**Communication:** Nickel(II) and palladium(II) complexes of the general type [MCl$_2$\{Ph$_2$P(CH$_2$)$_n$PPh$_2$\}] with $n = 2$, 3 and M = Ni (**2**, **3**), Pd (**4**, **5**) have been utilized as catalysts for the polymerization reaction of norbornene. It was found that the use of B(C$_6$F$_5$)$_3$/triethylaluminium (TEA) in comparison to methylaluminoxane as an activator towards complexes **2**, **3** and **5** gave comparable polymerization activities, and the system **4**/B(C$_6$F$_5$)$_3$/TEA even led to an extremely high polymerization activity of 10^7 g$_{polymer}$/mol$_{metal}$ · h.

M = Ni (**2**), M = Pd (**4**)

M = Ni (**3**), M = Pd (**5**)
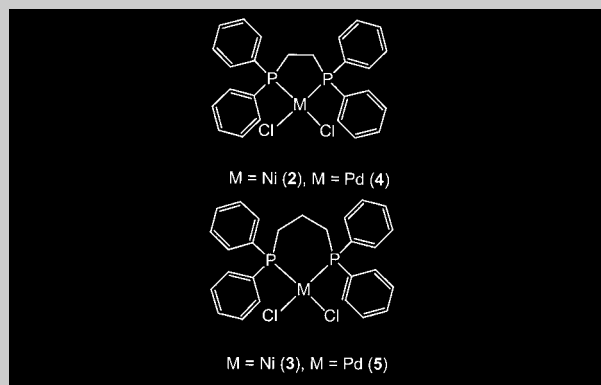
Borane Activators for Late-Transition Metal Catalysts in Norbornene Polymerization

Dedicated to Prof. Dr. Gerhard Herberich on the occasion of his 65th birthday

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Introduction

The majority of polyolefins is produced with titanium- (Ziegler catalysts), zirconium- (metallocene catalysts), and chromium-based catalysts (Unipol, Phillips catalysts) or by a free radical process (low-density polyethylene (LDPE)). Recently, late-transition metals, in particular nickel and palladium, are seeing a renewed interest as olefin polymerization catalysts.[1–3] Some of these late-transition metal complexes are directly active polymerization catalysts, mostly towards ethene, because they are cationic species with weakly bound ligands.[3,4] Others have to be activated with methylaluminoxane (MAO)[5] or so-called phosphane scavengers, such as Ni(cod)$_2$ (cod: 1,5-cyclooctadiene) or rhodium complexes to abstract phosphorus-bound ligands.[6] The use of the organic Lewis acid tris(pentafluorophenyl)borane (B(C$_6$F$_5$)$_3$, **1**)[7] in combination with and without TEA as an activator of late-transition metal complexes in olefin polymerization is also known and described in the literature.[8] Tris(perfluoroaryl)boranes also play an important role in catalyst activation and in the mechanistic under-standing of early-transition-metal group IV metallocene catalysts in olefin polymerization.[9–11] The borane abstracts an alkyl or hydride group from the metallocene precatalysts, becomes an anion and generates a highly active cationic metallocenium olefin polymerization catalyst. To the best of our knowledge, the use of the cocatalyst system **1**/TEA in the polymerization of norbornene has been described only once in a patent of the B.F. Goodrich Company (USA)[12] and communicated by the same author at conferences[13] but not published in regular journals. Here, we describe the use of **1**, in comparison to MAO as an activator towards nickel and palladium complexes **2**–**5** in the vinyl polymerization of norbornene. Phosphane complexes **2**–**5** have not been mentioned before for norbornene polymerization as well.[14]

The homopolymer vinyl-polynorbornene (**6**) is of inter-est as a specialty polymer with good mechanical strength, heat resistivity, and optical transparency for applications, such as deep ultraviolet photoresists, interlevel dielectrics in microelectronics applications, or as cover layers for liquid-crystal displays. Catalysts described in the litera-

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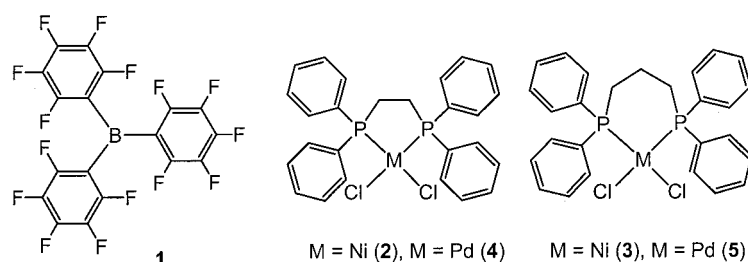
ture for the vinyl homopolymerization of norbornene are commonly activated with MAO except for the cationic palladium complexes $[Pd(NCR)_4]^{2+}2L^-$ (NCR: weakly bound nitrile ligand; L: non-coordinating counterion).[14]

norbornene   **6**   (1)
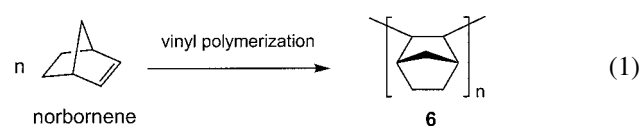
Experimental Part

Materials

1,2-Bis(diphenylphosphino)ethane (dppe; Aldrich), 1,3-bis-(diphenylphosphino)propane (dppp; Strem Chemicals), palladium(II) chloride (Merck-Schuchardt), $NiCl_2 \cdot 6H_2O$ (Acros), **1** (Aldrich), MAO (10% solution in toluene, Witco), and TEA (1 M solution in hexane, Merck-Schuchardt) were used as received. Toluene was dried over sodium metal and distilled under nitrogen. Methylene chloride was dried over CaH_2. Norbornene (bicyclo[2.2.1]hept-2-ene; Aldrich) was purified by distillation and used as a solution in toluene. All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or glovebox techniques.

Instruments

NMR spectra were recorded on a Varian O-300 (300 MHz) instrument. IR spectra (KBr pellets) were measured on a Bruker Optik IFS 25 and elemental analysis were obtained on a VarioEL from Elementaranalysensysteme GmbH. Gel permeation chromatography (GPC) analyses were performed on PL-GPC 220 with a polymer solution in 1,2,4-trichlorobenzene. The dried polymer samples were dissolved in 1,2,4-trichlorobenzene. The polymer solution was filtered (Schleicher & Schuell, Rezist 30/0, 45 PTFE, 0.45 μm, Grünrand) and the clear solution stored at 4–6 °C in a glass vial with a bakelite sealing and a polytetrafluoroethylene stopper. Filtration of the polymer solution should remove any catalyst residues for the protection of the GPC columns (PL gel 10 μm MIXED-B). The GPC was conducteded at 140 °C with an injection volume of 200 μl and with a rate of 1 mL/min. Thermal properties of the polymer samples were investigated under nitrogen with a heating rate of 10 K/min by thermogravimetric analysis (TGA), differential thermal analysis (DTA) on a Netzsch STA 409 and by differential scanning calorimetry (DSC) on a Netzsch DSC 200.

Preparation of the Precatalysts

Nickel(II) Complexes

Nickel(II) complexes were synthesized by the addition of dppe and dppp, respectively, in CH_2Cl_2 to a solution of $NiCl_2 \cdot 6H_2O$ in ethanol.[15]

Ni(dppe)Cl_2 (**2**): 90% yield; m.p. >215 °C.
^{1}H NMR (CDCl$_3$): δ = 2.14 (d, 4 H, CH$_2$, $^2J_{PH}$ = 17.5 Hz), 7.60–7.44 (m, 12 H, H$_{arom.}$), 8.05–7.94 (m, 8 H, H$_{arom.}$).
C$_{26}$H$_{24}$P$_2$NiCl$_2$ (528.0): Calcd. C 59.14, H 4.58; Found C 59.12, H 3.95.

Ni(dppp)Cl_2 (**3**): 82% yield; m.p. >215 °C.
^{1}H NMR (CDCl$_3$, paramagnetic sample): δ = −1.42 (s, br, 2 H, P—C—CH$_2$), 1.71 (s, 4 H, P—CH$_2$), 4.15 (s, br, 4 H, H$_{arom.}$), 5.63 (s, br, 8 H, H$_{arom.}$), 11.2 (s, br, 8 H, H$_{arom.}$).
C$_{27}$H$_{26}$P$_2$NiCl$_2$ (542.1): Calcd. C 59.83, H 4.83; Found C 59.25, H 4.18.

Palladium(II) Complexes

PdCl$_2$ was dissolved in hot conc. HCl. The cold solution was diluted with ethanol, filtered and the residue was washed with ethanol. A solution of dppe and dppp, respectively, in CH_2Cl_2 was added dropwise to the combined filtrates. The resulting suspension was stirred for 90 min at room temperature, filtered and dried in vacuo.

Pd(dppe)Cl_2 (**4**): 72% yield; m.p. >215 °C.
^{1}H NMR (DMSO-d_6): δ = 2.65 ("d", 4 H, CH$_2$, $^2J_{PH}$ = 24.4 Hz), 7.61–7.49 (m, 12 H, H$_{arom.}$), 7.87–7.80 (m, 8 H, H$_{arom.}$).
C$_{26}$H$_{24}$P$_2$PdCl$_2$ (575.8): Calcd. C 54.24, H 4.20; Found C 51.39, H 4.43.

Pd(dppp)Cl_2 (**5**): 83% yield; m.p. >215 °C.
^{1}H NMR (DMSO-d_6): δ = 1.69 (tquint, 2 H, P—CH$_2$—CH_2—CH$_2$—P, $^3J_{PH} \approx$ 23 Hz, $^3J_{HH} \approx$ 4 Hz), 2.65 ("quint", 4 H, P—CH$_2$), 7.51–7.40 (m, 12 H, H$_{arom.}$), 7.80–7.73 (m, 8 H, H$_{arom.}$).
C$_{27}$H$_{26}$P$_2$PdCl$_2$ (589.8): Calcd. C 54.99, H 4.44; Found C 54.27, H 4.11.

Polymerization Procedure

General

Precatalysts **2**, **3**, and **5** were applied as solutions in methylene chloride (4 mL). Complex **4** was dispersed in 4 mL of CH_2Cl_2 in an ultrasonic bath to give a fine slurry. Polymerizations were conducted at room temperature in a water bath to ensure a constant temperature during the reaction. Polymerization runs were carried out at least twice to ensure

reproducibility. The polymerizations with the borane activator were performed at least three times.

Procedure for the Homopolymerization of Norbornene with MAO as the Cocatalyst

A 50 mL Schlenk flask was charged with the norbornene solution and the MAO solution was added. After 1 min the solution of the precatalyst was added via syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped through the addition of 30 mL of a methanol/conc. HCl mixture (10:1). The precipitated polymer was isolated by filtration, washed with methanol and dried in vacuo for 5 h.

Procedure for the Homopolymerization of Norbornene with $B(C_6F_5)_3$/TEA as the Cocatalyst

A 100 ml Schlenk flask was charged with the norbornene solution. The solutions of the catalyst components (precatalyst and **1**) were quickly added consecutively via syringe and the mixture was stirred with a magnetic stirrer. The polymerization was started by adding TEA and was stopped through the addition of 40 mL of a methanol/conc. HCl mixture (10:1). The precipitated polymer was separated by filtration, washed with methanol and dried in vacuo for 5 h.

Results and Discussion

The results of the polymerization of norbornene using the different catalytic systems (complexes and activators) are summarized in Table 1 and Figure 1.

The metal-phosphane complexes **2**–**5** give rise to norbornene polymerization catalysts when activated with MAO or **1**/TEA. When borane **1** was used as the activator, TEA had to be simultaneously applied for the halide/alkyl exchange and as a scavenger for impurities. We
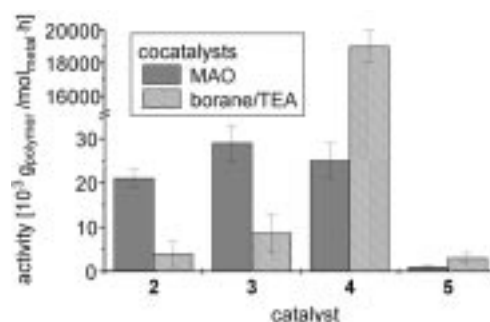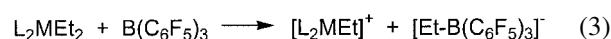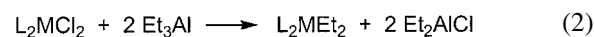

Figure 1. Polymerization activities of **2**–**5** with different cocatalysts in the polymerization of norbornene. Detailed conditions are given in Table 1. Error bars include the maximum/minimum deviation of the average activity in parallel experiments.

suggest that a chloride/ethyl exchange between the metal complex and TEA (Equation (2)) precedes the activation by the borane through alkyl abstraction as outlined in Equation (3). Alkylaluminium compounds are known as alkyl transfer agents.[16]

$$L_2MCl_2 + 2\,Et_3Al \longrightarrow L_2MEt_2 + 2\,Et_2AlCl \qquad (2)$$

$$L_2MEt_2 + B(C_6F_5)_3 \longrightarrow [L_2MEt]^+ + [Et\text{-}B(C_6F_5)_3]^- \qquad (3)$$

Borane alone is probably not capable of activating the metal-halide complex. With respect to zirconocene complexes, Cp_2ZrMe_2 instead of Cp_2ZrCl_2 had to be used in combination with the borane activator.[9a, 10] An alternative would have been a separate preparation of the metal-alkyl complex here. Yet, the possible in-situ formation of the labile and sensitive metal-alkyl species appears advantageously. The (expensive) borane is moreover not an efficient scavenger when applied in low molar excess. This necessitates the presence of TEA to avoid the

Table 1. Polymerization of norbornene (N) with catalysts **2**–**5**. General conditions: toluene/methylene chloride solution, room temperature.

Catalyst	Conversion %	Activity $g_{polymer}/mol_{metal} \cdot h$	$\overline{M}_w$ g/mol	$\overline{M}_w/\overline{M}_n$
2/MAO[a]	1.9	2.1×10^4	2.7×10^6	1.7
3/MAO[a]	2.5	2.9×10^4	2.6×10^6	1.9
4/MAO[a]	2.2	2.5×10^4	not soluble	not soluble
5/MAO[a]	0.1	1.1×10^3	not soluble	not soluble
2/$B(C_6F_5)_3$/TEA[b]	4.1	3.9×10^3	1.0×10^6	2.5
3/$B(C_6F_5)_3$/TEA[b]	9.0	8.6×10^3	8.1×10^5	2.4
4/$B(C_6F_5)_3$/TEA[c]	54.3	1.9×10^7	not soluble	not soluble
5/$B(C_6F_5)_3$/TEA[b]	3.1	3.0×10^3	not soluble	not soluble
2–**5**/$B(C_6F_5)_3$/–[d]	–	no activity observed	–	–
2–**5**/–/TEA[e]	–	no activity observed	–	–

[a] 10.6 mmol N, [cat]/[N] = 1:1000, [cat]/[Al] = 1:100, total volume: 10.0 mL, time: 5 min.
[b] 30.1 mmol N, [cat]/[N] = 1:1000, [cat]/[Bor]/[Al] = 1:9:10, total volume: 40.0 mL, time: 60 min.
[c] 30.1 mmol N, [cat]/[N] = 1:1000, [cat]/[Bor]/[Al] = 1:9:10, total volume: 40.0 mL, time: 10 s.
[d] 30.1 mmol N, [cat]/[N] = 1:1000, [cat]/[Bor]/[Al] = 1:9:0, total volume: 40.0 mL, time: 60 min.
[e] 30.1 mmol N, [cat]/[N] = 1:1000, [cat]/[Bor]/[Al] = 1:0:10, total volume: 40.0 mL, time: 60 min.

decomposition of the active species upon reaction with trace impurities. On the other hand, it was ascertained in separate experiments that TEA alone did not act as a cocatalyst or activator towards **2–5** in norbornene polymerization. MAO combines the function of alkyl-transfer agent, activator and scavenger.[10, 17] The molar metal/borane/TEA and metal/MAO ratios were 1:9:10 and 1:100, respectively. We would like to emphasize that the cocatalyst quantities required were much less with borane/TEA than with MAO for similar monomer conversions and activities. This leads to less cocatalyst residues in the polymer, which in term is highly advantageous for any prospective optical applications of polynorbornene.

The IR spectra of the polymers obtained with catalysts **2–5** proved the absence of a double bond at 1620 cm^{-1} to 1680 cm^{-1}, ensuring the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization (ROMP). The polymer samples obtained with precatalysts **2** and **4** and the two different cocatalyst systems MAO and **1**/TEA were investigated by means of TGA, DTA and DSC. TGA studies showed that the polymer samples were very stable up to about $400\,°C$ (under nitrogen). A more accurate decomposition temperature was obtained from DTA to be in the range of 435 to $438\,°C$ ($424\,°C$ for the polymer derived from **4**/MAO). Heating under air showed an earlier onset of decomposition around 250 to $300\,°C$. The determination of the glass transition temperature (T_g) of vinyl homo-polynorbornene has been described as being difficult, since it is apparently located close to the temperature range where decomposition tends to set in.[18 b] DSC studies did not show an endothermic signal upon heating up to $390\,°C$. Possibilities to determine T_g involve the extrapolation of the T_gs of copolymers towards that of polynorbornene (DSC) and the measurement of thermal density fluctuations through absolute small-angle X-ray scattering.[18]

The polymerization activities of precatalysts **2**, **3**, and **5** with the cocatalyst systems MAO and **1**/TEA show no dramatic differences. It is, of course, not appropriate to enter a detailed comparison because of the different complex/cocatalyst ratios and the different mode of cocatalyst action. Noteworthy is solely the extremely high activity of palladium-dppe complex **4** together with **1**/TEA in the reproducible order of 10^7 g$_{polymer}$/mol$_{Pd}$ · h. A conversion of 50% was reached after a polymerization time of 10 s. So far, only one other phosphane complex, Co(dppe)Cl$_2$ activated with MAO, has been described for the polymerization of norbornene.[19] A polymerization activity of up to 4.7×10^3 g$_{polymer}$/mol$_{Co}$ · h could be obtained with this cobalt complex, similar to the activities for nickel and palladium complexes **2–5** with MAO. No other phosphane ligands appear to have been used in the vinyl-polymerization of norbornene. It is not straightforward to rationalize the striking difference in activity between catalyst **4** and the other systems. We suggest that the four-membered chelate ligand provides a more open coordination sphere than the five-membered dppp ligand. The phenyl groups on the phosphorus atoms are more likely to block the access to the metal in the case of the dppp ligand. We note, however, that little is known about the active nickel or palladium species or the insertion mechanism in norbornene polymerization.[14] If the difference in activity can indeed be associated with the changes in the ligand, this suggests that the phosphane chelate remains bound to the metal in the active species.

Polymer solubilities were as expected from the literature. Polymers obtained with nickel catalysts **2** and **3** were soluble in 1,2,4-trichlorobenzene in a concentration of 2–3 mg/mL, whereas the palladium-derived polymers were insoluble in common solvents. Thus, only GPC data of the nickel-catalyzed polymers are available. The polymer samples displayed a monomodal molar mass distribution. The molar mass distribution $Q = \overline{M}_w/\overline{M}_n$ for the polymer samples is rather narrow and close to a value of 2. A value of $Q = 2$ is the theoretical dispersity for a Schulz-Flory-type distribution arising from an ideally behaved polymerization reaction with a chain-termination reaction. A dispersity of $Q \approx 2$ indicates a single-site character, i.e. a highly homogeneous structure of the active catalyst species.

Conclusions

Nickel(II) and palladium(II) complexes bearing bidentate phosphane ligands were used as precatalysts for the polymerization of norbornene. New precatalysts **2–5** were activated both with the already known cocatalyst MAO and the cocatalyst system B(C$_6$F$_5$)$_3$/TEA in separate experiments. With the exception of palladium system **4**, the cocatalysts MAO or B(C$_6$F$_5$)$_3$/TEA gave similar polymerization activities of about 10^3–10^4 g$_{polymer}$/mol$_{metal}$ · h. The polymerization of norbornene with PdCl$_2$(dppe) (**4**) and with B(C$_6$F$_5$)$_3$/TEA instead of MAO led to a high activity of 10^7 g$_{polymer}$/mol$_{Pd}$ · h. Polydispersities around $\overline{M}_w/\overline{M}_n = 2$ for the soluble, nickel-catalyzed polymer samples indicated a coordination polymerization with a single-site character of the active species.

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