Palladium(II) salts containing [PdCl$_4$]$^{2-}$ and [Pd$_2$Cl$_6$]$^{2-}$ ions as pre-catalysts for the vinyl-polymerization of norbornene— evidence for the *in situ* formation of PdCl$_2$ as the active species†

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The polymerization behaviour of a new series of palladium(II) pre-catalysts in the vinyl-polymerization of norbornene has been investigated. Compounds containing [PdCl$_4$]$^{2-}$ or [Pd$_2$Cl$_6$]$^{2-}$ anions and the organic cations [K(18-crown-6)]$^+$, [H$_3$O(18-crown-6)]$^+$, [Ph$_3$PCH$_2$C(O)CH$_3$]$^+$ or [Him]$^+$ (im = imidazole) can be activated with the Lewis acids methylalumoxane (MAO), tris(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$ or a combination of B(C$_6$F$_5$)$_3$/ triethylaluminum (TEA). The catalytic systems show very high norbornene polymerization activities of up to 10^7 g$_{polymer}$ mol$_{Pd}$$^{-1}$ h^{-1}. In the case of an activation with B(C$_6$F$_5$)$_3$ alone it is possible to obtain soluble palladium-catalyzed poly(norbornene)s which exhibit a fully saturated polymer backbone and a molar mass (M_n) between 8 × 10^3 and 3 × 10^5 g mol^{-1}. The activation process of the pre-catalyst [Ph$_3$PCH$_2$C(O)CH$_3$]$_2$[Pd$_2$Cl$_6$] (**2C**) in combination with B(C$_6$F$_5$)$_3$ can be followed by multinuclear (^{1}H, ^{13}C, ^{19}F and ^{31}P) NMR investigations and points to the *in situ* formation of PdCl$_2$ which then represents the active species for the polymerization process. The X-ray structure of compound **2C** is reported.

Introduction

Norbornene (bicyclo[2.2.1]hept-2-ene) can be polymerized *via* ring-opening metathesis polymerization (ROMP),[1–3] cationic or radical polymerization[4] and by olefin addition polymerization (vinyl-type polymerization)[5] (Scheme 1). In the latter case the bicyclic structure remains intact and only the π-bond of the cycloolefin will be opened.
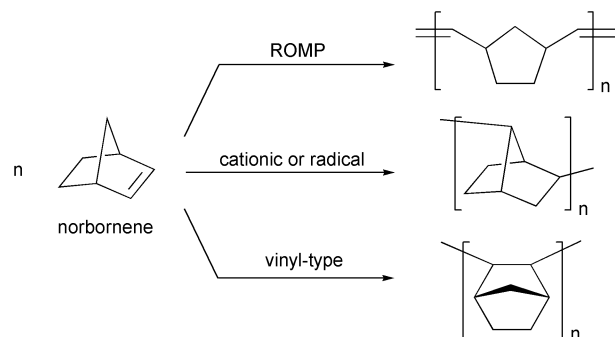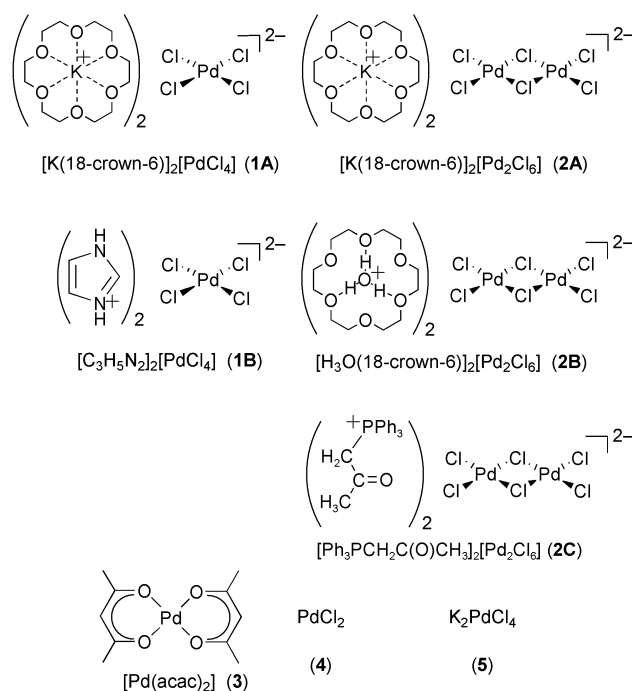

Scheme 1

Besides the well-known metallocene catalysts containing the early transition metals titanium[6] and zirconium[7] the late transition metals cobalt,[8] nickel[9–13] and palladium[14–18] are seeing a renewed interest as catalysts for the vinyl-polymerization of norbornene.[5,19,20] Typical palladium complexes employed in norbornene polymerization are cationic systems of type [Pd(NCR)$_4$]$^{2+}$2A$^-$ (ref. 14) or [L$_2$Pd(NCR)$_2$]$^{2+}$2A$^-$ (ref. 16) (NCR = weakly bound nitrile ligand, A = "non"-coordinating counter ion, L$_2$ = nitrogen or phosphorus donor ligand).[5] These cationic palladium complexes are polymerization-active without an additional co-catalyst, while neutral palladium complexes, *e.g.* L$_2$PdCl$_2$,[17] or nickel complexes[5,9,10,18] usually have to be activated with co-catalysts such as methylalumoxane (MAO) or tris(pentafluorophenyl)borane. The organo-Lewis acid tris-(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$[21] is probably best known

as a co-catalyst for the activation of early transition metal group 4 metallocene catalysts in olefin polymerization.[22–24] Recently, B(C$_6$F$_5$)$_3$ has been utilized in the activation process of late transition-metal complexes for the polymerization of cyclopentene,[25] ethene,[26] and norbornene.[10,17] Furthermore, the co-catalyst system B(C$_6$F$_5$)$_3$/TEA has been described for the polymerization of norbornene and norbornene derivatives in patents,[12,19,20,27,28] and communicated at conferences.[29] Contrary to metallocene catalysis[23,24] little is often known about the nature of the active species in MAO- or borane-activated late transition-metal olefin-polymerization catalysis.[5]

This work addresses the vinyl-polymerization of norbornene in the presence of a new class of palladium(II) pre-catalysts containing [PdCl$_4$]$^{2-}$ or [Pd$_2$Cl$_6$]$^{2-}$ anions and different organic counter-ions (Scheme 2). Anionic palladium complexes have not

Scheme 2 Pre-catalysts employed in the vinyl-polymerization of norbornene.

Scheme 3
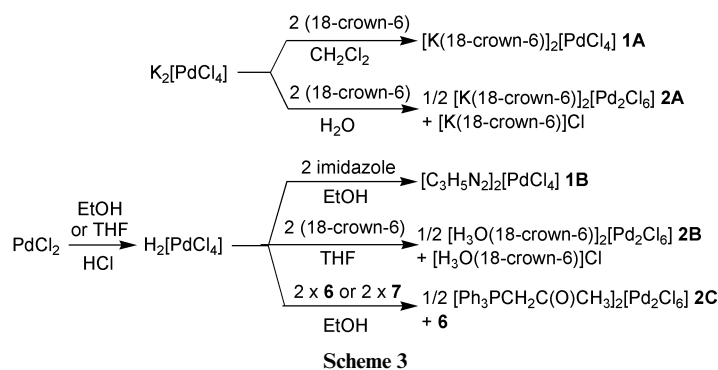
been employed in norbornene polymerization before.[5] Further comparison is made between MAO and the $B(C_6F_5)_3$ activator.

The homopolymer vinyl-poly(norbornene) is of interest as a specialty polymer with good mechanical strength, heat resistivity, and optical transparency, *e.g.* for deep ultraviolet photoresists, interlevel dielectrics in microelectronics applications or as cover layer for liquid-crystal displays.[5,30]

Results and discussion

Synthesis

Pre-catalysts **1A** and **2A** were synthesized by adding a solution of 18-crown-6 to a solution or a suspension of K_2PdCl_4. For the synthesis of **1B**, **2B** and **2C**, $PdCl_2$ was dissolved by the addition of small amounts of conc. HCl forming *in situ* the $[PdCl_4]^{2-}$ or $[Pd_2Cl_6]^{2-}$ anion. Addition of imidazole, 18-crown-6 or either acetonyltriphenylphosphonium chloride (**6**) or (acetylmethylene)triphenylphosphorane [(acetylmethylene)triphenyl-λ^5-phosphane] (**7**) to this solution resulted in the formation of the product complexes (Scheme 3).

Molecular structure of $[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]$ (2C)

The structure of complex **2C** was determined by single-crystal X-ray diffraction. The cation and anion moiety of **2C** are shown in Fig. 1. Distances for the hexachlorodipalladate(II) unit are as those seen before in other Pd_2Cl_6 structures.[31,32] There are no short interionic contacts.
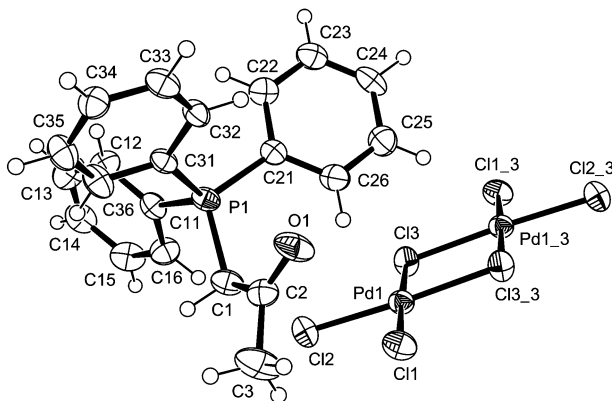

Fig. 1 Asymmetric unit of $[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]$ (**2C**). Selected distances [Å] and angles [°]: Pd1–Cl1 2.279(2), Pd1–Cl2 2.269(2), Pd1–Cl3 2.329(2), Pd1–Cl3_3 2.321(2), Pd1–Pd1_3 3.3781(9). P1–C1 1.813(6), O1–C2 1.203(7), C1–C2 1.530(8), Cl2–Pd1–Cl1 92.41(6), Cl2–Pd1–Cl3_3 176.11(6), Cl1–Pd1–Cl3_3 91.05(6), Cl2–Pd1–Cl3 89.73(6), Cl1–Pd1–Cl3 177.86(6)Cl3_3–Pd1–Cl3 86.81(5), C2–C1–P1 114.6(4), O1–C2–C3 123.0(6), O1–C2–C1 120.5(5), C3–C2–C1 116.5(5); symmetry transformation _3 = −x + 1, −y, −z. The second hydrogen atom of C1 is obscured by C2.

Polymerization activities

Palladium(II) complexes **1A**–**2C** containing anionic $[PdCl_4]^{2-}$ or $[Pd_2Cl_6]^{2-}$ moieties in combination with different cations were found to be active in the homopolymerization of norbornene. The results of the polymerization activities using methylaluminoxane (MAO) as co-catalyst are summarized in Table 1 and Fig. 2. To calibrate the polymerization activities of these anionic pre-catalysts the known compound bis(acetylacetonato)palladium(II) (**3**) and the simple inorganic palladium(II) salts $PdCl_2$ (**4**) and K_2PdCl_4 (**5**) were also tested under the same polymerization conditions.
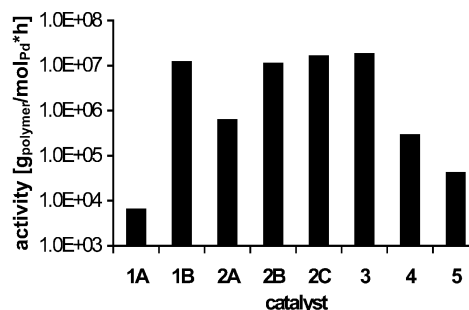
Fig. 2 Activities of **1A**–**5** with MAO as co-catalyst in the polymerization of norbornene. Detailed conditions are given in Table 1.

The polymerization activities of complexes **1A**–**2C** with MAO as co-catalyst covered a range of 6.3×10^3 (**1A**/MAO) to 1.6×10^7 /$g_{polymer}$ mol_{Pd}^{-1} h^{-1} (**2C**/MAO). In particular, the catalysts based on **2C**, **2B** and **1B** were as active as the reference catalyst **3**. Pre-catalyst **3** is known as a palladium ion source in the polymerization of norbornene and norbornene derivatives.[12,19,28] Complex **3** has been described as a catalyst in the presence of activating agents like hexachloroacetone/TEA.[27] To the best of our knowledge the use of **3** in combination with MAO as activating agent has not yet been described in the literature.[5] It is interesting that the protic cations [Himi]$^+$ (**1B**) and [H_3O(18-crown-6)]$^+$ (**2B**) do not seem to effect the activation process by MAO whereas the polymerization activities of the compounds **1A** and **2A** which contain the cations [K(18-crown-6)]$^+$ are considerably lower and similar to the polymerization activities of the simple palladium salts **4** and **5**. The polymers were not soluble in common solvents and could therefore not be investigated by gel permeation chromatography (GPC) except for the polymer obtained with the low-active pre-catalyst **1A**. The insolubility of some palladium(II)-catalyzed poly(norbornene)s compared to polymers derived from analogous nickel(II) catalysts is well established in the literature.[5,17,14,18,19,33]

Mechanistic investigations with MAO as a co-catalyst are problematic since the exact composition and structure of MAO is still not entirely clear.[23,34–36] In order to gain additional information about the activation process the activator was changed from MAO to the well-defined co-catalyst $B(C_6F_5)_3$ with or without triethylaluminum (TEA). The results of the polymerization of norbornene with the pre-catalysts **1A**–**2C** in combination with $B(C_6F_5)_3$/TEA or with $B(C_6F_5)_3$ alone are summarized in Table 2 and Fig. 3. For comparison the poly-

Table 1 Polymerization of norbornene (NB) with the catalysts **1A**–**5** in combination with methylalumoxane (MAO)

Catalyst	Time/min	Conversion (%)	Polymer yield/g	Activity/$g_{polymer}$ mol_{Pd}^{-1} h^{-1}
1A/MAO[a]	60	6.7	0.067	$6.3 \times 10^{3\,d}$
1B/MAO[a]	1/6	36.5	0.365	1.2×10^7
2A/MAO[a]	1	10.9	0.109	6.2×10^5
2B/MAO[a]	1/6	33.7	0.337	1.1×10^7
2C/MAO[a]	1/6	46.0	0.460	1.6×10^7
3/MAO[b]	1/6	51.7	0.517	1.8×10^7
4/MAO[b]	2	10.0	0.500	2.8×10^5
5/MAO[b]	2	1.4	0.072	4.1×10^4
1A/**5**[c]	60	–	–	No activity

Conditions: room temperature; toluene–methylene chloride solution for catalysts **1A**–**2C**; toluene solution for catalysts **3**–**5**. [a] 10.6 mmol NB, [Pd] : [NB] = 1 : 1000, [Pd] : [Al] = 1 : 100, total volume 10.0 mL. [b] 53.2 mmol NB, [Pd] : [NB] = 1 : 1000, [Pd] : [Al] = 1 : 100, total volume 50.0 mL. [c] 10.6 mmol NB, [Pd] : [NB] = 1 : 1000, total volume 10.0 mL. [d] The sample was only partly soluble in 1,2,4-trichlorobenzene and the GPC data correspond to the data of the soluble part of the polymer: $M_n = 1.1 \times 10^5$ g mol^{-1}, $M_w = 2.2 \times 10^5$ g mol^{-1}, $M_w/M_n = 2.1$.

Table 2 Polymerization of norbornene (NB) with the catalysts **1A**–**5** in combination with B(C$_6$F$_5$)$_3$ and triethylaluminum (TEA)

Catalyst	Time/min	Conversion (%)	Polymer yield/g	Activity/$g_{polymer}$ mol_{Pd}^{-1} h^{-1}	M_n/g mol^{-1}	M_w/g mol^{-1}	$Q = M_w/M_n$
1A/B(C$_6$F$_5$)$_3$/TEA[a]	1/6	35.0	0.992	1.2×10^7		Not soluble	
1B/B(C$_6$F$_5$)$_3$/TEA[a]	1/6	12.4	0.351	4.2×10^6		Not soluble	
2A/B(C$_6$F$_5$)$_3$/TEA[a]	1/6	95.7	2.712	3.3×10^7		Not soluble	
2B/B(C$_6$F$_5$)$_3$/TEA[a]	1/6	84.9	2.406	2.9×10^7		Not soluble	
2C/B(C$_6$F$_5$)$_3$/TEA[a]	1/6	44.4	1.258	1.5×10^7		Not soluble	
3/B(C$_6$F$_5$)$_3$/TEA[a]	1	90.2	2.556	5.1×10^6		Not soluble	
4/B(C$_6$F$_5$)$_3$/TEA[a]	1	3.9	0.111	2.2×10^5		Not measured	
1A/**4**/–/TEA[b]	60	–	–	No activity	–	–	–
1A/B(C$_6$F$_5$)$_3$/–[c]	60	46.1	1.306	4.4×10^4	8.2×10^3	1.5×10^4	1.8
1B/B(C$_6$F$_5$)$_3$/–[c]	60	29.3	0.830	2.8×10^4	3.2×10^5	5.6×10^5	1.8
2A/B(C$_6$F$_5$)$_3$/–[c]	60	76.9	2.179	7.3×10^4	2.1×10^4	3.2×10^4	1.5
2B/B(C$_6$F$_5$)$_3$/–[c]	60	73.5	2.083	6.9×10^4	5.4×10^4	8.1×10^4	1.6
2C/B(C$_6$F$_5$)$_3$/–[c]	60	99.7	2.825	9.4×10^4	3.3×10^4	4.2×10^4	1.3
3/B(C$_6$F$_5$)$_3$/–[c]	1	25.7	0.728	1.5×10^6		Not soluble	
4/B(C$_6$F$_5$)$_3$/–[c]	60	1.3	0.038	1.3×10^3		Not measured	

Conditions: room temperature; toluene–methylene chloride solution for catalysts **1A**–**2C** and toluene solution for catalyst **3**. [a] 30.1 mmol NB, [Pd] : [NB] = 1 : 1000, [Pd] : [Bor] : [Al] = 1 : 9 : 10, total volume 40.0 mL. [b] 30.1 mmol NB, [Pd] : [NB] = 1 : 1000, [Pd] : [Bor] : [Al] = 1 : – : 10, total volume 40.0 mL. [c] 30.1 mmol NB, [Pd] : [NB] = 1 : 1000, [Pd] : [Bor] : [Al] = 1 : 9 : –, total volume 40.0 mL.
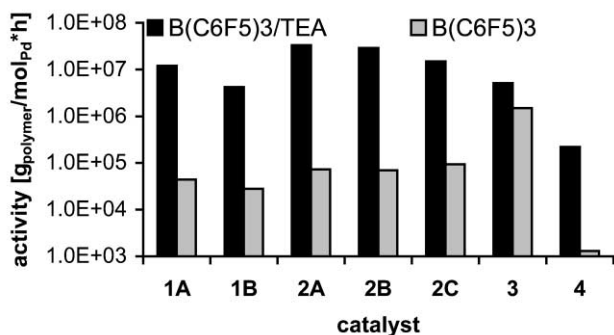
Fig. 3 Activities of **1A**–**4** with B(C$_6$F$_5$)$_3$/TEA or B(C$_6$F$_5$)$_3$ alone as co-catalysts in the polymerization of norbornene. Detailed conditions are given in Table 2.

merization data of bis(acetylacetonato)palladium(II) (**3**) and PdCl$_2$ (**4**) are included.

The different catalysts show similar polymerization activities with B(C$_6$F$_5$)$_3$/TEA. The polymerization activities cover a smaller range of 4.2×10^6 (**1B**/B(C$_6$F$_5$)$_3$/TEA) to 3.3×10^7 $g_{polymer}$ mol_{Pd}^{-1} h^{-1} (**2A**/B(C$_6$F$_5$)$_3$/TEA) than seen for MAO. The activities are even higher than that of the reference compound **3** and the simple palladium salt **4**. Activation of **3** by B(C$_6$F$_5$)$_3$/TEA has not been reported in the literature but a nearly similar polymerization activity of 2.0×10^5 $g_{polymer}$ mol_{Pd}^{-1} h^{-1} could be achieved using hexachloroacetone/TEA as co-catalyst system.[27] The polymerization activity of **1A**–**2C** with B(C$_6$F$_5$)$_3$/TEA was influenced less by the nature of the complex than with MAO. Furthermore, we note that for similar monomer conversions

and polymerization activities the required co-catalyst quantities were much lower with B(C$_6$F$_5$)$_3$/TEA than with MAO (molar ratios of Pd : borane : TEA = 1 : 9 : 10 and Pd : MAO = 1 : 100). This leads to fewer co-catalyst residues in the polymer which should be highly advantageous for the prospective optical applications of poly(norbornene).

Activation of the pre-catalysts **1A**–**2C** with B(C$_6$F$_5$)$_3$ alone led to a substantial drop in the polymerization activities by a factor of 100 to 500 when compared to the activation with B(C$_6$F$_5$)$_3$/TEA. However, the activity of **3** with B(C$_6$F$_5$)$_3$ was only slightly lower than that of **3** with B(C$_6$F$_5$)$_3$/TEA. PdCl$_2$ (**4**) with B(C$_6$F$_5$)$_3$ showed a considerably lower polymerization activity in comparison to the pre-catalysts **1A** to **2C** with B(C$_6$F$_5$)$_3$. Also, catalysts based on **2A** and **2B** display a similar high activity for polymerization when they are activated with B(C$_6$F$_5$)$_3$/TEA (Fig. 3), however the polymerization activity differs by more than one order of magnitude when MAO is used as the co-catalyst (Fig. 2). The activity trends are difficult to explain in the absence of a more profound knowledge of the active species. Generally, the active species in MAO- or B(C$_6$F$_5$)$_3$-activated Ni- or Pd-complexes are not well known.[5] Some investigations to be discussed below were aimed at increasing the understanding of the activation process of these pre-catalysts. The high Lewis acidity of B(C$_6$F$_5$)$_3$ with its perfluorated phenyl ligands plays an important role in the formation of the active species. It was shown for the otherwise highly active complexes bis(acetylacetonato)nickel(II) and bis(2-ethylhexanoato)nickel(II) that the weaker Lewis acid B(C$_6$H$_5$)$_3$ led to no polymerization activity.[10]

Surprisingly, poly(norbornene)s obtained with **1A**–**2C**/B(C$_6$F$_5$)$_3$ were completely soluble in 1,2,4-trichlorobenzene

and it was possible to characterize them with GPC and ^{1}H NMR measurements. The ^{1}H NMR spectra (Fig. 4) as well as the IR spectra are characteristic for the fully saturated polymer backbone of vinyl poly(norbornene) and showed no traces of double bonds which are typical for metathesis-type poly(norbornene).
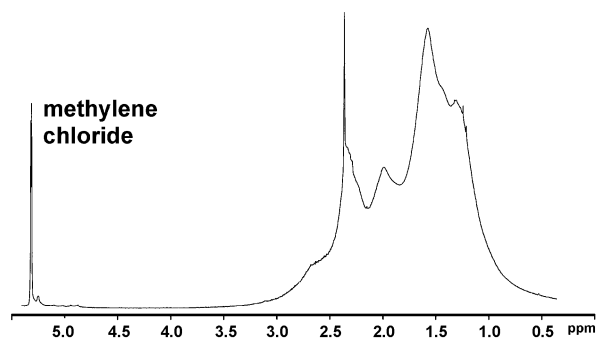

Fig. 4 ^{1}H NMR spectrum of a poly(norbornene) obtained in the presence of [K(18-crown-6)]$_2$[PdCl$_4$] (**1A**) and B(C$_6$F$_5$)$_3$ and recorded in 1,2,4-trichlorobenzene (0.4 mL) and CD$_2$Cl$_2$ (0.2 mL) at room temperature.

In the GPC, all soluble polymer samples displayed a monomodal molar mass distribution and the number-average molar mass (M_n) was found between 8.2×10^3 and 3.2×10^5 g mol^{-1}. Thus, the average chain length for the polymers laid between 90 [**1A**/B(C$_6$F$_5$)$_3$] and 3400 [**1B**/B(C$_6$F$_5$)$_3$] monomer units ($M_{norbornene} = 94.16$ g mol^{-1}). The molar mass distributions Q for these soluble polymer samples were extremely narrow with dispersities M_w/M_n in the range 1.3–1.8. Dispersities smaller than 2 seem to contradict a Schulz–Flory distribution for an insertion polymerization with chain transfer. However, Schulz–Flory demands a long chain polymerization process. Towards shorter chain oligomers the statistical treatment with $Q \geq 2$ does not hold anymore.[37] A dispersity of $Q < 2$ can also be explained by a chain-length dependent insertion rate in the case of oligomeric products.[38] The possibility to synthesize well defined poly(norbornene)s with low molar mass and high solubility may be an important step for the determination of the polymerization mechanism and for investigations concerning the structure of the polymer chain.[39]

Investigations of the activation process with complex 2C and the co-catalysts B(C$_6$F$_5$)$_3$/TEA

For pre-catalyst **2C** the activation process with the Lewis acid B(C$_6$F$_5$)$_3$ was investigated by using IR and multinuclear NMR measurements. For an understanding of the spectral features the interaction of compounds **6** and **7** with B(C$_6$F$_5$)$_3$ was studied separately. The NMR spectra of **6** are indicative of a keto–enol tautomerism (Scheme 4).[40] The origin of enol formation may be hydrogen bonding to the chloride anion in non-coordinating solvents (see below).
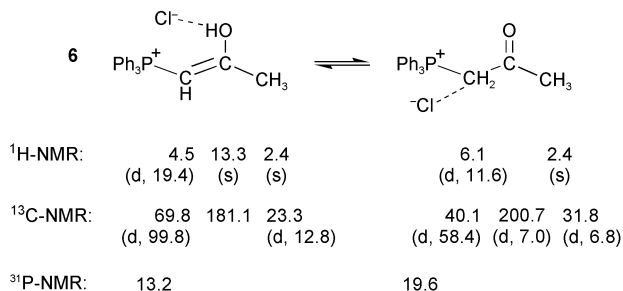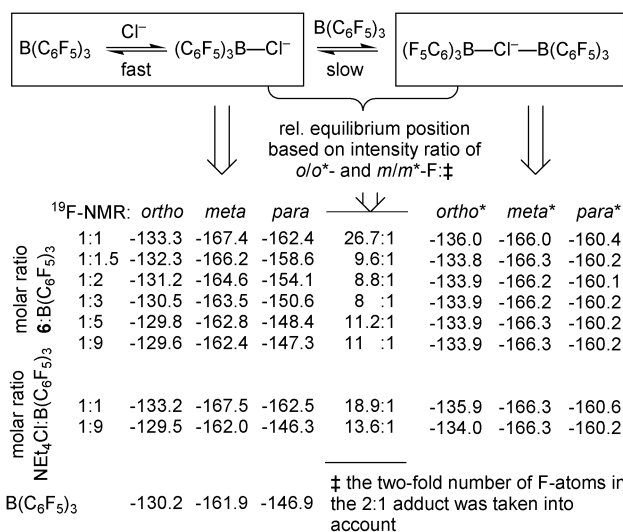

Scheme 4 ^{1}H, ^{13}C and ^{31}P NMR data of the keto–enol tautomerism of compound **6** (CD$_2$Cl$_2$, room temperature, data given in ppm including J_{PH} in Hz). See the ESI †for complete spectroscopic details.

The keto–enol ratio from ^{1}H NMR of 56 : 44 matches the literature data of "close to 50 : 50".[40] In the enol form the Ph$_3$P group and the oxygen atom are *cis* to each other, because of the repulsion between Ph$_3$P and the methyl group.[41–43] Reaction of **6** with B(C$_6$F$_5$)$_3$ (molar ratios from 1 : 1 to 1 : 9) involves mainly formation of a boron–chloride adduct (see below). This leaves the [Ph$_3$PCH$_2$C(O)CH$_3$]$^+$ cation solely in the keto form as shown by NMR (Scheme 5). Binding of the chloride anion by B(C$_6$F$_5$)$_3$ apparently removes the incentive for enol formation. All NMR signals correspond to the "free" cation [Ph$_3$PCH$_2$-C(O)CH$_3$]$^+$. Most of the signals remain mostly unchanged and there are no additional signals with increase in B(C$_6$F$_5$)$_3$, hence, no strong interaction between the cation and the borane can be seen. Some weak B · · · O coordination may be present, however, as deduced from IR spectroscopy (see below). The high-field ^{1}H NMR chemical shift for –CH$_2$– from 6.1 ppm in [Ph$_3$PCH$_2$C(O)CH$_3$]$^+$Cl$^-$ (Scheme 4) to 4.5 ppm in [Ph$_3$-PCH$_2$C(O)CH$_3$]$^+$ (Scheme 5) can be traced to the removal of C–H · · · Cl$^-$ interactions.[44]
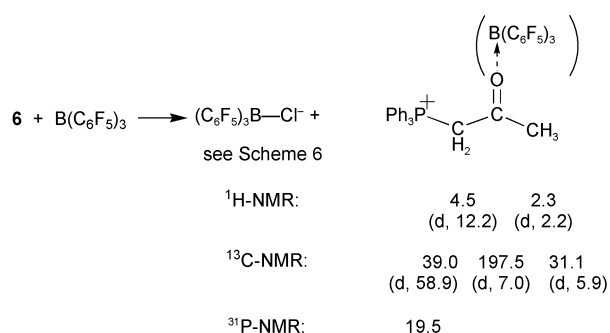
Scheme 5 ^{1}H, ^{13}C and ^{31}P NMR data of the interaction between **6** and B(C$_6$F$_5$)$_3$ (CD$_2$Cl$_2$, room temperature, data given in ppm including J_{PH}, J_{PC} in Hz). See the ESI †for complete spectroscopic details.

The features in the ^{19}F NMR of the B(C$_6$F$_5$)$_3$ moiety (Fig. 5) have to be explained by a fast equilibrium on the NMR time scale between free borane and a 1 : 1 boron–chloride adduct together with an additional slow equilibrium to a 2 : 1 boron–chloride adduct as depicted in Scheme 6. The averaged signals for the fast equilibrium between free borane and the 1 : 1 adduct are shifted towards the signals for pure B(C$_6$F$_5$)$_3$ with increasing borane ratio. The signals for the 2 : 1 adduct remain constant. The assignment and the formation of a boron–chloride adduct was verified by an independent invest-

^{19}F-NMR:	ortho	meta	para		ortho*	meta*	para*
1:1	-133.3	-167.4	-162.4	26.7:1	-136.0	-166.0	-160.4
1:1.5	-132.3	-166.2	-158.6	9.6:1	-133.8	-166.3	-160.2
1:2	-131.2	-164.6	-154.1	8.8:1	-133.9	-166.2	-160.1
1:3	-130.5	-163.5	-150.6	8 :1	-133.9	-166.2	-160.2
1:5	-129.8	-162.8	-148.4	11.2:1	-133.9	-166.3	-160.2
1:9	-129.6	-162.4	-147.3	11 :1	-133.9	-166.3	-160.2
1:1	-133.2	-167.5	-162.5	18.9:1	-135.9	-166.3	-160.6
1:9	-129.5	-162.0	-146.3	13.6:1	-134.0	-166.3	-160.2
B(C$_6$F$_5$)$_3$	-130.2	-161.9	-146.9				

molar ratio **6**:B(C$_6$F$_5$)$_3$ / molar ratio NEt$_4$Cl:B(C$_6$F$_5$)$_3$

‡ the two-fold number of F-atoms in the 2:1 adduct was taken into account

Scheme 6 ^{19}F NMR data of the interaction between Cl$^-$ (from **6** or NEt$_4$Cl) and B(C$_6$F$_5$)$_3$ (CD$_2$Cl$_2$, room temperature, data given in ppm). See the ESI † for signal multiplicity, FF coupling constants, ^{13}C NMR signals and further details.
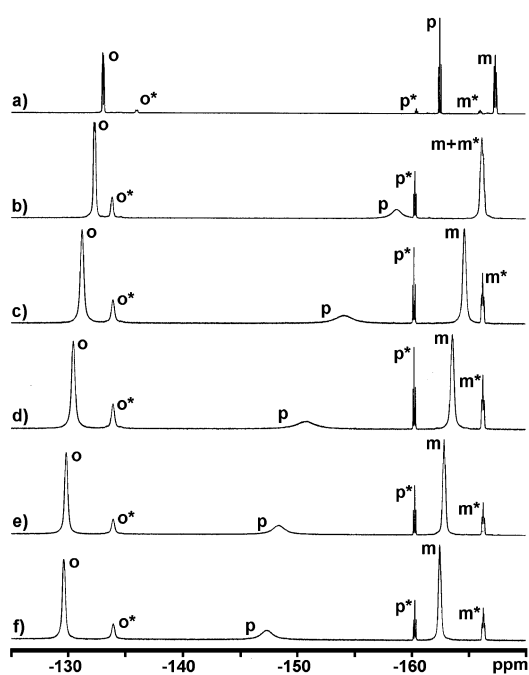
Fig. 5 ^{19}F NMR spectra of acetonyltriphenylphosphonium chloride (**6**) in combination with different amounts of B(C$_6$F$_5$)$_3$. The molar equivalents of **6** : B(C$_6$F$_5$)$_3$ in the different spectra were as follows: (a) 1 : 1, (b) 1 : 1.5, (c) 1 : 2, (d) 1 : 3, (e) 1 : 5 and (f) 1 : 9. The letters *o*, *m*, *p* indicate the *ortho*, *meta* and *para* fluorine atoms of B(C$_6$F$_5$)$_3$ in the fast equilibrium between B(C$_6$F$_5$)$_3$ and (F$_5$C$_6$)$_3$B–Cl$^-$. The letters *o**, *m**, *p** indicate the *ortho*, *meta* and *para* fluorine atoms of B(C$_6$F$_5$)$_3$ in the 2 : 1 B–Cl$^-$–B species (*cf.* Scheme 6). The spectra were measured in CD$_2$Cl$_2$ at room temperature (0.07 mmol B(C$_6$F$_5$)$_3$ for the spectra (a)–(e) and 0.063 mmol for spectrum (f)).

Scheme 7 ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR data of the interaction between **7** and B(C$_6$F$_5$)$_3$ (CD$_2$Cl$_2$, room temperature, data given in ppm including J_{PH} or J_{PC} in Hz); * indicates overlapping signals. See the ESI † for ^{19}F signal multiplicity, FF coupling constants and further details.

igation of tetraethylammonium chloride, NEt$_4$$^+Cl^-$ with B(C$_6$F$_5$)$_3$ where the same signal pattern could be observed.

The IR spectrum of **6** in CD$_2$Cl$_2$ exhibits two characteristic bands at 1718 and at 1608 cm^{-1} (in the range between 1800 and 1500 cm^{-1}) which can be assigned to the valence vibrations v(C=O) and v(C=C) of the keto–enol tautomers. After the addition of 1 or 9 equivalents of B(C$_6$F$_5$)$_3$ to **6** the v(C=C) band disappeared and the v(C=O) band was shifted slightly from 1718 to 1725 or 1727 cm^{-1}, respectively, perhaps due to some weak C=O $\cdots$ B interaction.

In accordance with literature data, compound **7** exists predominantly in the cisoid form because of repulsion between Ph$_3$P and the methyl group (*cf.* **6**).[43,45,46] In addition there are mesomeric forms for **7** (see Scheme 7). NMR data for **7**[47,48] and complexes thereof[49,50] can be found in the literature. Based on a known coordination of **7** to palladium,[51] a boron adduct of **7** may be envisioned through the oxygen atom (conformational isomeric cisoid or transoid form) or the (carb)anionic methine carbon.

The NMR spectral features of **7**/B(C$_6$F$_5$)$_3$ (molar ratio 1 : 1) can be explained by an equilibrium between B–O and B–C coordination. The latter leads to an asymmetric carbon atom and two enantiomeric forms (Scheme 7). A high-field shift in the ^{31}P NMR spectrum of **7**/acceptor *vs.* **7** (12.5 *vs.* 14.3 ppm) is known to be indicative of an oxygen coordination, a low-field shift (19.4 *vs.* 14.3 ppm) is indicative of a carbon adduct.[52,53] The remaining signal (15.6 ppm) was assigned to boron coordinating to the oxygen atom of the transoid form.[51] The signal intensity ratio for cisoid : transoid of 3.4 : 1 matches the ratio found in the literature for the palladium complex [Pd(C$_6$H$_4$CH$_2$N(CH$_3$)$_2$-2)(PPh$_3$)(Ph$_3$PCHC(O)CH$_3$)][ClO$_4$] of **7** (3.2 : 1).[51] The transoid form, absent in **7**, is observed in the boron adduct because of the increased steric interaction between the triphenylphosphorus and the borane moiety. In ^{1}H NMR spectrum the three groups of signals are assigned based
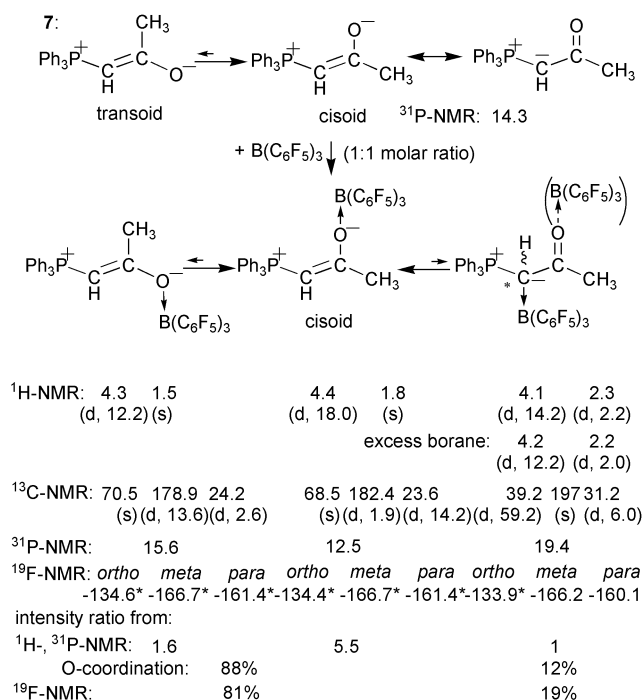
on the intensities in the ^{31}P NMR spectrum. The proton chemical shifts for the three coordination modes correspond well to those of respective palladium complexes.[51,53–55] Also, the cisoid : transoid (B–O) ratio is 3.4 : 1 in ^{1}H NMR. Similarly, the three groups of signals in ^{13}C NMR are assigned to the three isomers.[51] Furthermore, in ^{19}F NMR three groups of signals can be found, with the *ortho*-fluorine atoms of all three species overlapping.

IR spectroscopy for **7**/B(C$_6$F$_5$)$_3$ (1 : 1) shows one band for the C=O vibration at 1553 cm^{-1} which is indicative of B–O coordination and a second one at 1727 cm^{-1} indicative of B–C coordination. A distinction between cisoid and transoid form has not been described.[51,53,54,56] No band is observed anymore at 1536 cm^{-1} for the v(C=O)$\leftrightarrow v$(C–O$^-$) vibration in **7**.

At a molar ratio of 1 : 9 for **7**/B(C$_6$F$_5$)$_3$ only the set of signals which was attributed to the B–C coordination remained visible in ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR with some very minor changes only in proton NMR (see Scheme 7). Fluorine NMR shows, of course, also peaks for the free borane. At excess borane the equilibrium is, thus, shifted to a single species, perhaps with the support of some weak B $\cdots$ O coordination. The IR spectrum of **7**/B(C$_6$F$_5$)$_3$ (1 : 9) shows the band for B–C coordination at 1727 cm^{-1} and a weak band at 1531 cm^{-1}.

Reaction of complex **2C** with B(C$_6$F$_5$)$_3$ [molar ratio Pd : B(C$_6$F$_5$)$_3$ = 1 : 9] in CD$_2$Cl$_2$ resulted in the formation of a soluble part and a red precipitate which was investigated separately (see below). The ^{1}H, ^{19}F and ^{31}P NMR spectra of the soluble part of **2C**/B(C$_6$F$_5$)$_3$ (molar ratio Pd : B = 1 : 9) correspond completely to the spectra of **6** in combination with 9 equivalents of B(C$_6$F$_5$)$_3$. The ^{19}F NMR spectra demonstrates again the presence of the two different equilibria with different boron–chloride adducts as explained in the case of **6**/B(C$_6$F$_5$)$_3$. The intensity ratio of the two boron–chloride species from **2C**/B(C$_6$F$_5$)$_3$ with a molar ratio Pd : B(C$_6$F$_5$)$_3$ = 1 : 9 matches the intensity ratio observed for **6**/B(C$_6$F$_5$)$_3$ with a molar ratio of 1 : 9 (see Fig. 6). This agreement suggests that one chlorine is provided by each palladium and supports the formulation of the activation reaction in Scheme 8.

The red precipitate mentioned above could be redissolved in [D$_6$]DMSO. The ^{1}H, ^{31}P and ^{19}F NMR spectra of this solution
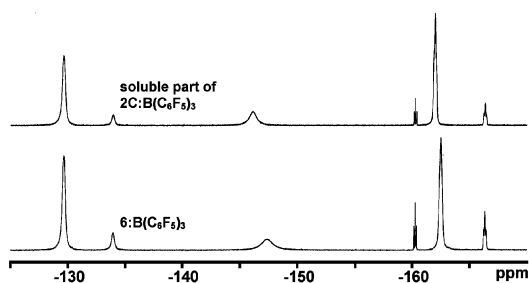
Fig. 6 ^{19}F NMR spectra of $[Ph_3PCH_2C(O)CH_3^+]_2[Pd_2Cl_6]$ (**2C**, 0.0035 mmol) and acetonyltriphenylphosphonium chloride (**6**, 0.007 mmol) in combination with $B(C_6F_5)_3$ (0.063 mmol) (molar ratios P or Pd : B = 1 : 9). See caption to Fig. 5 for the assignment of *o*, *m*, *p*. The spectra were measured in CD_2Cl_2 at room temperature.
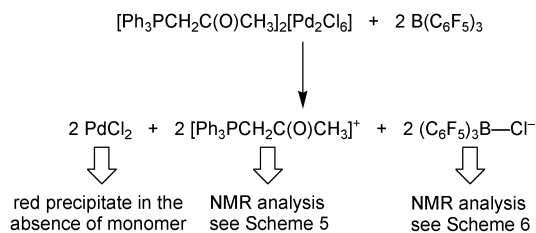
Scheme 8 Activation process of pre-catalyst **2C** with the Lewis acid $B(C_6F_5)_3$ for the vinyl-polymerization of norbornene.

showed no signals. Therefore, the red precipitate is proposed to be the purely inorganic compound $PdCl_2$. Bulk (commercial) $PdCl_2$ is a red solid which has very little solubility in CD_2Cl_2 even in the presence of $B(C_6F_5)_3$.

The red precipitate shows a shoulder at 345 cm^{-1} and a peak at 327 cm^{-1} in the IR spectrum between 400 and 200 cm^{-1}. This agrees with the reported IR frequencies for the β- or α-form of $PdCl_2$,[57] *i.e.* discrete molecular Pd_6Cl_{12} clusters or infinite chains of edge-sharing $PdCl_4$ squares.[58] $PdCl_2$ is polymorphic with α-$PdCl_2$ being the high-temperature form (above 500 °C) and β-$PdCl_2$ the low-temperature form.[59] In addition, evidence of a third form, γ-$PdCl_2$, also a low-temperature modification, is provided but no structural details are known. Commercial $PdCl_2$ may usually be this γ-form.[60–62] X-Ray powder diffractometry (radiation at 0.7093 Å) of the red precipitate gave the following peaks at $2\theta/°$ (*d*/Å) 5.930 (6.857), 6.245 (6.510), 8.612 (4.724), 10.125 (4.019), 10.796 (3.770), 12.486 (3.261), 13.436 (3.032), 13.838 (2.944), 15.218 (2.678), 15.559 (2.620) and 16.108 (2.531) which correspond perfectly to the diffractogram reported for β-$PdCl_2/Pd_6Cl_{12}$.[62]

We also attempted a mass spectroscopic (MS) investigation of the red precipitate. The mass spectrum of β-$PdCl_2/Pd_6Cl_{12}$ shows the molecular ion as the base peak.[59,60,62,63] From α- or γ-$PdCl_2$ the β-form may be formed at elevated temperature (>400 °C) under mass spectrometric conditions.[59,63] Here, an MS signal for $Pd_6Cl_{12}^+$ with the expected isotopic pattern, albeit of low intensity has been observed for the red precipitate at 460 °C/70 eV. At low temperature (<200 °C) the most prominent MS peaks were those for $C_6F_5H^+$ (*m/z* 168), $B(C_6F_5)_3^+$ (*m/z* 512) and for $[Cl–Cl–B(C_6F_5)_3]^+$ (*m/z* 582).

The multinuclear NMR investigations suggest that the activation process of pre-catalyst **2C** with $B(C_6F_5)_3$ can be formulated as a reaction of the Lewis acid with the chloride atoms of **2C** resulting in the formation of boron–chloride adducts and $PdCl_2$. The latter may be the active species for the polymerization of norbornene (see Scheme 8). It has been noted above that the polymerization activity of solid $PdCl_2$ is substantially lower than that of the potentially *in situ* formed $PdCl_2$ from **2C**/$B(C_6F_5)_3$ or the other pre-catalysts. This can be explained by the insolubility of commerical α- or γ-$PdCl_2$ in non-complexing organic solvents[60,62] or in the reaction mixture or by the small surface area of the $PdCl_2$ particles in case of a heterogeneous catalysis. Whereas the *in situ* formation initially leads to $PdCl_2$

or Pd_6Cl_{12} molecules which can start the polymerization in solution before further agglomeration occurs. Also, β-$PdCl_2$, *i.e.* Pd_6Cl_{12}, has been reported as soluble in aromatic solvents (*cf.* toluene used here in the polymerization runs), albeit still insoluble in non-donor organic solvents such as hydrocarbons or halogenated solvents.[62] The growing polymer chain and catalyst–monomer interaction can stabilize the $PdCl_2$ molecule or oligomer for some time and prevent the formation of solid $PdCl_2$. There was never a visible red precipitate in the polymerization flask. Even if colloidal oligomeric $PdCl_2$ species form they can still be considered more active than solid $PdCl_2$. $PdCl_2$ has also been described for norbornene polymerization in a water dispersion at 70 °C over 24 h.[64]

From the polymerization results in Table 2 activation of the pre-catalyst **2C** with $B(C_6F_5)_3$ was even more effective in combination with TEA. The combination of $B(C_6F_5)_3$ and $AlMe_3$ led to facile aryl/alkyl group exchange and resulted in the formation of $Al(C_6F_5)_3$ as the main product.[65,66] $B(C_6F_5)_3$ in combination with TEA (molar ratio 9 : 10) should undergo an analogous ligand exchange reaction and the ^{19}F NMR spectrum showed the expected signals of $Al(C_6F_5)_3$ at -122.3 ppm (*o*-F), -152.2 ppm (*p*-F) and -161.7 ppm (*m*-F). Also, the ^{19}F NMR spectrum revealed the formation of heteroleptic and possibly dimeric aluminum species of the type $[Al(C_6F_5)_x(C_2H_5)_{3-x}]_2$ (x = 1–2) as side products.[33]

As expected, the addition of TEA to the soluble part of the catalyst **2C**/$B(C_6F_5)_3$ showed the same ^{19}F NMR spectrum than the combination of **6**/$B(C_6F_5)_3$ and TEA. In this case an interaction of $Al(C_6F_5)_x(C_2H_5)_{3-x}$ with chloride and/or the oxygen atom of **6** will take place. The addition of TEA to the already active system **2C**/$B(C_6F_5)_3$ increases the polymerization activity by factor of 160. The role of TEA in the activation process of pre-catalyst **2C** lies in a possible higher reactivity of $Al(C_6F_5)_x(C_2H_5)_{3-x}$ compared to $B(C_6F_5)_3$,[33] the function of aluminum alkyls as alkyl chloride transfer agents[67] and the use as scavengers towards impurities. Due to the immiscibility of DMSO and *n*-hexane it was not possible to investigate the interaction of the red precipitate as the possible active species with TEA. The poly(norbornene)s obtained with $B(C_6F_5)_3$/TEA were not soluble and showed slight differences in the IR spectra compared to the polymers obtained with $B(C_6F_5)_3$ alone.

Conclusion

Palladium(II) compounds containing $[PdCl_4]^{2-}$ or $[Pd_2Cl_6]^{2-}$ fragments and different organic counter-ions represent a new class of pre-catalysts for the vinyl-type polymerization of norbornene. These pre-catalysts can be activated with the Lewis acids methylalumoxane (MAO) or $B(C_6F_5)_3$ and a combination of $B(C_6F_5)_3$/triethylaluminum (TEA). With the exception of the K$^+$ containing pre-catalysts **1A** and **2A** the new pre-catalysts showed high polymerization activities in combination with MAO which were in the range of the reference catalyst bis(acetylacetonato)palladium(II) (**3**) (1.8×10^7 g$_{polymer}$ mol$_{Pd}^{-1}$ h^{-1}). No influence of the counter-ion could be seen when using the co-catalyst $B(C_6F_5)_3$ alone or in combination with TEA. The use of a $B(C_6F_5)_3$/TEA mixture as co-catalyst increased the polymerization activity by factor of 150 (pre-catalyst **1B**) to 450 (pre-catalyst **2A**) when compared to $B(C_6F_5)_3$ alone. The poly(norbornene)s from MAO and $B(C_6F_5)_3$/TEA as co-catalysts were insoluble and showed slight differences in the IR spectra compared to the poly(norbornene)s from the $B(C_6F_5)_3$ activator. In the case of an activation with $B(C_6F_5)_3$ it was possible to obtain soluble poly(norbornene)s with palladium catalysts. These soluble poly(norbornene)s showed a fully saturated polymer backbone and a molar mass (M_n) between 8.2×10^3 and 3.2×10^5 g mol^{-1}. Multinuclear NMR investigations opened the door to explore the activation process and showed in the case of the system **2C**/$B(C_6F_5)_3$ the possible *in situ*

formation of $PdCl_2$ which is suggested here to be the active species for the polymerization of norbornene. The activation process and polymerization mechanism will continue to be the topic of future investigations.

Experimental

General remarks

All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques. IR spectra (KBr pellet) were measured on a Bruker Optik IFS 25 or a Bruker Vector 22 (PE pellet between 400 and 200 cm^{-1} for $PdCl_2$). NMR spectra were recorded with a Bruker AXS 200 at 300 K and 200 MHz (^{1}H NMR), 50 MHz (^{13}C NMR), 81 MHz (^{31}P NMR), and 188 MHz (^{19}F NMR). The NMR experiments were measured under inert gas atmosphere using NMR tubes with caps or Teflon covered septa and CD_2Cl_2 or [D_6]DMSO as solvent. ^{1}H and ^{13}C NMR spectra were calibrated against the solvent signal (CD_2Cl_2 5.32 ppm, 53.5 ppm, [D_6]DMSO 2.53 ppm, 39.5 ppm), ^{31}P NMR spectra against the external standard of 85% H_3PO_4, ^{19}F NMR spectra against the external standard $CDFCl_2$. Elemental analysis were obtained on a VarioEL from Elementaranalysensysteme GmbH. Mass spectrometric investigations for "$PdCl_2$" were carried out on a Varian MAT311A/AMD instrument in EI mode at 70 eV. X-Ray powder diffractometry was done on a Stoe STADI P with Debye-Scherrer geometry, Mo-Kα radiation ($\lambda = 0.7093$ Å) and a Ge(111) monochromator. Gel permeation chromatography (GPC) analyses were performed on a PL-GPC 220 (columns PL gel 10 μm MIXED-B) with polymer solutions in 1,2,4-trichlorobenzene (concentration of 2–3 mg mL^{-1}). The GPC was measured at 140 °C with an injection volume of 200 μL and with a rate of 1 mL min^{-1}. Acetonyltriphenylphosphonium chloride (Aldrich), palladium(II) chloride (Merck-Schuchardt), 18-crown-6 (Aldrich), potassium tetrachloropalladate(II) (Merck), imidazole (Acros), palladium(II) acetylacetonate (Aldrich), methylalumoxane (10% solution in toluene, Witco), tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, (Aldrich), and triethylaluminum (TEA, 1 mol L^{-1} 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. [18-crown-6]potassium tetrachloropalladate(II) (**1A**), [18-crown-6]potassium hexachlorodipalladate(II) (**2A**),[31] [H_3O^+(18-crown-6)]$_2$[Pd_2Cl_6] (**2B**)[32] and (acetylmethylene)triphenylphosphorane (**7**)[68] were synthesized according to literature procedures.

Synthesis

Bis(imidazolium) tetrachloropalladate(II) (1B). A solution of $PdCl_2$ (0.355 g, 2.00 mmol) in hot conc. HCl (2 mL) and ethanol (10 mL) was added dropwise to a solution of imidazole (0.272 g, 4.00 mmol) in ethanol (10 mL). A red–brown precipitate appeared instantly. After stirring the suspension for 1 h at room temperature, the red–brown solid was filtered off and dried *in vacuo* (yield 0.419 g, 54%, mp > 200 °C). $C_6H_{10}N_4PdCl_4$ (386.40): calc.: C 18.65, H 2.61, N 14.50; found: C 19.63, H 2.67, N 15.44%. ^{1}H NMR ([D_6]DMSO): δ 7.71 (s, 2 H, N–CH= CH–N), 9.13 (s, 1 H, N=CH–N), 14.5 (s, br, 2 H, N–H).

Acetonyltriphenylphosphonium hexachlorodipalladate(II) (2C)[69,70]**.** A solution of $PdCl_2$ (0.080 g, 0.45 mmol) was dissolved in hot conc. HCl (3 mL) and ethanol (10 mL). The red–brown solution was filtered and the residue was washed with 2 × 2 ml ethanol. A solution of (acetylmethylene)-triphenylphosphorane (**7**) (0.143 g, 0.45 mmol) or acetonyl-triphenylphosphonium chloride (**6**) (0.160 g, 0.45 mmol) in

ethanol (10 mL) was added dropwise to the collected filtrates. After stirring the clear, red–brown solution for 3 h at room temperature, diethylether was condensed onto the reaction mixture over a period of several days resulting in orange- to red–brown needles which were separated by filtration and washed with diethyl ether (crystal yield from **7** 0.101 g, 42%, from **6** 0.056 g, 23%, mp > 200 °C). The needles were suitable for study by X-ray diffraction. $C_{42}H_{40}Cl_6O_2P_2Pd_2$ (1064.28): calc.: C 47.40, H 3.79; found: C 47.42, H 3.69%. ^{1}H NMR ([D_6]DMSO): δ 2.14 (d, 3 H, J_{PH} = 2.2 Hz, C(O)–CH_3), 5.32 (d, 2 H, J_{PH} = 12.6 Hz, P–CH_2–C(O)), 7.3–7.8 (m, 15 H, aromatic H); ^{31}P NMR ([D_6]DMSO): δ 19.5 (s).

Polymerization procedures

General. The pre-catalysts were applied as solutions (**1A**, **2A**, **2B**) or as a fine suspension *via* ultrasonication (**2C** and **1B**) in methylene chloride. The pre-catalysts **3**–**5** were used as solution (**3**) or as suspension (**4** and **5**) in toluene for the polymerization with MAO as co-catalyst and in methylene chloride for the polymerization with $B(C_6F_5)_3$/TEA. 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 but often three to five times to ensure reproducibility. The polymerizations with the borane activator have been performed at least three times. The IR spectra of the poly(norbornene)s obtained with the catalysts **1**–**5** showed the absence of a double bond at 1620–1680 cm^{-1}. This ensured the vinyl-type polymerization instead of a ring-opening metathesis polymerization (ROMP).

General procedure for the homopolymerization of norbornene with MAO as co-catalyst. A Schlenk-flask was charged with the norbornene solution in toluene and the MAO–toluene solution was added. After 1 min the CH_2Cl_2 or toluene solution of the pre-catalyst 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 10 : 1 methanol–conc. HCl mixture. The precipitated polymer was filtered off, washed with methanol and dried *in vacuo* for 5 h.

General procedure for the homopolymerization of norbornene with $B(C_6F_5)_3$ or TEA alone and $B(C_6F_5)_3$ in combination with TEA as co-catalysts. A Schlenk-flask was charged with the norbornene solution in toluene. The solutions of the palladium pre-catalyst (in CH_2Cl_2) followed by the co-catalyst components [$B(C_6F_5)_3$ as toluene, triethylaluminum (TEA) as hexane solution] were quickly added *via* syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped through the addition of 40 mL of a 10 : 1 methanol–conc. HCl mixture. The precipitated polymer was filtered off, washed with methanol and dried *in vacuo* for 5 h.

X-Ray crystallographic study of 2C

Crystal data. Molecular formula $C_{42}H_{40}Cl_6O_2P_2Pd_2$, formular mass 1064.22 g mol^{-1}, $a = 9.737(1)$, $b = 21.764(2)$, $c = 11.807(1)$ Å, $\beta = 119.088(7)°$, $V = 2186.6(4)$ Å^3, $Z = 2$, $D_c = 1.616$ g cm^{-3}, $F(000) = 1064$, monoclinic, space group $P2_1/c$. *Data Collection*: Bruker AXS with CCD area-detector, Mo-Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, crystal size 0.18 × 0.06 × 0.05 mm^3, 203(2) K, double-pass method ϕ–ω-scan, 4.4 ≤ 2θ≤ 56.6°, $-10 \leq h \leq 12$, $-29 \leq k \leq 22$, $-15 \leq l \leq 15$, 13845 reflections measured, 5333 independent, R_{int} = 0.072, μ(Mo-Kα) 12.97 cm^{-1}. Data collection and cell refinement with SMART,[71] data reduction with SAINT.[71] An experimental absorption correction (SADABS)[72] was performed with T_{min}/T_{max} of 0.6417/0.9380. *Structure Analysis and Refinement*: The structure was solved by direct methods (SHELXS-97);[73] refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite.[73] All non-hydrogen positions were found and refined with

anisotropic temperature factors. The hydrogen atoms were placed at calculated positions, using appropriate riding models (HFIX 43 for aromatic C–H, HFIX 33 for CH$_3$, and HFIX 23 for CH$_2$) and isotropic temperature factors of $U(H) = 1.2\ U_{eq}$-(C_{arom} and CH$_2$) or $U(H) = 1.5\ U_{eq}$(CH$_3$). 244 refined parameters, final $R1 = 0.0566$, $wR2 = 0.0959$ for 2732 reflections with $I > 2\sigma I$, $R1 = 0.1300$, $wR2 = 0.1202$ for all reflections, goodness-of-fit on $F^2 = 1.021$, largest difference peak and hole 1.056/-1.286 e Å^{-3} in the vicinity of CH$_3$ and the Pd atom. Graphics were obtained with ORTEP 3 for Windows.[74] Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

CCDC reference number 194665.

See http://www.rsc.org/suppdata/dt/b2/b209633a/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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