Oligomerization of $\alpha$-olefins by the dimeric nickel bisamido complex [Ni\{1-N(PMes$_2$)-2-N(\mu-PMes$_2$)C$_6$H$_4$-κ$^3$N,N',P,-κ$^1$P\}]$_2$ activated by methylalumoxane (MAO)

Felicite Majoumo-Mbe$^{a,c}$, Peter Lönecke$^{a}$, Victoria Volkis$^{b}$, Manab Sharma$^{b}$, Moris S. Eisen$^{b,*,}$, Evamarie Hey-Hawkins$^{a,*,}$

$^a$Institut für Anorganische Chemie der Universität, Johannisallee 29, D-04103 Leipzig, Germany
$^b$Shulich Faculty of Chemistry, The Institute of Catalysis Science and Technology, Haifa 32000, Israel
$^c$University of Buea, Faculty of Science, Department of Chemistry, Inorganic Chemistry Laboratory, P.O. Box 63, Buea, Cameroon

A R T I C L E I N F O

Article history:
Received 31 March 2008
Received in revised form 1 May 2008
Accepted 6 May 2008
Available online 10 May 2008

Keywords:
P,N ligand
Nickel complex
Oligomerization reaction
$\alpha$-Olefins

A B S T R A C T

The reaction of Li$_2$[1,2-{N(PMes$_2$)}$_2$C$_6$H$_4$], formed in situ from n-BuLi and the corresponding amines, with 1 equiv. of [NiBr$_2$(DME)] gives [Ni\{1-N(PMes$_2$)-2-N(\mu-PMes$_2$)C$_6$H$_4$-κ$^3$N,N',P,-κ$^1$P\}]$_2$ (1). After activation by methylalumoxane (MAO), 1 is a highly active catalyst in the oligomerization and isomerization of $\alpha$-olefins such as ethene, propene, isobutene, 1-hexene and 1,5-hexadiene. For ethene oligomerization turn-over frequencies (TOFs) range from 3000 to 79015 h$^{-1}$, depending on the reaction conditions. The TOF for propene oligomerization reaches 1190730 h$^{-1}$. To our knowledge, catalyst 1, activated by MAO, is the most active catalyst for the oligomerization of propene and outperforms the best known complexes for this reaction. In the reactions with 1-hexene, 1,5-hexadiene and isobutene dimerization and oligomerization products were observed.

Catalytic polymerization and oligomerization of $\alpha$-olefins, especially to give dimeric and trimeric products, are of special interest in industry [1] due to the use of olefin oligomers as building blocks and intermediates for specialty chemicals [1a,2]. In addition, olefin oligomerization is widely studied to gain better insight into the reaction mechanisms of the corresponding catalysts, because of the homogeneity of the reaction mixture and easier characterization of oligomeric products as compared to high molar mass polymers [3].

Recently, different organometallic catalysts, including homogeneous vanadium-based catalysts, zeolites, alkyl aluminum compounds, group IV and late transition metal catalysts, have been reported as good precursors for olefin oligomerization [2,4], with special focus on nickel catalysts [5].

The pronounced ability of Ni complexes for chain termination via a β-hydrogen elimination process is important for their successful application in the production of dimers and/or oligomers of ethene, propene and other olefins. Nickel catalysts have been found to be active in a wide spectrum of olefin transformations, including dimerization [6], oligomerization [7], polymerization [8], and copolymerization [9] with different comonomers. Their reduced oxophilicity and enhanced tolerance to functional groups makes them very effective in copolymerization of polar and nonpolar monomers to give new polymers with unusual microstructures [10].

Among the myriad of nickel precursors containing chelating acetylacetonate [11], 2-(diphenylamino)benzoate [12], pyrrolidine [13], salen [14], Schiff base [15], salicylideneiminato [16], and many other ligands which were found to be active for the dimerization and oligomerization of ethene and propene, the following activators are the most active: (i) catalytic systems based on a P,O chelate ligand for the production of C$_4$–C$_{20}$ oligomers from ethene, which were developed by Keim et al. and later modified in the Shell Higher Olefin Process (SHOP) for the synthesis of linear oligomers of ethene [17], (ii) P,N chelate complexes of Ni reported by Brauneit et al. [18], (iii) Grubbs' catalysts [19], and (iv) Brookhart's catalysts [20]. In addition, much attention has been focused on Ni catalysts supported on zeolites such as Y-zeolite, L-zeolite, mordenite, and mesoporous MCM-41 or on amorphous silica–alumina [21]. These systems were found to be very effective for the dimerization of ethene.

One of the industrially most important dimerization reactions is that of isobutene, as hydrogenation of the resulting dimers gives isooctane (2,2,4-trimethylpentane), which is a reference compound for the measurement of octane number that, by definition,
has a research octane number (RON) and motor octane number (MON) of 100. In attempts to replace the industrially used acid catalysts and ion-exchange resins for the dimerization of isobutene, some inorganic catalysts such as titanium complexes [22], organo-f-element complexes [23], and the system AlEt3/TiCl4 [24] were studied. However, none of them has industrial future due to the low activity compared to acidic ion-exchange resins [25].

Recently, the catalytic activity of many nickel complexes in the oligomerization of ethene was reported. For example, paramagnetic complexes [NiBr2(L)] (L = cone-5,17-dibromo-11,23-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix-4-arene or cone-5,17-bis(diphenylphosphino)-25,26,27,28-tetrapropoxycalix-4-arene) [26] activated with methylalumoxane selectively produced 1-butene with turnover frequencies (TOFs) up to 106 (mol C2H4) (mol Ni)−1 h−1. Complexes with phosphinopyridine (P,N) ligands [18a] have shown TOFs for catalytic oligomerization of ethene with good catalytic activity (104–105 g mol−1 C2H4) (mol Ni)−1. Complexes activated by MAO and modified MAO (MMAO) are highly selective in the range of 70–85% for the C4 olefins and 33–38% for 1-butene in the C4 fraction. Nickel complexes with oxazoline- or phospholane ligands [18a] have shown TOFs for catalytic oligomerization of ethene with turnover frequencies (TOFs) up to 106 (mol C2H4) (mol Ni)−1 h−1 [28].

Here, we report the catalytic dimerization and oligomerization of ethene, propene, isobutene, 1-hexene, and 1,5-hexadiene by the novel nickel bisamide complex [Ni{1-N(PMes2)-2-N((NPPh3)2C6H4)}2] (1) activated by MAO. Complex 1 was synthesized and was characterized by various analytical techniques, including X-ray crystallography. This complex was found to be an active catalyst in the dimerization of ethene and propene, and, to the best of our knowledge, for the latter this catalyst exhibits the best activity to date. The influence of the reaction conditions on the oligomerization activity and properties of the resulting dimers and oligomers are presented.

1. Results and discussion

1.1. Synthesis and spectroscopic properties of the nickel bisamide complex [Ni{1-N(PMes2)-2-N(μ-PMes2)C6H4-κ3'N,N,P-κ1'P}]2 (1)

The reaction of 1,2-(NH(PMes2)2)2C6H4 [29] with 2 equiv. of n-BuLi in toluene at room temperature leads to the formation of the anionic ligand [1,2-(N(PMes2)2)C6H4]2−, which reacts in situ with 1 equiv. of [NiBr2(DME)] to give 1 (Scheme 1).

In the 31P{1H} NMR spectrum of 1, two doublets are observed for the two nonequivalent phosphorus atoms. The doublet at 61.8 ppm (3JpN = 299.4 Hz), assigned to Ni–P–N (bridging mode), is shifted to lower field in comparison to the free ligand (24.9 ppm), and the second doublet at −68.3 ppm (3JpN = 299.4 Hz), assigned to Ni(P–N) (chelating mode), is shifted to higher field, probably due to the effect of the small ring and the delocalization of the lone pair of electrons on nitrogen into antibonding orbitals at phosphorus, as was observed in the structures of model compounds of phosphanylamide anions [30]. A high-field shift was also observed for [TiCl2[N(PPh2)2]2] [31] (−10 ppm), a complex with P–N in a chelating mode and Ti in an octahedral configuration, whereas the chemical shift of the free ligand is 46 ppm. Details of the 1H and 13C NMR spectra are given in Section 3.

1.2. Molecular structure of 1

Violet crystals of 1 were obtained from diethyl ether/petroleum ether at 4 °C. Compound 1 crystallizes in the monoclinic space group C2/c with four molecules of 1 and four noncoordinating diethyl ether molecules in the unit cell. The molecular structure of 1 (Fig. 1) reveals a dimeric complex with a crystallographic C2 axis located at the center of the hexagon formed by the two P–N bridges and the two Ni atoms. Compound 1 exhibits unusual coordination at the Ni atoms. Each Ni atom is coordinated by two nitrogen and two phosphorus atoms. The geometry around the Ni atom is highly distorted, and consists of a five-membered chelate ring via the nitrogen atoms, a threemembered chelate ring via the P–N group, and formation of a dimer in which the two rings are bridged by two phosphorus atoms. The five-membered rings have an envelope conformation in which the atoms N(1), C(19), C(24), and N(2) are coplanar, while the Ni atom lies 0.64(2) Å above this plane.

The (N(1)–Ni(1)–N(2) bond angle of 83.6(4)° is comparable to that of 83.6(6)° observed for the chelating nitrogen donor ligands in the Ni-1,2-dimino phosphinophane complex [NiCl2(1,2-(NPPPh3)2C6H4)] [32]. The sum of the bond angles [N(1)–Ni(1)–P(1) 46.0(3)°, N(1)–Ni(1)–N(2) 83.6(4)°, N(2)–Ni(1)–P(2) 108.7(3)° and P(1)–Ni(1)–P(2) 123.9(1)°] of 362.3° around the Ni atom indicates a distorted planar geometry. The sum of bond lengths at N(2) [C(24)–N(2)–P(2) 121.8(7)°, C(24)–N(2)–Ni 108.8(7)°, P(2)–N(2)–Ni 126.8(5)°] of 357.6° indicates trigonal-planar coordination, while at N(1) [C(19)–N(1)–P(1) 132.0(8)°, C(19)–N(1)–Ni 110.8(7)°, P(1)–N(1)–Ni 77.7(4)°] the sum of 320.7° indicates a pyramidal environment due to the chelating mode of the P–N group.

The N(1)–Ni and N(2)–Ni bond lengths of 1.872(9) and 1.965(8) Å, respectively, are shorter than those observed in other chelating N-donor Ni complexes [1.996(2)–2.017(5) Å] [32]. The shorter P(2)–N(1) bond length of 1.617(8) Å compared to the P(2)–N(2) bond length of 1.676(9) Å indicates double-bond character, as in the case of Ni complexes with iiminophosphane ligands.
[1.585(5)–1.618(2) Å] [32]. The P(1)–Ni bond of the three-membered ring is stronger than the P(2)–Ni bond of the bridging unit, as the bond length of 2.234(4) Å for the latter is larger than the 2.197(3) Å for the former. This may indicate delocalization of the π-bered ring is stronger than the P(2)–Ni bond of the bridging unit, [1.585(5)–1.618(2) Å][32].

1.3. Oligomerization reactions promoted by complex 1 activated by MAO

Complex 1 was activated by methylalumoxane prior to the oligomerization reaction. Only one broad signal at ~58 ppm is observed in the $^{31}$P NMR spectrum for the active species. The oligomerizations of ethene, propene, and isobutene were carried out in a high-pressure stainless steel reactor, whereas the oligomerization reactions for 1-hexene and 1,5-hexadiene were performed in Schlenk heavy duty glass vessels. For ethene, the pressure of the reactor was kept constant at 20 atm via a solenoid pressure transducer, whereas for propene and isobutene liquid pressure of the reactor was kept constant at 20 atm via a solenoid pressure transducer, whereas for propene and isobutene liquid monomer was used and as soon as the pressure was slightly reduced (~1 atm) quenching was immediately performed. This procedure was followed to allow a constant monomer concentration in the reaction vessel and to avoid pressure-velocity polymerization side effects.

The oligomerization data for ethene, propene, and isobutene are presented in Table 2. The reactions of oligomerization/polymerization were studied as batch conditions and performing the same procedure was followed to allow a constant monomer concentration in the active sites with almost no change in composition of products.

It can be seen from Table 2 that the catalytic activity of complex 1 in the oligomerization of ethene increases with increasing Al:Ni ratio. In addition, the catalyst is more active in the polar solvent methylene chloride than in toluene. However, depending on the oligomerization conditions, liquid or liquid and solid products may be obtained. The formation of both oligomers and polymers with preferential selectivity for oligomers has already been reported in the literature. For example, nickel(II) complexes containing neutral N,N- and anionic N,O-bidentate ligands activated by MMAO produced a mixture of ethene trimers and polymers with moderate activity and very high selectivity towards the oligomer [33]. Tables 3 and 4 illustrate the properties of the resulting solid and liquid ethylene oligomerization products, respectively. The polymerization products are high density polyethylene with similar melting points of 127.0–127.5 °C. Moreover, the higher the amount of MAO the higher the amount of the polymeric fraction obtained, but in all cases the amount of the oligomers is always much higher than that of the polymers. In the reaction with ethene, complex 1 exhibits a high activity but a low chemoselectivity as compared to previously described catalysts; it produces a mixture of dimers (where 1-butene is always the major component >77%) and branched trimers (>80% 3-methyl-1-pentene) with a small preference for the linear product. The TOF exhibited for complex 1 in dichloromethane (79015 h$^{-1}$) is indeed higher than those
TOFs observed for the P,N chelate nickel complexes reported in the last few years [18]. However, our TOFs are somewhat lower than those obtained using Grubbs’ [19] and Brookhart’s [20] catalysts.

The oligomerization of propene, promoted by complex 1 and activated by MAO, was performed in liquid propene using a double jacket wall reactor with a mechanical stirrer (>100 RPM), an internal thermocouple and the reactor vessel thermostated to the requested temperature. When the oligomerization reaction was carried out at room temperature, the process was found to be extremely fast and exothermic. The pressure in the reactor dropped in a few minutes, and full conversion was reached. No solids or elastomeric materials were detected in any of the reactions with propene.

Among the many previously reported active nickel catalysts for the oligomerization of propene the following complexes are noteworthy: [Ni(COD)2], prepared in situ and activated by MAO, poly-merizes propene with TOFs of up to 24800 h⁻¹ and is regioselective towards 2,3-dimethyl-1-butene (2,3-DMB) in the C6 fraction (>82%) [34]. [Ni(η5-indenyl)2] activated by organoaluminum cocatalysts displayed an extremely high productivity (TOF up to 169000 h⁻¹) and a moderate regioselectivity for 2,3-DMB (66.4%) [35]. Poly-salen-type NiII complexes reached TOFs of up to 221000 h⁻¹.C, the temperature raised to 0 °C, the pressure increased to 11 atm, and the reaction was performed in toluene. In all these cases where toluene was used as the solvent at both MAO/cat ratios, the product distribution is very much alike. Among the linear products 1-hexene (75%) is obtained as the major isomer along with 2-hexene (mostly cis and trans) and 3-hexene (mostly trans), which are obtained via a simple isomerization of 1-hexene, as minor products. The amount of the isomerized dimers is an indication that the speed of formation of the dimers and trimers is by far more rapid than the isomerization process. Although lower temperatures do not lead to the formation of higher oligomers, using methylene chloride results in the partial formation of C9–C12 oligomers without changing the activity (Table 2, run 10).

As can be seen from Table 2, the nickel complex 1 is an extremely active catalyst for the oligomerization of propene. The activity increases with increasing the Al:Ni ratio. Moreover, to try to control the exothermicity of the reaction without reducing the catalytic activity we have found that when the reaction is performed at −5 °C, the temperature raised to 0 °C yielding the best turnover frequency of 1190734 h⁻¹ (run 10). Comparison of this result with the most active catalyst described in the literature allows us to conclude that for the oligomerization of propene, catalyst 1 has the highest activity to date. Under all studied conditions, complex 1 is an order of magnitude more active than the best literature catalysts [20]. Interestingly, to put the result into perspective, at room temperature and at low Al:Ni ratio, the activity of complex 1 is comparable to those catalysts reported by Wu and Lu [35–38].

Table 2
Oligomerization/polymerization data for different olefins in the presence of complex 1 activated by MAO*.

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Ni:Al</th>
<th>Time (h)</th>
<th>Solvent</th>
<th>Initial temperature (°C)</th>
<th>Maximum temperature (°C)</th>
<th>Solid product (g)</th>
<th>Liquid product (g)</th>
<th>Activity (g/mol cat × h)</th>
<th>TOF (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethene</td>
<td>1:100</td>
<td>3</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>0.02</td>
<td>1.78</td>
<td>8.4 × 10⁴</td>
<td>3001</td>
</tr>
<tr>
<td>2</td>
<td>Ethene</td>
<td>1:700</td>
<td>0.5</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>0.11</td>
<td>4.61</td>
<td>2.2 × 10⁵</td>
<td>7868</td>
</tr>
<tr>
<td>3</td>
<td>Ethene</td>
<td>1:700</td>
<td>0.5</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>0.06</td>
<td>0.86</td>
<td>2.6 × 10⁴</td>
<td>9202</td>
</tr>
<tr>
<td>4</td>
<td>Ethene</td>
<td>1:700</td>
<td>0.5</td>
<td>CH₂Cl₂</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>17.1</td>
<td>8.0 × 10⁴</td>
<td>28505</td>
</tr>
<tr>
<td>5</td>
<td>Ethene</td>
<td>1:700</td>
<td>0.5</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>Traces</td>
<td>3.53</td>
<td>5.0 × 10⁴</td>
<td>17653</td>
</tr>
<tr>
<td>6</td>
<td>Ethene</td>
<td>1:700</td>
<td>0.5</td>
<td>CH₂Cl₂</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>15.8</td>
<td>2.2 × 10⁴</td>
<td>79015</td>
</tr>
<tr>
<td>7</td>
<td>Propene</td>
<td>1:200</td>
<td>0.33</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>25</td>
<td>1.1 × 10⁴</td>
<td>252580</td>
</tr>
<tr>
<td>8</td>
<td>Propene</td>
<td>1:700</td>
<td>0.07</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>25</td>
<td>5.0 × 10⁴</td>
<td>1190734</td>
</tr>
<tr>
<td>9</td>
<td>Propene</td>
<td>1:700</td>
<td>0.07</td>
<td>CH₂Cl₂</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>25</td>
<td>5.0 × 10⁴</td>
<td>1190734</td>
</tr>
<tr>
<td>10</td>
<td>Propene</td>
<td>1:700</td>
<td>0.07</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>25</td>
<td>5.0 × 10⁴</td>
<td>1190734</td>
</tr>
<tr>
<td>11</td>
<td>Isobutene</td>
<td>1:500</td>
<td>3</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>3.7</td>
<td>1.7 × 10⁴</td>
<td>3084</td>
</tr>
<tr>
<td>12</td>
<td>Isobutene</td>
<td>1:500</td>
<td>3</td>
<td>Toluene</td>
<td>25</td>
<td>25</td>
<td>–</td>
<td>17.2</td>
<td>8.0 × 10⁴</td>
<td>14337</td>
</tr>
</tbody>
</table>

* 10 mg of catalyst 1.
  b Ethene 20 atm, propene 50 ml = 11 atm, 10 ml of solvent.
  c 7.6 ml of solvent.
  d Clean product without catalyst or solvent.
  e mol of monomer/(mol of catalyst + h).

Table 3
Properties of solid products of the reaction with ethene.

<table>
<thead>
<tr>
<th>Run</th>
<th>Mw (g/mol)</th>
<th>Mn (g/mol)</th>
<th>MWD*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99000</td>
<td>258000</td>
<td>2.60</td>
</tr>
<tr>
<td>2</td>
<td>122000</td>
<td>330000</td>
<td>2.70</td>
</tr>
<tr>
<td>3</td>
<td>12000</td>
<td>2400</td>
<td>2.20</td>
</tr>
</tbody>
</table>

* MWD = molecular weight distribution = Mw/Mn.

Table 4
Amounts of different fractions in liquid products of ethene oligomerization*.

<table>
<thead>
<tr>
<th>Run</th>
<th>Dimer Cx (%)</th>
<th>Linear Cx (%)</th>
<th>Branched Cx (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>82</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>87</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>85</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>49</td>
<td>23</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>77</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>54</td>
<td>34</td>
<td>12</td>
</tr>
</tbody>
</table>

* GCMS and GC data.

Unexpectedly, and in contrast to the results observed for ethene, in propene the oligomerization activity is not affected by the solvent (Table 2, runs 9 and 10) presumably due to the large amount of liquid propene serving as a co-solvent. However, a very strong effect is observed for the regioselectivity of the products as presented in Table 5. For all the reactions linear and branched dimers are obtained with a slight preference for the branched compound when the reaction is performed in toluene. In all these cases where toluene was used as the solvent at both MAO/cat ratios, the product distribution is very much alike. Among the linear products 1-hexene (75%) is obtained as the major isomer along with 2-hexene (cis + trans) and 3-hexene (mostly trans), which are obtained via a simple isomerization of 1-hexene, as minor products. The amount of the isomerized dimers is an indication that the speed of formation of the dimers and trimers is by far more rapid than the isomerization process. Although lower temperatures do not lead to the formation of higher oligomers, using methylene chloride results in the partial formation of C9–C12 oligomers without changing the activity (Table 2, runs 8 and 9). Interestingly, the distribution of the products for the dimers remains almost unchanged but for the branched trimer 2,3-DMB is the major isomer (>82%). For the higher oligomers a myriad of isomers were obtained.
The reaction of 1/MAO with isobutene was also studied in a high-pressure reactor at room temperature. Although the TOFs were not very high for these reactions as compared to propene, but the selectivity was remarkable, only one dimeric product (2,5-dimethyl-3-hexene) was produced (Table 2).

Complex 1 was also found to be active in the oligomerization of 1-hexene and 1,5-hexadiene (Table 6). For these olefins, the reaction in toluene was again slower than for ethene and propene and as compared in dichloromethane a similar behavior is obtained inducing slightly to better activities in the more polar solvent. In toluene the selectivity was exclusively for dimers for both substrates whereas for dichloromethane trimers were obtained for 1,5-hexadiene. For 1-hexene in both solvents, the linear 1-dodecene was the major product (>75%) but isomerization of the double bond to different diastereomers is observed producing a myriad of products as a function of time which were difficult to separate or compare. For 1,5-hexadiene, the dimer 5-methyleneundeca-1,10-diene is obtained as the major isomeric product (>50%) but a number of compounds are also observed. In dichloromethane, a mixture of dimers and trimers was obtained as a low melting wax. The reaction mixture was stirred overnight, and then filtered. The solvent was removed, and the residue was dissolved in diethyl ether. The solution was concentrated and layered with petroleum ether. The product was obtained as violet crystals at 4°C. Yield: 0.58 g (68%), M.p.: 255–257°C. 1H NMR (CDCl3, ppm): 7.39 (br. s, 2H in C6H4), 7.04 (br. s, 2H in C6H4), 6.90 (br. s, 2H, C6H4), 6.63 (s, 8H, m–H in Mes), 6.53 (s, 8H, m–H in Mes), 6.10 (br. s, 2H, 2C=C in C6H4), 3.57 (s, Et2O), 2.73 (s, 24H, o–CH2 in Mes), 2.73 (s, 24H, o–CH2 in Mes), 2.00 (s, 12H, p–CH3 in Mes), 1.92 (s, 12H, p–CH3 in Mes), 1.42 (s, Et2O). 31P NMR (CDCl3, ppm): 61.8 (d, 2P, PC = 11.2 Hz, C6H4), 133.6 (d, 2P, PC = 11.2 Hz, p–C in Mes), 140.02 (s, PC = 19.4 Hz, C6H4), 131.6 (d, PC = 38.0 Hz, ipso-C in Mes), 131.7 (d, PC = 38.0 Hz, ipso-C in Mes), 130.7 (d, PC = 7.6 Hz, m–C in Mes). 31P NMR (CDCl3, ppm): 61.8 (d, 2P = 299.4 Hz), –68.3 (d, 2P = 299.4 Hz), 131(C) NMR (CD2Cl2, ppm): 142.3 (d, 2JPC = 11.2 Hz, o–C in Mes), 141.4 (s, p–C in Mes), 140.2 (d, 2JPC = 11.2 Hz, o–C in Mes), 140.02 (s, p–C in Mes), 134.3 (d, 2JPC = 11.2 Hz, C6H4), 133.6 (d, 2JPC = 19.4 Hz, C6H4), 131.6 (d, 2JPC = 38.2 Hz, ipso-C in Mes), 131.7 (d, 2JPC = 38.0 Hz, ipso-C in Mes), 130.7 (d, 2JPC = 7.6 Hz, m–C in Mes). 13C NMR spectra are reported in parts per million (ppm) at 200 MHz and 10160 h. Microanalysis for compound 1 was obtained. To the best of our knowledge, catalyst 1 activated by MAO exhibits the largest activity to propene oligomerization to date. In addition, the activated complex 1 was also found to be highly effective in the dimerization reactions of 1-hexene, 1,5-hexadiene, and isobutene.

### 3. Experimental

All reactions were carried out in an atmosphere of dry nitrogen using standard Schlenk or vacuum line techniques. The solvents were purified (diethyl ether, THF, toluene: reflux over Na/benzophenone; petroleum ether: reflux over LiAH4) and distilled under nitrogen. The infrared spectrum was recorded on a Perkin–Elmer System 2000 FT-IR spectrometer scanning between 400 and 4000 cm−1 using KBr disks. The chemical shifts for the 1H and 13C NMR spectra are reported in parts per million (ppm) at 400.13 and 100.63 MHz, respectively, with tetramethylsilane as external standard. The chemical shifts for the 31P NMR spectrum are reported in ppm at 161.97 MHz, with 85% H3PO4 as external standard. The FAB mass spectrum was recorded on a ZAB-HSQ-VC with 3-nitrobenzyl alcohol as matrix. The elemental analyses were recorded on a VARIO EL (Heraeus). The melting point was determined in a sealed capillary and was not corrected. The 2.50 M solution of n-ButLi in n-hexane (Aldrich) was used as purchased. [NiBr2(DME)] was prepared according to the literature [39].

Crystallographic data of 1 are listed in Table 1. The data were collected with a Siemens CCD (SMART) diffractometer using ω–scan rotation. Data reduction was performed with SADABS including the program SADABS for empirical absorption correction [40]. The structure was solved by heavy-atom methods and the refinement of all non-hydrogen atoms was performed with SHELX97 [40]. Due to the weakly diffracting, small crystal, the quality of our experimental results are relatively poor, although they are good enough for a structural confirmation of 1. The presentation of the molecular structure in this paper was generated with ORTEP [40].

#### 3.1. [Ni(1-NP(Mes2)2)-2-N(μ-P(Mes2)2)C6H4-k2N,N,P,k2P)]2 (1)

The anionic ligand [1,2-{N(PMes2)2}C6H4]2− was produced by the reaction of 1,2-{NP(Mes2)2}C6H4 with 2 equiv. of n-ButLi in toluene at room temperature.Treating the latter in situ with 1 equiv. of [NiBr2(DME)] resulted in the formation of precatalyst 1, which was characterized by NMR spectroscopy and X-ray diffraction.

The activation of complex 1 in toluene or dichloromethane by an excess of MAO results in the formation of species which are extremely active in the oligomerization of ethene and propene. For ethene oligomerization high TOF numbers were obtained and for propene TOFs of up to 1.2 × 106 h−1 was obtained. To the best of our knowledge, catalyst 1 activated by MAO exhibits the largest activity to propene oligomerization to date. In addition, the activated complex 1 was also found to be highly effective in the dimerization reactions of 1-hexene, 1,5-hexadiene, and isobutene.

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Ni:Al</th>
<th>Solvent</th>
<th>Time (h)</th>
<th>Product (g)</th>
<th>Activity (g mol−1 cat−1 h−1)</th>
<th>TOF (h−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Hexene</td>
<td>1:500</td>
<td>Toluene</td>
<td>4</td>
<td>2.4</td>
<td>8.4 × 10^4</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>1-Hexene</td>
<td>1:500</td>
<td>CH2Cl2</td>
<td>4</td>
<td>3.1</td>
<td>1.1 × 10^4</td>
<td>1292</td>
</tr>
<tr>
<td>3</td>
<td>1,5-Hexadiene</td>
<td>1:500</td>
<td>Toluene</td>
<td>4</td>
<td>1.2</td>
<td>4.2 × 10^4</td>
<td>512</td>
</tr>
<tr>
<td>4</td>
<td>1,5-Hexadiene</td>
<td>1:500</td>
<td>CH2Cl2</td>
<td>4</td>
<td>Dimers (60%), trimers (40%)</td>
<td>1.7 × 10^5</td>
<td>2050</td>
</tr>
</tbody>
</table>

Table 6. Oligomerization data for 1-hexene and 1,5-hexadiene with the complex 1.
C$_{4}$H$_{8}$Na$_{2}$Ni$_{2}$P$_{2}$: M = 1403.00. Anal. Calc. for C$_{4}$H$_{8}$Na$_{2}$Ni$_{2}$P$_{2}$ - 40E$_{2}$ (1699.49): C, 70.7; H, 8.0; N, 3.3. Found: C, 70.0; H, 9.4; N, 3.2%.

3.2. Reaction of complex 1 with ethene

In a glove box a high-pressure reactor (100 ml) was charged with complex 1 (10 mg, 7.13 × 10$^{-3}$ mmol), the desired amount of MAO according to the Ni:Al ratio, and 10 ml of solvent. Then the reactor was connected to a high-pressure line and filled with ethene (99.999%) at 20 atm. To maintain a constant pressure of 20 atm a solenoid valve was used. Hence, when the pressure in the reactor was reduced it was refilled constantly. After a specific amount of time, the reactor (kept at –30°C) was opened in a well-ventilated hood, the raw content was weighed, and the amount of products was calculated as the difference between the mass of raw content and the sum of the masses of the catalyst, MAO, and the solvent. The raw product was maintained at –30°C to keep the C$_{4}$ fraction liquid and filtered. From the resulting liquid samples for NMR and GCMS were taken. The solid material obtained at room temperature was washed with a 1:1 mixture of methanol and HCl (10 wt% solution), filtered again, washed with acetone, and dried under vacuum.

3.3. Reaction of complex 1 with propene

In a glove box, a high-pressure stainless steel reactor (100 ml) was charged with complex 1 (10 mg, 7.13 × 10$^{-3}$ mmol), the desired amount of MAO according to the Ni:Al ratio, and 10 ml of solvent. The reactor was connected to a high-vacuum line, and propene (50 ml, 25 g) was transferred to the reactor (propene was frozen with liquid nitrogen, and the volume measured in a heavy-duty calibrated glass vessel). The reactor was brought to room temperature and the mixture was stirred during the reaction time. At the beginning of the reaction the pressure of propene was 10–11 atm. A quick and exothermic reaction occurred, the pressure dropped to zero, and the reactor was opened. Immediately after opening the reactor the raw content was weighed and the amount of products was calculated as the difference between the mass of the raw contents and the sum of the masses of the catalyst, MAO, and the solvent. The raw product was filtered off. From the resulting liquid, samples were taken for NMR and GCMS.

3.4. Reaction of complex 1 with 1-hexene and 1,5-hexadiene

These reactions were carried out in a Schlenk tube, charged in a glove box with catalyst 1 (10 mg, 7.13 × 10$^{-3}$ mmol), the desired amount of MAO according to the Ni:Al ratio, and 10 ml of solvent. Then the Schlenk tube was connected to a vacuum line, and a measured amount (10 ml or 40 ml) of isobutene was transferred under vacuum to the reactor (by a similar procedure as for propene but at –30°C). After the reaction was finished the excess of isobutene was released in a well-ventilated hood. The products were separated similar to the procedure described for 1-hexene: a 1:1 mixture of methylene chloride and HCl (10 wt% in water) was added to the Schlenk tube. After neutralization of the catalytic mixture, the contents of the Schlenk tube were transferred to a separating funnel. The organic fraction was separated and dried with MgSO$_4$. After filtration the mixture was analyzed by NMR and GCMS.

4. Supplementary material

CCDC 652339 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References
