waymouth, Organometallics, 2000, 19, 1870.
- 5 K. H. Shaughnessy and R. M. Waymouth, J. Am. Chem. Soc., 1995, 117, 5873.
- 6 (a) E. Negishi and D. Y. Kondakov, J. Am. Chem. Soc., 1995, 117, 10771; (b) E. Negishi and D. Y. Kondakov, Chem. Soc. Rev., 1996, 25, 417.
- 7 (a) K. H. Shaughnessy and R. M. Waymouth, Organometallics, 1998, 17, 5728; (b) B. H. Lipshutz, T. Butler and A. Lower, J. Am. Chem. Soc., 2006, 128, 15396; (c) R. A. Petros and J. R. Norton, Organometallics, 2004, 23, 5105.
- 8 G. A. Molander and E. M. Sommers, Tetrahedron Lett., 2005, 46, 2345.
- 9 R. Emrich, O. Heinemann, P. W. Jolly, C. Krüger and G. P. J. Verhovnik, Organometallics, 1997, 16, 1511.
- 10 (a) M. Enders, P. Fernández, G. Ludwig and H. Pritzkow, Organometallics, 2001, 20, 5005; (b) M. Enders, J. Hack, G. Ludwig, S. Mihan, U. Rief, R. Rudolph, U. Handrich, P. Lange, D. Lilge, M. Schneider and G. Schweier, US Pat., 6,919,412 B1, 1999; (c) S. Mihan, D. Lilge, G. Schweier, M. Enders, Eur. Pat., 1204685 B1, 1999; (d) S. Derlin and W. Kaminsky, Macromolecules, 2008, 41, 6280; (e) M. Enders, Macromol. Symp., 2006, 236, 38.
- 11 V. R. Jensen, K. Angermund and P. W. Jolly, Organometallics, 2000, 19, 403.
- 12 (a) B. J. Thomas and K. H. Theopold, J. Am. Chem. Soc., 1988, 110, 5902; (b) B. J. Thomas, S. K. Noh, G. K. Schulte, S. C. Sendlinger and K. H. Theopold, J. Am. Chem. Soc., 1991, 113, 893; (c) K. H. Theopold, Eur. J. Inorg. Chem., 1998, 15; (d) J. S. Rogers and G. C. Bazan, Chem. Commun., 2000, 1209; (e) D. W. Norman, R. McDonald and J. M. Stryker, Organometallics, 2005, 24, 4461.
- 13 (a) G. Mani and F. P. Gabbai, Angew. Chem., Int. Ed., 2004, 43, 2263; (b) R. A. Heintz, S. Leelasubcharoen, L. M. Liable-Sands, A. L. Rheingold and K. H. Theopold, Organometallics, 1998, 17, 5477.
- 14 P. Fernández, H. Pritzkow, J. J. Carbo, P. Hofmann and M. Enders, Organometallics, 2007, 26, 4402.
- 15 M. Bochmann and L. M. Wilson, J. Chem. Soc., Chem. Commun., 1986, 1610.
- 16 R. Taube and L. Krukowka, J. Organomet. Chem., 1988, 347, C9.
- 17 H. W. Turner, Chem. Abstr., 1989, 110, 58290a.
- 18 In hydroalumination reactions with alkynes the assignment of the organoaluminium compound by analysis of the hydrolysis product is not always possible. See: W. Uhl, *Coord. Chem. Rev.*, 2008, 252, 1540.
- 19 (a) C. Müller, C. Loos, N. Schulenberg and S. Doye, *Eur. J. Org. Chem.*, 2006, 2499; (b) P. D. Knight, I. Munslow, P. N O'Shaughnessy and P. Scott, *Chem. Commun.*, 2004, 894; (c) D. V. Gribkov and K. C. Hultzsch, *Angew. Chem., Int. Ed.*, 2004, **43**, 5542.