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New Functionalized Vinyl Monomers by Ethylene-(Functionalized)-Norbornene Hetero-Trimerization Catalyzed by Cobalt(II)-(Imino)pyridine Complexes

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Abstract: On activation by MAO the (imino)pyridine cobalt(II) complex $CoCl_2N_2^{Ph/i\text{-}Pr_2}$ catalyzes the enchainment of one norbornene (NB) molecule with two ethylene molecules to give *exo*-2,*exo*-3-ethylvinylnorbornane with high activity and complete diastereoselectivity. Turnover frequencies [TOF, mol NB (mol Co × h)$^{-1}$] as high as 270,000 have been obtained. The 2E-1NB hetero-trimerization reaction has been also accomplished with NBs bearing polar substituents such as norbornenemethanol and norbornenecarboxylic acid provided that the substrate is protected with triisobutylaluminum and the less sterically demanding complex $CoCl_2N_2^{Ph/Me_2}$ is used as catalyst precursor. A mechanism for the hetero-trimerization reactions is proposed on the basis of experimental evidence.

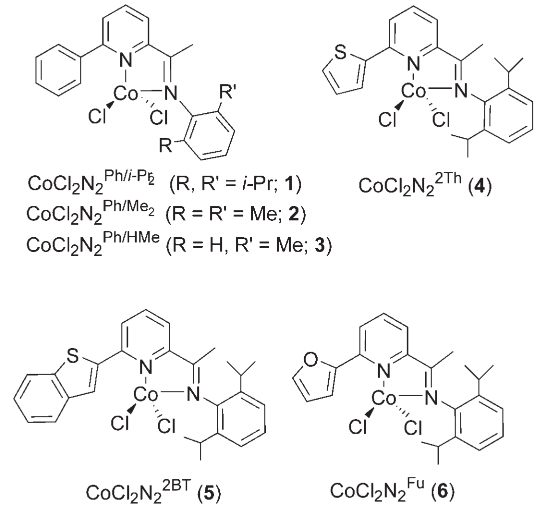
Keywords: cobalt catalysis; co-oligomerization; ethylene-norbornene; (imino)pyridine ligands; vinyl monomers

Introduction

We have recently reported that tetrahedral Co(II) dichloride complexes supported by 6-organyl-2-(imino)pyridine ligands (Figure 1) generate, on activation by methylaluminoxane (MAO), effective catalyst precursors for the oligomerization of ethylene (E)[1,2] and higher α-olefins.[3] A crucial role in determining both the catalytic activity and the selectivity is apparently played by the substituent on the 6-position of the pyridine ring. Among the various precursors scrutinized, $CoCl_2N_2^{Ph/i\text{-}Pr_2}$ (**1**), bearing a 6-phenyl substituent and 2,6-*i*-Pr groups on the imine aryl ring (Figure 1), has been found to generate a very active catalyst for the dimerization of E and propene.[3]

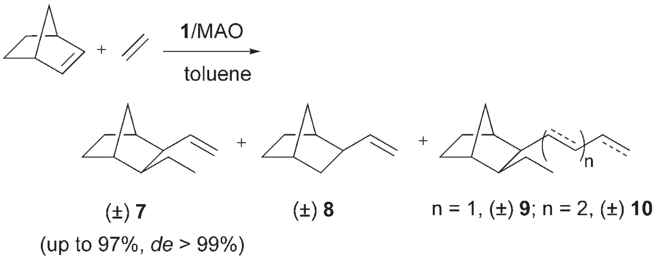
In a recent communication, we have also shown that **1**/MAO fails in catalyzing the polymerization/oligomerization of cyclic olefins such as norbornene (NB), whereas, it is very active for the stereoselective ethyl-vinylation of the latter substrate on feeding the reactor with a mixture of E and NB (Scheme 1).[4]

Since vinyl monomers are attractive building blocks for the preparation of fine chemicals[5] and macromolecular materials,[6] we decided to carry out an in-depth study of the ethyl-vinylation of NB (2E-1NB hetero-trimerization) catalyzed by **1**/MAO as well as explore the applicability of this reaction to norbornenes bearing hydroxy and carboxylic acid groups.



$CoCl_2N_2^{Ph/i\text{-}Pr_2}$ (R, R' = *i*-Pr; **1**)
$CoCl_2N_2^{Ph/Me_2}$ (R = R' = Me; **2**)
$CoCl_2N_2^{Ph/HMe}$ (R = H, R' = Me; **3**)
$CoCl_2N_2^{2Th}$ (**4**)
$CoCl_2N_2^{2BT}$ (**5**)
$CoCl_2N_2^{Fu}$ (**6**)

Figure 1. $CoCl_2$ (imino)pyridine pre-catalysts for olefin oligomerization.



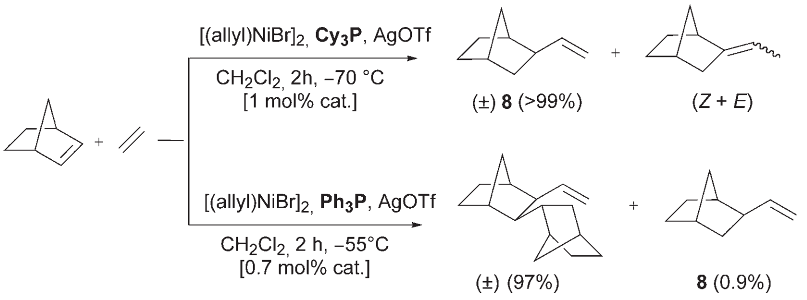
Scheme 1. **1**/MAO catalyzed 2E-1NB hetero-trimerization.

Indeed, such compounds are of great industrial relevance as polymerizable polar vinyl monomers or dissolution rate modifiers for chemically amplified photoresistors.[7]

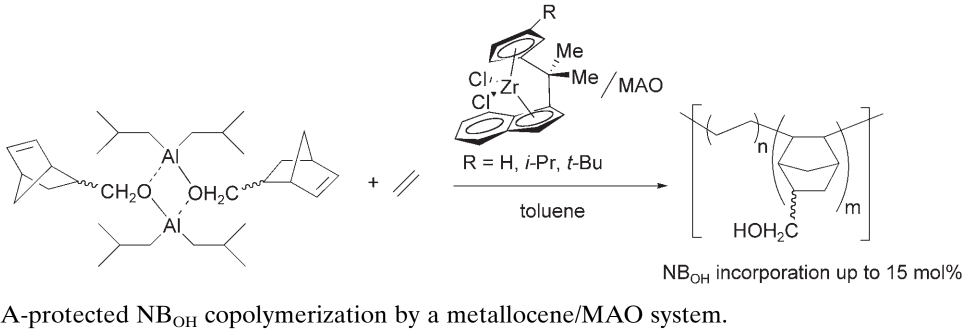
Current methods for the synthesis of vinylnorbornanes involve the hydrovinylation of NB by nickel-catalyzed 1E-1NB coupling.[8] One of the very first examples of this reaction was reported by Wilke who accomplished the highly stereoselective E/NB hetero-dimerization using π-allylnickel catalysts stabilized by optically pure phosphine ligands.[9] More recently, RajanBabu reported an effective way of tuning the selectivity of the 1E-1NB coupling by varying the phosphine that reacts with the π-allylnickel precursor (Scheme 2).[10]

A much more challenging task is the catalytic synthesis of vinylnorbornanes bearing polar groups (hydroxy or carboxylic acid, for instance) that are generally incompatible with oxophilic catalysts as well as the most common activators of metal complexes.[11] However, some pioneering work on the direct copolymerization of α-olefins with monomers containing polar functional groups using either metallocene-type catalysts[12] or Ni/Pd systems bearing bulky diimine ligands,[13] have been recently reported. As a matter of fact, the catalytic system **1**/MAO was found to be totally inactive for the vinylation of 5-norbornene-2-methanol (NB_{OH}) and 5-norbornene-2-carboxylic acid (NB_{COOH}) following the protocol illustrated in Scheme 1. In the course of the research aimed at designing suitable catalysts for the latter reaction, we met some illuminating examples of copolymerization of ethylene with polar olefins successfully accomplished by pre-treating the polar monomers with aluminum alkyls.[14,15] The example that mostly attracted our attention was reported by Fink and co-workers who achieved the copolymerazion of ethylene with either NB_{OH} (Scheme 3) or NB_{COOH} by zirconocene/MAO catalysis upon "protection" of the polar groups with triisobutylaluminum (TIBA).[15] The sterical and chemical protection of the polar functionalities by TIBA is apparently sufficient to prevent the poisoning of the catalyst.[15,16]

In this paper, we provide a full account of the 2E-1NB hetero-trimerization catalyzed by **1**/MAO and report on the use of the 6-organyl-2-(imino)pyridine Co(II) complexes **4–6** in Figure 1 as catalyst precursors for the same reaction. Also, for the first time it is demonstrated that the TIBA-protected norbornenes NB_{OH} and NB_{COOH} can be effectively and diastereose-



Scheme 2. Phosphine ligand dependance in the NB hydrovinylation.



Scheme 3. E/TIBA-protected NB_{OH} copolymerization by a metallocene/MAO system.

lectively hetero-trimerized with E to give new polymerizable vinylnorbornanes containing polar functionalities.

Results and Discussion

2E-1NB Hetero-Trimerization

As shown in Scheme 1, the enchainment of one NB molecule with two E molecules to give the *exo*-2,*exo*-3-ethyl-vinylnorbornane **7** can be achieved with high activity and complete diastereoselectivity by reacting the two monomers in the presence of a catalytic amount of **1** activated by an excess of MAO in toluene. Table 1 reports the results obtained with two procedures differing from each other for the reagent addition sequence (see the Supporting Information). In procedure **A**, the pre-catalyst, the activator and NB were introduced into the reactor prior to pressurization with E, while in procedure **B**, the pre-catalyst was added after all the other reagents were already mixed. It should be pointed out that the two procedures used did not show any major effect either on the activity or on selectivity of the hetero-oligomerization process (entries 16 and 17). On the other hand, procedure **B** was used to evaluate the effective ethylene consumption throughout the catalysis (*vide infra*).

The **1**/MAO system led to the production of **7** with chemoselectivities in the range from 87.4 to 96.8%, complete diastereoselectivity in the *exo* disubstituted compound (*de* > 99%) and TOFs as high as 270,000 mol of NB converted (mol Co × h)$^{-1}$ (entry 18). Overall, the 3E-1NB adduct **9** was produced in rather modest yields (< 1.3%), while the 4E-1NB adduct **10** was never detected.

Unequivocal identification of **7** as a single diastereomer in its racemic form was obtained by GC analysis, NMR spectroscopy, including a 2D phase-sensitive NOESY, showing positive cross-peaks as depicted in Figure 2 (see the Supporting Information). Most importantly, the ^{13}C NMR spectrum of the compound

Table 1. Diastereoselective alkyl-vinylation of NB catalyzed by (imino)pyridine Co(II) catalysts.[a]

Entry	Method	Pre-cat./ µmol	Al [µmol]	T [°C]	Time [min]	P [bar]	[E][b]	[NB]	χ_{NB}[c]	NB Conv.[d] [%]	TON[e]	TOF[f]	Yield **7** [%]	Yield **8** [%]	Yield **9** [%]	Yield **10** [%]
1	**A**	**1**/12	7200	−20	30	4	1.15	0.18	13.53	17.9	269	537	96.8	2.1	1.1	
2	**A**	**1**/12	7200	0	20	8	1.58	0.18	10.20	100	1500	4500	96.4	2.8	0.8	
3	**A**	**1**/12	7200	0	20	4	0.79	0.18	18.52	93.7	1406	4217	96.5	2.2	1.3	
4	**A**	**1**/12	7200	0	30	4	0.79	0.18	18.52	100	1500	3000	96.1	3.0	0.9	
5	**A**[g]	**1**/12	7200	0	30	4	0.79	0.18	18.52	100	1500	3000	94.9	4.4	0.7	
6	**A**	**1**/12	7200	10	20	4	0.67	0.18	21.17	83.2	1248	3744	96.0	3.2	0.7	
7	**A**	**6**/12	7200	10	20	4	0.67	0.18	21.17	78.5	1178	3533	94.8	4.3	0.9	
8	**A**	**4**/12	7200	10	10	4	0.67	0.18	21.17	98.3	1475	8847	82.1	3.3	8.7	5.9
9	**A**	**5**/12	7200	10	10	4	0.67	0.18	21.17	91.5	1373	8235	79.9	2.1	12.1	5.9
10	**A**	**1**/12	7200	10	30	4	0.67	0.18	21.17	100	1500	3000	95.9	3.1	1.0	
11	**A**	**1**/12	7200	10	30	4	0.67	0.35	34.31	100	2917	5833	93.7	5.6	0.7	
12	**A**	**1**/12	7200	30	3	4	0.50	0.18	26.63	67.1	1007	20130	90.3	8.8	0.8	
13	**A**	**1**/12	7200	30	30	4	0.50	0.18	26.63	100	1500	3000	90.5	8.8	0.8	
14	**A**	**1**/12	7200	30	30	1	0.12	0.18	59.21	57.6	864	1728	87.4	11.3	1.3	
15	**A**	**1**/12	7200	50	30	4	0.38	0.18	32.08	65.6	984	1968	88.9	9.7	1.3	
16	**A**	**1**/1.2	3600	0	20	8	1.58	0.35	18.10	100	29167	87500	92.4	6.5	1.0	
17	**B**	**1**/1.2	3600	0	20	8	1.58	0.35	18.10	100	29167	87500	96.5	2.9	0.5	
18	**B**	**1**/1.2	3600	0	2	4	0.79	0.18	18.52	59.9	8985	269550	96.4	3.0	0.6	
19	**B**	**1**/1.2	3600	0	10	4	0.79	0.18	18.52	100	15000	90000	96.6	2.7	0.7	
20	**B**[g]	**1**/1.2	3600	0	20	8	1.58	0.35	18.10	100	29167	87500	95.8	3.9	0.3	
21	**B**	**1**/1.2	3600	0	30	3.55	0.70	0.18	20.39	100	15000	30000	96.0	3.4	0.6	
22	**B**	**1**/1.2	3600	20	30	4.90	0.70	0.18	20.39	52.4	7857	15714	92.9	6.8	0.2	
23	**B**	**1**/1.2	3600	40	30	6.50	0.70	0.18	20.39	21.0	3146	6291	92.3	7.0	0.7	

[a] *Reaction conditions:* co-catalyst, MAO; toluene, 100 mL.

[b] Calculated according to Henry's law: $C_E = P_E \times H_0 \exp[\Delta H_L \times (RT)^{-1}]$, C_E (mol L^{-1}), P_E (atm), $H_0 = 0.00175$ mol L^{-1} atm^{-1}, ΔH_L = *enthalpy of solvatation of E in toluene* = 2569 cal mol^{-1}, $R = 1.989$ cal mol^{-1} K^{-1}.

[c] $\{[NB]/([NB]+[E])\} \times 100$.

[d] Determined by GC.

[e] Calculated as mol of NB (mol of Co)$^{-1}$.

[f] Calculated as mol of NB (mol of Co × h)$^{-1}$.

[g] Co-catalyst, MMAO; *n*-pentane, 100 mL.

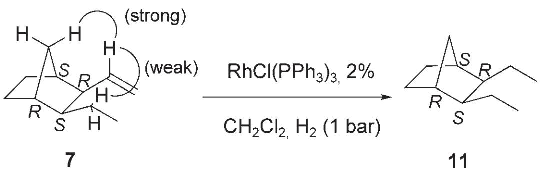


Figure 2. NOE effect on **7** and catalytic hydrogenation to **11**.

Table 2. $^{13}C\{^1H\}$ NMR parameters for **11** (100.62 MHz, 23 °C, $CDCl_3$).

Nucleus	δ (ppm)
CH_3^{Et}	14.28
CH_2^{Et}	22.25
-CH_2-CH_2-	30.02
-CH-CH_2-CH-	32.60
-CH-CH_2-CH-	40.27
-CH-Et	46.78

exo,*exo*-2,3-diethyl-norbornane **11**, obtained by hydrogenation of **7**, showed two chemically and magnetically equivalent ethyl groups (Figure 2, Table 2, see also the Supporting Information).

Low temperatures and low NB molar fractions were found to favor the formation of **7** while high temperatures and high NB molar fractions increased the amount of the hydrovinylation product **8** (entries 11–15, 22 and 23). Although the higher the initial NB concentration the higher was the yield of the plain hydrovinylated compound **8**, short time experiments demonstrate that this side-product is regularly produced throughout all the process (entry 12 *vs.* 13 and 18 *vs.* 19). The effect of the temperature on the catalysis outcome has been also evaluated at equal NB molar fractions (entries 21–23). The hetero-trimerization process was apparently best accomplished by using a very low catalyst loading at high E concentrations and low temperatures (entries 17–19). No major effect on catalyst activity and/or selectivity was observed for reactions conducted in *n*-pentane using modified aluminoxane (MMAO) as activator (entries 4 *vs.* 5 and 17 *vs.* 20).

Figure 3 shows typical curves of E consumption (mL sec^{-1}) with time (sec), as acquired with a mass-flow controller calibrated on the E feed, during selected reactions of E oligomerization (**A**) and E/NB co-oligomerization (**B** and **C**) catalyzed by **1**/MAO. The curve reported in Figure 3 **A** shows the oligomerization starting with no induction period but featured by a gradual decrease in catalyst activity with time. The latter effect is likely due to the early production of butenes (92% selectivity in 1-butene) that can compete with E for the interaction with the cobalt center as well as contribute to reduce the E partial pressure in the reactor. It is noteworthy to recall that the latter is connected to an ethylene reservoir which maintains a constant pressure throughout the catalytic runs.

Notably, the presence of NB in the feed strongly reduced the production of butenes (Figure 3 B; entry 4), leading to a low and constant E consumption up to very low NB molar fractions. A rapid enhancement in the E consumption, simultaneously accompanied by the production of butenes, was observed after *ca.* 15 min, which highlights the remarkable lifetime of the present catalytic system. Indeed, almost complete conversion of NB occurred in 20 min (entry 3).

Figure 3 C reports the E consumption profile for an E/NB co-oligomerization experiment carried out with procedure **B** for 120 sec that gave a final NB conversion of 59.9% (entry 18). Integration of the amount of E consumed *vs.* time provided the overall volume of E transformed in the process with an approximate accuracy of ±1% (see the Supporting Information). Under these conditions, more than 80 mol% of E was consumed in the vinylation of NB, while less than 20 mol% was converted into butenes.

In addition to **1**, other 6-organyl-2-(imino)pyridine Co(II) complexes have been scrutinized as catalyst precursors for the hetero-trimerization reaction (Figure 1). Under comparable conditions (entry 6 *vs.* 7), the 6-furanyl complex **6** was slightly less active and selective. For this reason, it was not investigated further. The 6-thienyl complexes **4** and **5** were more

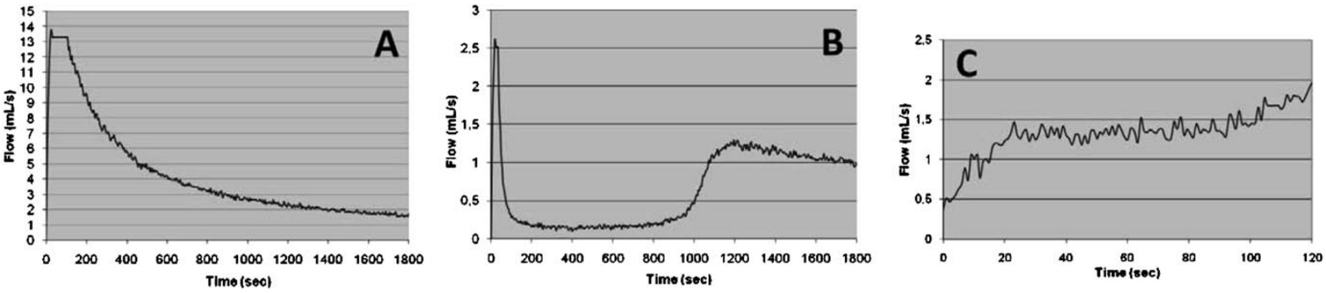
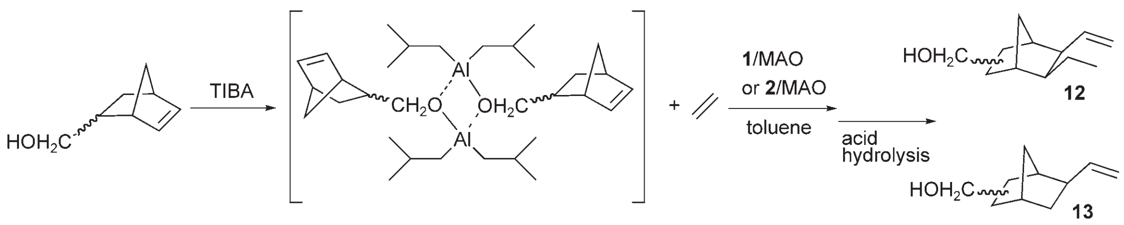


Figure 3. A) E consumption in E oligomerization (**1**, 12 μmol; E, 4 bar; toluene, 100 mL; MAO, 600 equiv; 30 min; 25 °C); **B**) E/NB co-oligomerization (Table 1, entry 4); **C**) E/NB co-oligomerization (Table 1, entry 18).



Scheme 4. E/TIBA-protected NB_{OH} Co-catalyzed hetero-trimerization.

efficient than **1** for the NB conversion into the vinylated derivatives **7–10** but significantly less selective for the 2E-1NB hetero-trimerization (entries 6, 8 *vs.* 9), which is consistent with the greater ability of the 6-thienyl complexes to oligomerize ethylene to α-olefins higher than 1-butene.[2a] Just the presence of a large amount of α-olefins higher than butenes in the reactor made the recovery and purification of the vinylated products obtained with **4** and **5** difficult to achieve. Conversely, the reactions catalyzed by **1** and **6**, yielding only butenes as homo-oligomerization by-product, allowed for an easy product recovery.

2E-1NB Hetero-Trimerization of NBs Containing Polar Functionalities

Having demonstrated the effectiveness of the system **1**/MAO to catalyze the 2E-1NB hetero-trimerization, we have investigated the feasibility of this reaction protocol with norbornenes bearing polar substituents such as NB_{OH} and NB_{COOH}. In fact, vinylnorbornanes bearing such groups are of great industrial relevance.[17] Under the conditions successfully used with the plain NB, no reaction occurred, which we ascribe to fast poisoning of the catalytic system. Indeed, the hydroxy and carboxylic acid groups react with MAO and may compete with the monomer for coordination to the cobalt center. This issue has been previously experienced in the ethylene copolymerization with polar monomers, including substituted NBs, by early and late transition metal catalysts and successfully overcome by a preliminary treatment of the polar functionalities on the comonomer with aluminum alkyls such as TIBA.[15,16] Therefore, we decided to follow this route, selecting TIBA as protecting agent for the polar groups.

Scheme 4 shows the way TIBA is believed to interact with NB_{OH} as well as the following vinylation reactions catalyzed by either **1**/MAO or $CoCl_2N_2^{Ph/Me_2}$ (**2**)/MAO. Table 3 reports the results of the 2E-1NB_{OH} hetero-trimerization reactions assisted by the catalytic precursors **1** and **2** (see the Supporting Information). These complexes differ from each other only in the

Table 3. Diastereoselective alkyl-vinylation of NB_{OH} catalyzed by **1** and **2**.[a]

Entry	Pre-cat.	T [°C]	Time [min]	P [bar]	[E][b]	[NB_{OH}]	χ_{NBOH}[c]	NB_{OH} Conv.[d] [%]	TON[e]	TOF[f]	Yield **12** [%]	Yield **13** [%]
1	**1**	0	30	4	0.79	0.08	9.18	<1	7	13	n.d.	n.d.
2	**1**	30	30	8	0.99	0.04	3.88	9.4	31	63	78.8	21.2
3	**1**	30	30	4	0.50	0.04	7.46	5.8	19	39	76.4	23.6
4	**1**	30	30	4	0.50	0.08	13.89	3.3	22	44	74.7	25.3
5	**1**	50	30	4	0.38	0.04	9.50	3.9	13	26	66.3	33.7
6	**2**	10	30	4	0.67	0.04	5.63	27.6	92	184	94.1	5.9
7	**2**	30	60	8	0.99	0.04	3.88	100	333	333	93.3	6.7
8	**2**	30	30	4	0.50	0.04	7.46	61.3	204	409	92.4	7.6
9	**2**	30	90	4	0.50	0.04	7.46	99.7	332	222	92.1	7.9
10	**2**	30	30	4	0.50	0.08	13.89	41.2	275	549	88.7	11.3

[a] *Reaction conditions:* pre-catalyst, 12 μmol; MAO equiv., 600; NB_{OH} pre-reacted with TIBA at a 1:1.1 molar ratio; toluene, 100 mL.

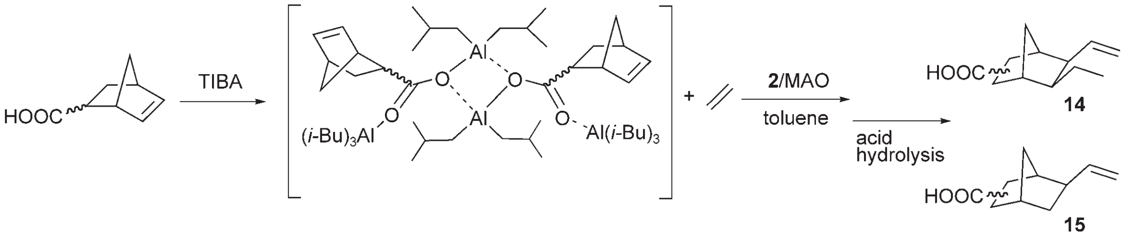
[b] Calculated according to Henry's law: $C_E = P_E \times H_0 \exp[\Delta H_L \times (RT)^{-1}]$, C_E (mol L^{-1}), P_E (atm), $H_0 = 0.00175$ mol L^{-1} atm^{-1}, ΔH_L = *enthalpy of solvatation of E in toluene* = 2569 cal mol^{-1}, $R = 1.989$ cal mol^{-1} K^{-1}.

[c] $\{[NB_{OH}]/([NB_{OH}]+[E])\} \times 100$.

[d] Determined by GC.

[e] Calculated as mol of NB_{OH} (mol of Co)$^{-1}$.

[f] Calculated as mol of NB_{OH} (mol of Co × h)$^{-1}$.



Scheme 5. E/TIBA-protected NB_{COOH} Co-catalyzed hetero-trimerization.

size of the 2,6-alkyl substituents at the imino-aryl ring, which has a remarkable effect on the catalytic activity, however (*vide infra*).[18]

NB_{OH} was pre-reacted with a slight excess of TIBA (1.1 equiv.) in toluene to ensure the complete protection of the hydroxy groups. According to previous studies, this reaction would produce mainly alkoxyaluminum dimers, although the formation of tetramers cannot be excluded.[15] Independent experiments of E oligomerization with both **1**/MAO and **2**/MAO were carried out in the presence of free TIBA to evaluate the compatibility of the two activators. Neither the activity nor the selectivity in the α-olefins changed as compared to the analogous reactions without TIBA.

The TOFs of NB_{OH} conversion into *exo*-5,*exo*-6-(ethyl-vinyl)-norbornanyl-2-methanol (**12**) were generally much smaller than those observed for NB, which seems to be due essentially to steric effects as the protection of the hydroxy groups by TIBA generates a sterically demanding co-monomer (Scheme 4). As a matter of fact, the less sterically congested system **2**/MAO proved to be much more active than **1**/MAO (Table 3, entries 4 *vs.* 10 and 3 *vs.* 8). In other words, the interaction between the metal center in **1** and TIBA-protected co-monomer would be sterically disfavored. On the other hand, it is not possible to get rid of the 2,6-alkyl substitution as just the presence of alkyl groups in these positions allows the corresponding 6-organyl-2-(imino)pyridine cobalt complexes to generate active catalysts for olefin oligomerization/polymerization. As reported and commented in a number of publications,[2b,19] the presence of 2,6-groups on the imino-aryl ring of either (imino)pyridine or bis(imino)pyridine ligands locks this aryl in a position orthogonal to the N–N plane, thus retarding the chain-transfer rate. To prove experimentally the importance of the 2,6-substitution, the *o*-tolyl complex $CoCl_2N_2^{Ph/HMe}$ (**3**) (Figure 1) was synthesized and tested as catalyst precursor for both 2E-1NB and 2E-$1NB_{OH}$ hetero-trimerization. As expected, complex **3** did not generate an active catalyst for either reaction upon activation with MAO.

Besides showing higher activity than **1**, complex **2** was more chemoselective leading to the formation of the ethyl-vinylated product **12** in up to 94.1% yield (Table 3, entry 6), while a maximum yield of 78.8% was obtained with **1**/MAO (Table 3, entry 2). Noteworthy, since NB_{OH} was purchased as a mixture of *exo-endo* diastereoisomers,[20] **12** was produced as a mixture of *exo* and *endo* forms with respect to the -CH_2OH substituent at the norbornane backbone (four diastereoisomers, see the Supporting Information). In agreement with previous papers describing the vinyl polymerization of *exo*/*endo* functionalized NBs,[21] the hetero-trimerization rate of our *endo* isomer was slower than that of the *exo* isomer.[22] The purification of **12** from **13** was conveniently achieved by evaporation of all volatiles under reduced pressure (*vide infra*).

Changing the substrate from NB_{OH} to NB_{COOH} required us to modify the experimental conditions to achieve an appreciable production of the vinylation and ethyl-vinylation compounds. In particular, the amount of TIBA had to be doubled as the protection of NB_{COOH} requires at least two equivalents of TIBA to form a reactive species. Scheme 5 illustrates a possible structure for the TIBA-NB_{COOH} adduct[15b] as well as the products obtained using **2**/MAO.

Table 4 illustrates the catalytic results obtained (see the Supporting Information). Compared to NB_{OH}, the conversion of NB_{COOH} was lower (entry 8 in Table 2 *vs.* entry 6 in Table 3), while the chemoselectivity in the desired product **14** was comparable (around 90%).[23] Like the reactions involving NB_{OH} and NB, the formation of the 2E-$1NB_{COOH}$ adduct was higher at low temperature and/or at low NB_{COOH} molar fractions (Table 4, entries 1 and 2). Under the present reaction conditions, however, the catalyst underwent deactivation within 1 h as shown by the corresponding conversions (entries 3–5). All our attempts to isolate compound **14** from the side product **15** by either fractional distillation or flash chromatography, were unsuccessful. The esterification (EtOH/*p*-toluenesulfonic acid – PTSA) of the crude acid mixture gave **16** and **17** which were easily separated by chromatography (Scheme 6). The $^{13}C\{^1H\}$ NMR spectra of **16** was consistent with the formation of both *exo* and *endo* forms with respect to the -COOEt substituent at the norbornane backbone (see the Supporting Information).

Table 4. Diastereoselective alkyl-vinylation of NB_{COOH} catalyzed by **2**.[a]

Entry	T [°C]	Time [min]	P [bar]	[E][b]	[NB_{COOH}]	χ_{NBCOOH}[c]	NB_{COOH} Conv.[d] [%]	TON[e]	TOF[f]	Yield **14** [%]	Yield **15** [%]
1	10	30	4	0.67	0.02	2.90	21.3	36	71	92.2	7.8
2	30	60	8	0.99	0.02	1.98	63.8	120	120	91.8	8.2
3	30	30	4	0.50	0.02	3.88	49.2	82	164	88.5	11.5
4	30	60	4	0.50	0.02	3.88	67.9	113	113	88.9	11.1
5	30	90	4	0.50	0.02	3.88	68.2	110	74	88.3	11.7
6	30	30	4	0.50	0.04	7.46	21.1	70	141	85.3	14.7

[a] *Reaction conditions:* pre-catalyst, 12 μmol; MAO equiv., 600; NB_{COOH}, 2 mmol (pre-reacted with TIBA at a 1:2.1 molar ratio); toluene, 100 mL.

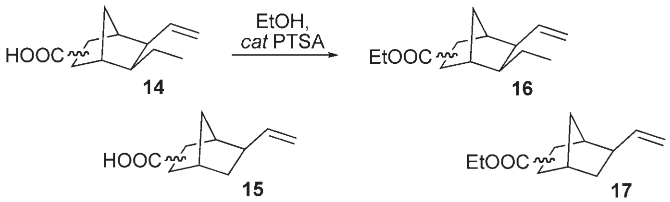
[b] Calculated according to Henry's law: $C_E = P_E \times H_0 \exp[\Delta H_L \times (RT)^{-1}]$, C_E (mol L^{-1}), P_E (atm), $H_0 = 0.00175$ mol L^{-1} atm^{-1}, ΔH_L = *enthalpy of solvatation of E in toluene* = 2569 cal mol^{-1}, $R = 1.989$ cal mol^{-1} K^{-1}.

[c] $\{[NB_{OH}]/([NB_{OH}]+[E])\} \times 100$.

[d] Determined by GC.

[e] Calculated as mol of NB_{COOH} (mol of Co)$^{-1}$.

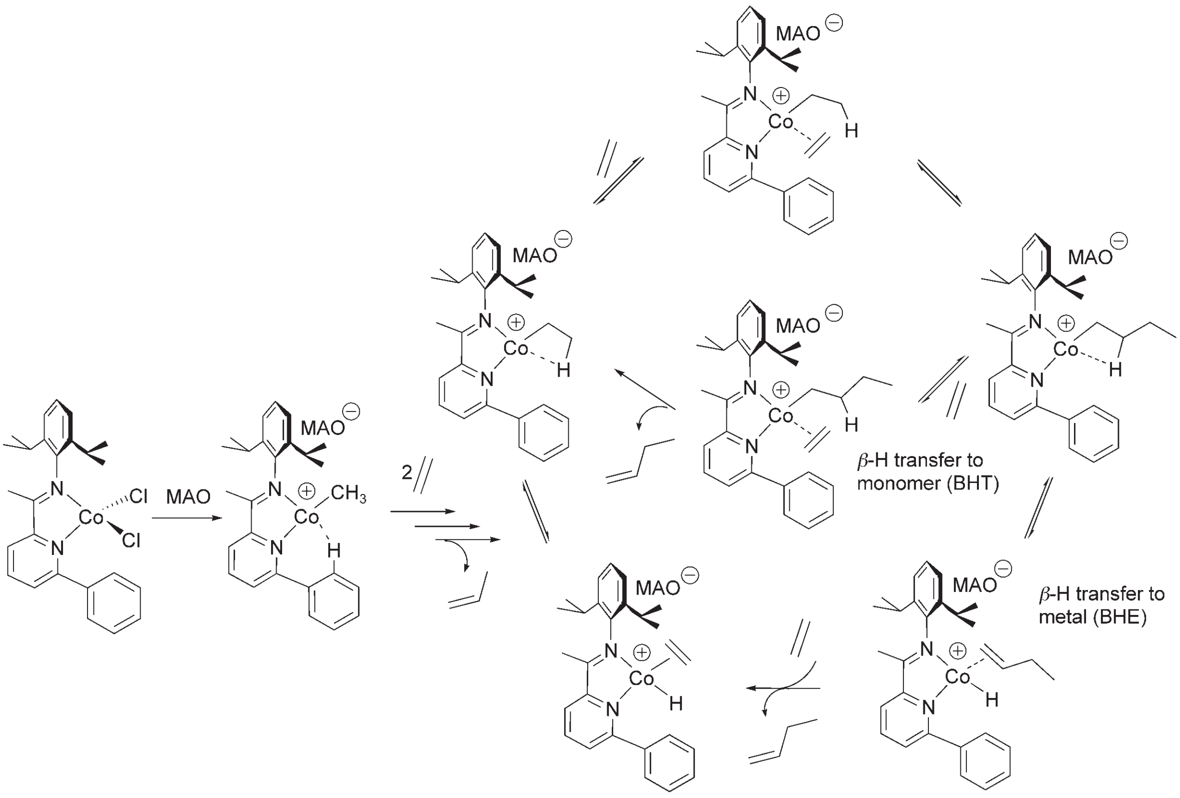
[f] Calculated as mol of NB_{COOH} (mol of Co × h)$^{-1}$.



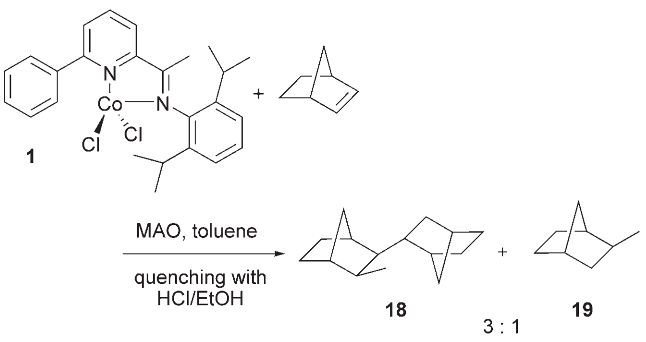
Scheme 6. Esterification of the crude acid mixture.

Mechanistic Considerations on the 2E-1NB Hetero-Trimerization Catalyzed by 1/MAO

It has been recently demonstrated that the tetrahedral high-spin complexes **1**, **2**, **4**, and **5** react with MAO in toluene to give a low-spin Co(II) square-planar methyl complex that becomes a square-planar alkyl complex during the propagation step of ethylene oligomerization.[2a] Scheme 7 illustrates the overall reac-



Scheme 7. Reaction paths for the dimerization of E catalyzed by **1**/MAO.



Scheme 8. Stoichiometric reaction of **1** with NB.

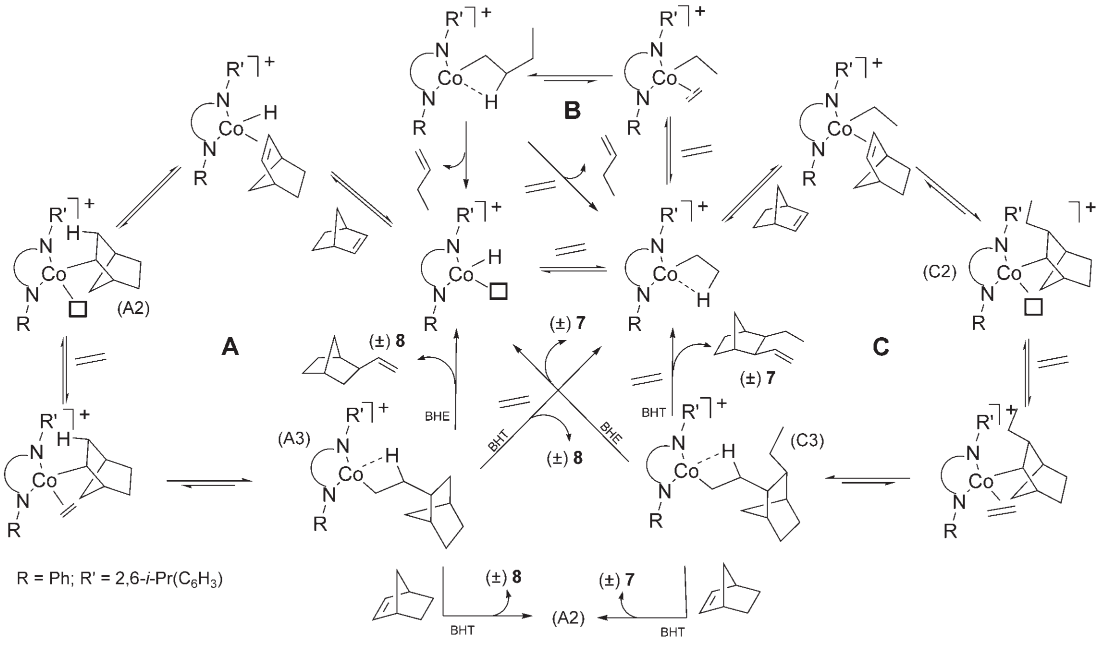
tion path for the dimerization of E catalyzed by **1**/MAO.

The propagating alkyl Co(II) complexes were intercepted by *in situ* and *operando* EPR experiments. Like any metal alkyl, the propagating Co(II) *n*-butyl complexes can transfer a β-H to give 1-butene and Co-H or Co-C_2H_5 species depending on the operating chain-transfer mechanism. When the β-H elimination to the metal (BHE) prevails over the β-H transfer to the monomer (BHT), the formation of Co-H predominates over that of Co-C_2H_5. The opposite will occur for the prevalence of the BHT. In the case of E oligomerization by the present (imino)pyridine catalysts, the two chain termination paths are kinetically indistinguishable and the question of the more favorable path could not be addressed experimentally.[24] The formation of internal olefins, due to α-olefin isomerization, was taken as an indirect proof of the formation of the Co-H initiator, but the small extent of this isomerization, compared to the very high catalytic activity, did not allow us to rule out an effective role also for the BHT. In fact, the occurrence of the latter termination mechanism is highly probable (*vide infra*).

Clear evidence of the formation of a Co-CH_3 initiator upon activation of the Co(II) dihalide **1** by MAO as well as of the irreversible insertion of NB into the Co-CH_3 moiety was provided by the result of the reaction shown in Scheme 8. In this experiment, **1** was reacted with an excess of MAO in toluene in the presence of a stoichiometric amount of NB for 30 min and then the reaction was quenched by adding an ethanol solution of HCl. Work-up of the resulting solution allowed us to detect the formation of a 3:1 mixture of *exo*-(2,3-methyl-norbornanyl)-norbornane (**18**) and *exo*-(2-methyl)-norbornane (**19**) in quantitative yield (see the Supporting Information). The formation of these products can exclusively occur through an NB migratory insertion in Co(methyl)(η^2-norbornene) and Co(2-methyl-norbornanyl)(η^2-norbornene), respectively.

Incorporation of the experimental results reported in this work, particularly in terms of chemo- and stereoselectivity, with the information gathered from previous studies of E oligomerization by **1**, **2**, **4**, and **5** catalysis has prompted us to suggest a mechanistic rationale for the present diastereoselective 2E-1NB hetero-trimerization (Scheme 9).

The high selectivity in **7** and the very low amount of 1-butene produced during the co-oligomerization reaction prove that i) cycle **C** (Scheme 9) is favored over cycles **A** and **B**; ii) NB generally prevails over E



Scheme 9. Possible mechanistic paths for the 2E-1NB hetero-trimerization reaction.

for the insertion into the Co-C_2H_5 moiety. Indeed, the preferred enchainment of the cyclic olefin is consistent with the drastic decrease in the E consumption observed during the E/NB co-oligomerization (Figure 3**B**). Once the Co(2-ethyl-norbornanyl) product (**C2**) has formed, the insertion of E apparently prevails over further NB insertion leading to intermediate **C3** which liberates the ethyl-vinylated compound **7** by β-H transfer (BHE and/or BHT).

The observed chemoselectivity seems to indicate that, in the presence of E, NB prefers to insert into the Co-C_2H_5 moiety rather than into the Co-H moiety. This preference might be essentially kinetic in nature or determined by the low concentration of Co-H initiator that would be rapidly consumed by E to form Co-C_2H_5. On the other hand, there is little doubt that the plain hydrovinylated compound **8** (cycle **A**) is mainly produced in the presence of high NB molar fractions (Table 1, entries 11–-15).

While the initiation and propagation mechanisms of the 2E-1NB enchainment is therefore quite clear, discriminating between the two possible ways (BHE or BHT) by which **7** is liberated from intermediate **C3** is a much more difficult task, even if, on the basis of chemoselectivity arguments (up to 96.8% of the hetero-trimerization product and almost negligible formation of internal butenes), one might be induced to think of a prevailing BHT mechanism.

The observed diastereoselective enchainment, yielding the *exo*-2,*exo*-3 ethyl-vinylnorbornane products, agrees with the known propensity of NB to insert into M–C bonds through the less hindered *exo* face.[25]

Conclusions

We have set up an efficient hetero-trimerization protocol for the highly selective synthesis of new vinyl monomers featured by an *exo*-2,*exo*-3-ethyl-vinylnorbornane structure. For the first time NB containing polar functionalities such as alcohols or carboxylic acids have been effectively transformed into the corresponding ethyl-vinylated products, which has required the preliminary *in-situ* pre-treatment of the polar groups with TIBA.

Appropriate experiments have allowed us to gain insight into the nature of some Co species involved in the catalysis cycle as well as into the experimental conditions that control the chemoselectivity.

Experimental Section

Characterization data for compounds **7, 11, 12** and **16** are available in the Supporting Information.

General Remarks

All air- and/or water-sensitive reactions were performed under either nitrogen or argon in flame-dried flasks using standard Schlenk-type techniques. Anhydrous toluene was obtained by means of an MBraun solvent purification system. *n*-Pentane was dried and distilled over Na. Solid MAO for polymerization was prepared by removing toluene and $AlMe_3$ under vacuum from a commercially available MAO solution (10 wt% in toluene, Sigma–Aldrich). The MAO solution was filtered on a D4 funnel and evaporated to dryness at 50 °C under vacuum. The resulting white residue was heated further to 50 °C under vacuum overnight. A stock solution of MAO was prepared by dissolving solid MAO in toluene (100 $mg\,mL^{-1}$). The solution was used within three weeks to avoid self-condensation effects of the MAO. Modified methylaluminoxane (MMAO) was purchased from Akzo Nobel (7 wt% solution in heptane) and used as received. Literature methods were used to synthesize the cobalt and nickel complexes **1–3**.[1,2] Norbornene was dried by treatment over Na at 80 °C for two days and then distilled. A stock solution of norbornene was prepared by dissolving 90 g of freshly distilled norbornene in 50 mL of toluene (toluene: 670 $mg\,mL^{-1}$, $d=0.872$, 23 °C). 5-Norbornene-2-methanol and 5-norbornene-2-carboxylic acid (purchased from Aldrich), were distilled under vacuum and stored under a nitrogen atmosphere in presence of activated 3 Å molecular sieves. Unless otherwise stated, all the other reagents and solvents were used as purchased from commercial suppliers. Catalytic reactions were performed with a 750-mL stainless steel reactor, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a mechanical stirrer, a Parr 4842 temperature and pressure controller, a mass flow meter equipped with a digital control for the connection to the PC and an external jacket for the temperature control. The reactor was connected to an ethylene reservoir to maintain a constant pressure throughout the catalytic runs. Ethylene was purified before use by passing it through two columns filled with activated molecular sieves 4 Å and BASF R3–11G catalysts, respectively. Deuterated solvents for NMR measurements were dried over molecular sieves. ^1H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Bruker Avance DRX-400 (400.13 and 100.62 MHz, respectively) spectrometer. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to the chemical shifts of residual solvent resonances (^1H and ^{13}C). The multiplicities of the $^{13}C\{^1H\}$ NMR spectra were determined with the DEPT 135 technique and quoted as: CH_3, CH_2, CH and C for primary, secondary, tertiary and quaternary carbon atoms, respectively. GC analyses of the reaction products were performed on a Shimadzu GC-17 gas chromatograph equipped with a flame ionization detector and a Supelco SPB-1 fused silica capillary column (30 m length, 0.25 mm i.d., 0.25 μm film thickness) or a CHIRALDEX G-TA (50 m length, 0.25 mm i.d). The GC-MS analyses were performed on a Shimadzu QP2010S apparatus equipped with a column identical with that used for GC analyses.

General Procedure for the Ethyl-Vinylation of Norbornene

Method A**:** A 750-mL stainless steel reactor was heated at 60 °C under vacuum overnight and then cooled to room temperature under a nitrogen atmosphere. The solid precatalyst (12 μmol) was charged into the reactor which was sealed, placed under vacuum and put at the operating temperature by means of an external circulating thermostatic bath. An oxygen-free MAO/cyclic monomer solution, prepared by diluting 4.2 mL of a stock toluene solution of MAO (7.2 mmol) and a proper amount of the cyclic olefin in toluene (final volume 100 mL), was introduced by suction into the reactor. The system was stirred for 3 min at 1500 rpm and then pressurized with ethylene. Ethylene was continuously fed to maintain the reactor pressure at the desired value. The temperature inside the reactor was maintained within ± 1 °C with respect to the operating temperature by means the external control. At the end of the reaction, stirring was stopped, the reactor was cooled at 10 °C and depressurized. Afterwards, 2 mL of acidic EtOH (5% HCl) were introduced by syringe and the system was maintained under stirring for further 3 min. The solution was analyzed by GC and GC-MS and in some cases, the compounds were fractionally distilled from the reaction mixture and characterized by ^{1}H and ^{13}C NMR spectroscopy. For the quantification of the products, 1-undecene was injected into the reactor as the GC internal standard. Some catalytic runs were carried out using *n*-pentane as solvent and MMAO (7 wt% solution in heptane) as co-catalyst.

Method B**:** A 750-mL stainless steel reactor was heated at 60 °C under vacuum overnight and then cooled to room temperature under a nitrogen atmosphere. Afterwards, the reactor was placed under vacuum and put at the operating temperature by means of an external circulating thermostatic bath. An oxygen-free MAO/cyclic monomer solution, prepared by diluting 2.1 mL of a stock toluene solution of MAO (3.6 mmol) and a proper amount of the cyclic olefin in toluene (final volume 95 mL), was introduced by suction into the reactor. The system was pressurized with ethylene to the desired pressure and stirred for 5 min. Afterwards, 5 mL of a solution, prepared by dissolving the solid precatalyst (12 μmol) in 50 mL of toluene, was syringed into the reactor. The system was continuously fed to the desired pressure and stirred at 1500 rpm. The temperature inside the reactor was maintained within ± 1 °C with respect to the operating temperature by means the external control. At the end of the reaction, stirring was stopped, the reactor was cooled at 10 °C and depressurized. Afterwards, 2 mL of acidic EtOH (5% HCl) were introduced by syringe and the system was maintained under stirring for further 3 min. The solution was analyzed by GC and GC-MS and in some cases, the compounds were fractionally distilled from the reaction mixture and characterized by ^{1}H and ^{13}C NMR spectroscopy. For the quantification of the products, 1-undecene was injected into the reactor as the GC internal standard. Some catalytic runs were carried out using *n*-pentane as solvent and MMAO (7 wt% solution in heptane) as co-catalyst.

exo-2,*exo*-3-Ethyl-vinylnorbornane (7)

The pure product was isolated as a colorless oil *via* solvent evaporation followed by fractional distillation of the crude mixture using a 15-cm Vigreaux column (130–140 °C, 760 mmHg).

exo,exo-2,3-Diethyl-norbornane (11)

A solution of **7** (0.1 g, 0.667 mmol) in CH_2Cl_2 (5 mL), was treated with 12 mg of $RhCl(PPh_3)_3$ (Wilkinson's catalyst) under nitrogen. Afterwards, nitrogen was replaced by hydrogen (1 bar). The reaction mixture was kept under stirring for 3 h then the solvent was removed under vacuum and the crude product was filtered through a silica pad using *n*-pentane as eluting solvent. Evaporation of the solvent under reduced pressure gave the product as a colorless oil which was analyzed by GC, GC-MS, ^{1}H NMR and $^{13}C\{^1H\}$ NMR.

exo-(2,3-Methylnorbornanyl)-norbornane (18) and *exo*-(2-Methyl)-norbornane (19)

To a suspension of **1** (100 mg, 0.205 mmol), in toluene (4 mL) a stock solution of NB (24 μL, 17.6 mg, 0.187 mmol) and MAO (200 equiv., 23.7 mL, 40.8 mmol) were added in sequence. The resulting dark brown solution was allow to stir for 2 h at room temperature. Afterwards, 5 mL of $EtOH/H^+$ were added and the organic phases extracted with 3×20 mL of Et_2O. The crude product was analyzed *via* GC and GC-MS analysis: 6.8 min, MS (EI): *m/z* (%): = 110 (M^+, 7); 95 (61); 67 (100); 21.2 min, MS (EI): *m/z* (%) = 204 (M^+, 5); 189 (3); 95 (100); 67 (77).

General Procedure for the Ethyl-vinylation of 5-Norbornene-2-methanol (NB_{OH}) and 5-Norbornene-2-carboxylic Acid (NB_{COOH})

A 750-mL jacketed stainless steel reactor was heated at 60 °C under vacuum overnight and then cooled to room temperature under a nitrogen atmosphere. Afterwards, the reactor was placed under vacuum and put at the operating temperature by means of an external circulating thermostatic bath. In a tipycal procedure, a 150-mL Schlenk flask cooled at 0 °C in an ice bath, a well stirred solution of TIBA (triisobutylaluminum, 1 M solution in toluene; 4.6 mL, 4.6 mmol) was treated drop-wise over 30 min, under nitrogen atmosphere, with a 0.4 M toluene solution of NB_{OH} (10 mL, 4.0 mmol) or a 0.2 M toluene solution of NB_{COOH} (10 mL, 2.0 mmol), respectively. The reaction mixture was kept under stirring at room temperature for 1 h, then treated with 4.8 mL of a stock toluene solution of MAO (10 wt%, 8.2 mmol). The mixture was raised to the final volume of 95 mL by adding degassed toluene and finally introduced by suction into the reactor. The system was pressurized with ethylene to the desired pressure and stirred for 5 min. Afterwards, 5 mL of a solution/suspension of the solid precatalyst (12 μmol) in 5 mL of toluene, was syringed into the reactor. The system was continuously fed to the desired pressure and stirred at 1500 rpm. The temperature inside the reactor was maintained within ± 1 °C with respect to the operating temperature by means the external control. At the end of the reaction, stirring was stopped, the reactor was cooled at 10 °C and depressurized. Afterwards, 2 mL of acidic EtOH (5% HCl) were introduced by syringe and the system was maintained under stirring for 3 min further. The solution was analyzed by GC and GC-MS and in some cases, the compounds were fractionally distilled from the reaction mixture and characterized by ^{1}H and ^{13}C NMR spectroscopy. For the quantification of the products, 1-undecene was injected into the reactor as the GC internal standard.

exo-5,*exo*-6-(Ethyl-vinyl)-norbornanyl-2-methanol (12)

The crude reaction mixture was washed with distilled water (3×20 mL) to remove all the aluminum salts. The aqueous layers were then extracted three times with CH_2Cl_2 and the collected organics (toluene+CH_2Cl_2) were evaporated at reduced pressure as to eliminate volatiles. The residual colorless oil was then keep under high vacuum at 60°C for 0.5 h to give the pure product (>98%, GC), as a viscous oil. Filtration on a silica gel pad (AcOEt:hexanes 10:90), provided a sample suitable for elemental analysis.

exo-5,*exo*-6-(Ethyl-vinyl)-norbornanyl-2-carboxylic Acid, Ethyl Ester (16)

The crude reaction mixture was washed with an HCl solution (5% v/v) (3×20 mL) to remove all the aluminum salts. The aqueous layers were then extracted three times with CH_2Cl_2 and the collected organics (toluene+CH_2Cl_2) were evaporated at reduced pressure as to eliminate all volatiles. The stinking crude acid mixture was treated in boiling ethanol with a catalytic amount of PTSA (2 mol%) for 12 h. Afterwards, the solution was neutralized with a saturated solution of $NaHCO_3$ and extracted three times with CH_2Cl_2 (3× 15 mL). The collected organics were evaporated under reduced pressure to give a yellow pale oil. Purification through flash chromatography (AcOEt:hexanes, 5:95) afforded the pure ester **16** as a colorless viscous oil.

Acknowledgements

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[18] **1**/MAO catalyzed the highly selective E oligomerization to butenes and E/NB heterotrimeriation to compound **7** with activity significantly higher than **2**/MAO. (Ethylene reaction conditions: 300-mL jacketed glass reactor, 100 mL toluene, 30 °C, 12 μmol pre-cat., MAO 600 equiv **1**) TOF $(10^{-3}) = 149.7$ $\mathrm{mol}_{C_2H_4}$ $(\mathrm{mol\ Co\ h})^{-1}$; $\alpha = 0.020$ **2**) TOF $(10^{--3}) = 72.2$ $\mathrm{mol}_{C_2H_4}$ $(\mathrm{mol\ Co\ h})^{-1}$; $\alpha = 0.022$. E/NB reaction conditions: 750-mL jacketed stainless steel reactor, 100 mL toluene, 30 °C, 12 μmol pre-cat., MAO 600 equiv **1**) TOF $(10^{-3}) = 20.1$ mol_{NB} $(\mathrm{mol\ Co\ h})^{-1}$; **2**) TOF $(10^{-3}) = 1.2$ mol_{NB} $(\mathrm{mol\ Co\ h})^{-1}$.

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[22] $\mathrm{NB_{OH}}$ *exo*/*endo* ratio = 35/65 (as received from the suppliers). After partial conversion (61,3%, see Table 3, entry 8): *exo/endo* ratio = 28/72.

[23] $\mathrm{NB_{COOH}}$ *exo*/*endo* ratio = 32/68 (as received from the suppliers). After partial conversion (67,9%, see Table 4, entry 4): *exo/endo* ratio = 16/84.

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