Dihalogeno(diphasphane)metal(II) complexes (metal = Co, Ni, Pd) as pre-catalysts for the vinyl/addition polymerization of norbornene – elucidation of the activation process with $\text{B(C}_6\text{F}_5)_3/\text{AlEt}_3$ or Ag[closo-1-CB$_{11}$H$_{12}$] and evidence for the \textit{in situ} formation of “naked” Pd$^{2+}$ as a highly active species

Paul-Gerhard Lassahn,* Vasile Lozani,* Biao Wu,* Andrew S. Weller* and Christoph Janiak**

* Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstr. 21, 79104 Freiburg, Germany. E-mail: janiai@uni-freiburg.de

** Department of Chemistry, University of Bath, Bath, UK BA2 7AY.

E-mail: a.s.weller@bath.ac.uk

Received 14th March 2003, Accepted 10th September 2003

Dihalogenometal(II) complexes with bidentate phosphate ligands of the general type $[\text{M}(\text{Ph}_{11}54)[\text{CB}_{11}12(H_2)]_{14}]$ (dppp)[$\text{CB}_{11}12(H_2)])_2$CH$_2$Cl$_2$. The stable [Pd(dppe)]$^{2+}$ cation from 6 could be crystallized as [Pd(dppe)(CB$_{11}$H$_{12}$)][CB$_{11}$H$_{12}$] (CB$_{11}$H$_{12}$ = mono-anionic carbaborane [closo-1-CB$_{11}$H$_{12}$]).

Introduction

The homopolymerization of norbornene can be accomplished by three different routes with each route leading to its own polymer type with different structure and properties (Scheme 1).

Polymers produced \textit{via} ring-opening-metathesis-polymerization (ROMP) still contain double bonds in the polymer backbone and can be obtained for a number of transition metals in high oxidation states.\textsuperscript{1–3} Only a few reports describe the formation of low molar mass oligomeric material with 2,7-connected rotationally constrained polymers in which the bicyclic structural unit remains intact and only the double bond of the \textit{n}-component is opened. Catalysts containing the metals titanium,\textsuperscript{4,5} zirconium,\textsuperscript{7,9} hafnium,\textsuperscript{8} and currently the late transition-metals cobalt,\textsuperscript{11–15} nickel\textsuperscript{16–18} and palladium\textsuperscript{29,32–48} are described in the literature for the vinyl/ addition polymerization of norbornene.\textsuperscript{49–58} The late transition-metal complexes are commonly activated with methylalumoxane (MAO),\textsuperscript{36–38,40} except for the cationic palladium-complexes [Pd(NCR)$_3$]$^{2+}$ 2A$^−$ (NCR weakly bound nitrile-ligand; A = “non”-coordinating counter ion).\textsuperscript{55–57} Another co-catalytic system for the activation of metal complexes is the organo-Lewis acid tris(pentafluorophenyl)borane, B(C$_6$F$_5$)$_3$, with or without triethylaluminium (AlEt$_3$). This co-catalytic system is known from the activation process of early transition-metal Group 4 metallocene catalysts in olefin polymerization\textsuperscript{56–58} and was recently also applied to the activation of late transition-metal complexes for the (co)polymerization of cyclopentene,\textsuperscript{66} ethene,\textsuperscript{67} norbornene and norbornene derivatives.\textsuperscript{66,58–66} Previously, we have communicated initial polymerization results of nickel(II) and palladium(II) dihalogeno complexes bearing bidentate phosphate ligands as pre-catalysts for the
vinyl polymerization of norbornene. These complexes can be activated with MAO as well as with B(C₆F₅)₃ and showed remarkable polymerization activities up to $2.0 \times 10^4 \, \text{g}_{\text{polym.}} \, \text{mol}^{-1} \, \text{h}^{-1}$. In this paper, we wish to present the polymerization results of the complete series of cobalt(ii), nickel(ii) and palladium(ii) complexes of the general type $[\text{M}\{\text{dppp}\} \{\text{PH}_{2}\text{P(CH}_2\text{)}_2\text{PPh}_2\} \text{Cl}_3]$ with $n = 2$ to 5 and $M = \text{Co, Ni, Pd}$ (Scheme 2). In the case of the palladium(ii) pre-catalysts 5 and 6 we were able to obtain information about the activation process with $\text{B(C}_6\text{F}_5)_3$ and $\text{AlEt}_3$ by using multinuclear ($^{1}H$, $^{13}P$, and $^{31}P$) NMR investigations and crystallization of reaction products with $\text{B(C}_6\text{F}_5)_3$ or the $\text{closo}$-carborane anion [$\text{CB}_{11}\text{H}_{13}$].

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

### Experimental

#### General procedures

All work involving air- and/or moisture-sensitive compounds was carried out using standard vacuum, Schlenk or drybox techniques. FT-IR spectra (KBr pellets) were measured on a Bruker Avance 500 at 300 K and 500 MHz ($^{1}H$), 125 MHz ($^{13}C$), and 195 MHz ($^{29}P$) NMR spectroscopy. $^{29}P$ NMR experiments were recorded with a Bruker Avance 500 at 300 K and 500 MHz ($^{1}H$). FT-IR spectra (KBr pellets) were measured on a Nicolet 7600 FT-IR spectrometer. $^{1}H$ NMR spectra were calibrated against the residual solvent signal (CDCl$_3$, 5.32 ppm). The NMR spectra for compound $[\text{Pd(dpppe)}]_{2}$$[\text{CB}_{11}\text{H}_{13}]_{2}$ (16) were recorded with a Bruker Avance 500 at 500 MHz ($^{1}H$ NMR) and 125 MHz ($^{13}C$ NMR). The NMR experiments with air-sensitive materials were performed under an inert gas atmosphere using NMR tubes with screw caps (Wilmad). Teflon-covered septa (Wheaton) and CD$_2$Cl$_2$ as solvent. Elemental analyses were obtained on a VarioEL from Elementaranalysetechnik GmbH. 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$^{-1}$.

#### X-Ray crystallography

X-Ray data were collected with a Bruker AXS with CCD area-detector and Mo-Kα radiation ($\lambda = 0.71073$ Å), graphite monochromator, double-pass method ϕ-ω-scan. Data collection and cell refinement with SMART were performed with SAINT. An experimental absorption correction was performed with SADABS. The structures were solved by direct methods (SHELXS-97); refinement was done by full-matrix least squares on $F^{2}$ using the SHELXL-97 program suite. 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 CH, HFIX 33 for CH$_2$, HFIX 23 for CH$_3$, HFIX 153 for CH and BH in the carborane, HFIX 83 for OH) and isotropic temperature factors of $U(H) = 1.2 \cdot U_{eq}(\text{C, CH and BH})$ or $(\text{H}) = 1.5 \cdot U_{eq}(\text{C, O, H})$. One of the chlorine atoms in each of the two independent CH$_3$Cl solvent molecules of crystallization in the structure of $[\text{Pd(dpppe)}]_{2}$$[\text{CB}_{11}\text{H}_{13}]_{2}$ (14) was found to be disordered. One of the CH$_3$Cl solvent molecules in $[\text{Pd(dpppe)}]_{2}$$[\text{CB}_{11}\text{H}_{13}]_{2}$ (15) is disordered around a crystallographic glide plane. In the structure of $[\text{Pd(dppp)}]_{2}$$[\text{CB}_{11}\text{H}_{13}]_{2}$ (16) about 22% of the carborane counter anions were found to contain a hydroxy group, and hence to be of formula $[\text{CB}_{11}\text{H}_{13}(\text{OH})]_{2}$. The OH-group may have been introduced by the solvent diethylether which contained traces of water. Thus, the crystal structure would have to be correctly formulated as $[\text{Pd(dppp)}]_{2}$$[\text{CB}_{11}\text{H}_{13}]_{2}$ (16) (OH)$_{2}$Cl, the carbon atom in CB$_{11}$H$_{13}$ (OH)$_{2}$Cl is disordered in the bound and free cage of CB$_{11}$H$_{13}$ or [CB$_{11}$H$_{13}(\text{OH})_{2}$] in 16 were located as their $B_{eq}$ bond lengths are slightly shorter than those for B-B. For 15 B-C = 1.701(6)–1.728(6) Å, B-B = 1.733(6)–1.778(6) Å; for 16, bound cage B-C = 1.693(7)–1.709(6), B-B = 1.748(6)–1.800(6) Å, free cage B-C = 1.687(8)–1.718(7), B-B = 1.726(9)–1.774(8) Å. The location may be different in CB$_{11}$H$_{13}$ (OH), since the carbon atom was not found opposite to the hydroxide-bound boron (B10) atom. The anion CB$_{11}$H$_{13}$Cl in 15 the carbon atom is opposite to the chlorine bound boron(12) atom. The B12 vertex is known to be most reactive for electrophilic substitution and thus would be expected to be substituted first. Also, the carbon atom was found opposite to one of the B12 groups bonded to palladium in the metal-bound cage in 16. This is as expected as metal fragments generally bind through B(H)12 and B(H)7 when the cage acts in a bidentate fashion. Details of the X-ray structure determinations and refinements are provided in Table 1. Graphical were obtained with ORTEP 3 for Windows. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

CCDC reference numbers 206046–206048.

See http://www.rcsb.org/pdb/submitdata/db/b3/b302937a for crystallographic data in CIF or other electronic format.

### Materials

- Cobalt(ii) chloride (Aldrich), nickel(ii) chloride (Aldrich), nickel(ii) chloride hexahydrate (Acrros), nickel(ii) bromide (Aldrich), palladium(ii) chloride (Merck-Schuchardt), 1,2-bis(diphenylphosphino)ethane (dppp, Aldrich), 1,3-bis(diphenylphosphino)propane (dppp, Strem Chemicals), potassium diphenylphosphide ([C$_{6}$H$_{5}$]$_{2}$PK, 0.5 M solution in tetrahydrofuran), 1,4-dichlorobutane (Aldrich), 1,5-dichloropentane (Aldrich), methylammonoxane (10 wt% solution in toluene, Witoce), tris(pentafluorophenyl)borane (B(C$_{6}$F$_{5}$)$_{3}$, Aldrich), and triethylaluminum (AlEt$_{3}$, 1 mol L$^{-1}$ solution in hexane, Merck-Schuchardt) were used as received.
- Toluene, tetrahydrofuran and n-hexane were dried over sodium metal, distilled and stored under nitrogen.
- Methylene chloride was dried over CaH$_{2}$, Norbornone (bicyclo[2.2.1]hept-2-ene, Aldrich) was purified by distillation and used as a solution in toluene.

### Preparation of the pre-catalysts

The nickel(ii) complexes Ni(dpppe)Cl$_{2}$ (1) and Ni(dppp)Cl$_{2}$ (2) were synthesized by addition of the ligand in CH$_{2}$Cl$_{2}$ to a solu-
tion of NiCl₂·6H₂O in ethanol according to a procedure given by Busby et al. The palladium(ii) complexes Pd(dppe)Cl₂ (5), Pd(dpdpCl)Cl₂ (6), Pd(dpdpCl)Cl (7) and Pd(dpdpCl)Cl (8) were synthesized by combining a solution of PdCl₂ in hot concentrated HCl and ethanol or 1-butanol with a solution of the appropriate ligand in CH₂Cl₂ or CHCl₃. The nickel(ii) complexes Ni(dpdpCl)Cl₂ (3), Ni(dpdpCl)Br₂ (4), Ni(dpdpCl)Br₃ (13) and the cobalt(ii) complexes Co(dpdpCl)₂ (9), Co(dpdpCl)Cl (10), Co(dpdpCl)Cl (11) and Co(dpdpCl)Cl (12) were synthesized according to a modified procedure given by Sacconi and Gelsomini. The yields were in the range of 70 to 97% and the purities were checked by CHN-analysis.

Synthesis of [Pd(dppe)]₂[CB₁₁H₁₂]₂·4CH₂Cl₂ (14). Pd(dppe)Cl₂ (0.115 g, 0.2 mol mmol) and B(C₂H₅)₃ (0.307 g, 0.6 mmol) were dissolved under an inert-gas atmosphere in a mixture of freshly dried toluene (5 mL) and methylene chloride (10 mL). Some colorless, air-sensitive crystals which were suitable for study by X-ray diffraction were obtained after 4 months at −18 °C and analyzed as the title compound. The small amount of crystalline material available (−10 mg) precluded any further analyses.

Synthesis of [Pd(dpdpCl)]₂[CB₁₁H₁₂]Cl₂·3CH₂Cl₂ (15). Ag-[CB₁₁H₁₂]₂ (0.075 g, 0.30 mmol) was placed under an inert-gas atmosphere into a Schlenk-flask which was covered with aluminum foil to protect the silver salt from light. Pd(dpdpCl)Cl₂ (0.089 g, 0.15 mmol) was dissolved in freshly dried CH₂Cl₂ (40 mL) and added dropwise to the silver salt. After stirring for 4 days the resulting suspension was filtered over Celite. The Celite was washed with 30 mL of CH₂Cl₂ and the solvent was removed in vacuo to a volume of 5 mL. Addition of dried n-hexane (30 mL) resulted in the formation of a yellow precipitate which was filtered off and dried in vacuo (yield 0.080 g, 66%, mp >200 °C). C₃H₂Ag₂Pd₂PdCl₄ (804.93); calcd. C 42.7, H 2.45, N 0.46%. ρH NMR (500 MHz, CDCl₃): δ = 1.0 −2.5 (br, 22H, CB₁₁H₁₂); 2.54 (s, br, 2H, CH₂Br₁₂H₁₁); 2.75 (t, br, 2H, P−CH₂−CH₂−CH₂−P); 2.83 (s, br, 2H, P−CH₂−CH₂−CH₂−P). Crystals suitable for X-ray diffraction were grown within several days after redissolving the solid product in a minimum of methylene chloride and overlaying this solution with diethyl ether at room temperature. The crystals were found to have the chemical composition of the title compound except for about 22% of the carbaborane counter anions that were found to contain a hydroxy group, and hence to be of formula [CB₁₁H₁₂(OH)]⁺.

Polymerization procedures

General. The pre-catalysts were applied as solutions (for precatalysts 1, 2, 6, 8, 9, 10 and 13) or as a fine suspensions via ultrasonication in methylene chloride (for precatalysts 3 to 5, 7, 11 and 12). 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 three times to ensure reproducibility. The IR spectra of the poly-(norbornene) obtained with the catalysts 1 to 12 showed the absence of a double bond at 1620 to 1680 cm⁻¹. This proved that vinyl/addition polymerization instead of a ring-opening metathesis polymerization (ROMP) had occurred. The conversion was calculated by gravimetric analysis of the polymer.

General procedure for the homopolymerization of norbornene with MAO as co-catalyst. A Schlenk-flask was charged with the norbornene solution and the MAO-solution was added. After 1 min the solution or suspension of the pre-catalyst was added.
via syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped by the addition of 30 mL of a 10 : 1 methanol/concentrated 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(C₆F₅)₃/AlEt₃ as co-catalysts. A Schlenk-flask was charged with the norbornene solution. The solution or suspension of the pre-catalyst followed by the separate co-catalyst components [B(C₆F₅)₃ and AlEt₃] were quickly added via syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped by the addition of 40 mL of a 10 : 1 methanol/concentrated HCl mixture. The precipitated polymer was filtered off, washed with methanol and dried in vacuo for 5 h.

From studies of a number of metal complexes which did not show any polymerization activity with B(C₆F₅)₃/AlEt₃ as co-catalysts, we conclude that the combination of B(C₆F₅)₃/AlEt₃ alone is not polymerization active.

Results and discussion

Norbornene polymerization

Nickel(ii), palladium(ii) and cobalt(ii) complexes of the general type [M{Ph₂P(CH₂)}₃PPh₂]X₃ with n = 2 to 5, X = Cl or Br and M = Ni (1 to 4), Pd (5 to 8) and Co (9 to 12) were tested in the homopolymerization of norbornene. The results of the polymerization activities using methyalumoxane (MAO) as co-catalyst are summarized in Table 2 and Fig. 1.

The polymerization activities of the metal–phosphane complexes 1 to 12 in combination with MAO covered a range of 3.0 × 10⁵ (11/MAO) to 4.1 × 10⁶ g polymer mol⁻¹ h⁻¹ (4/MAO). Only the nickel complexes 3 and 4 and perhaps the palladium complex 8 exhibit activities around or above 10⁶ g polymer mol⁻¹ h⁻¹. These complexes contain the six- or seven-membered dpdp and dppt ligands (Fig. 3). For the other complexes the conversion and activity with MAO was unremarkable. In accordance with the literature data, the cobalt(ii) complexes 9–12 delivered only traces of poly(norbornene) within a polymerization time of 1 h.° The polymers obtained with the nickel- and cobalt-containing catalysts were soluble in 1,2,4-trichlorobenzene and could be investigated by gel permeation chromatography (GPC) whereas the palladium(ii)-catalyzed poly(norbornenes) were insoluble in common solvents as expected from the literature.° The soluble polymer samples displayed a monomodal and narrow molar mass distribution with Q = Mₘ/Mₜ close to a value of 2 (except for the highly active 4/MAO with Q = 4.4). The number-average molar mass (Mₘ) was found between 1.5 × 10⁵ and 1.6 × 10⁶ g mol⁻¹. Thus, the average chain length for the polymers lies between 1,600 (12) and 17,000 (1) monomer units (Mₘ/norbornene = 94.16 g mol⁻¹). 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 = 2 indicates a single-site character, i.e. a highly homogeneous structure for the active catalyst species.

In order to gain additional information about the activation process the activator was changed from MAO to the better defined co-catalyst B(C₆F₅)₃ with or without triethylaluminium (AlEt₃). Mechanistic investigations with MAO as a co-catalyst are difficult since the exact composition and structure of MAO is still not entirely clear.° The results of the polymerization of norbornene with the pre-catalysts 1 to 8 and 10 in combination with B(C₆F₅)₃/AlEt₃ or with B(C₆F₅)₃ alone are summarized in Table 3 and Fig. 2.

Dichloro-nickel(ii) and palladium(ii) complexes bearing bidentate phosphane ligands can be activated with the co-catalytic system B(C₆F₅)₃/AlEt₃. Activation of the cobalt complex 10 under similar conditions essentially failed. The activity trends for the nickel complexes 1–4 and the palladium complexes 6–8 are the same as seen above for activation with MAO. Again, the nickel complexes 3 and 4 and the palladium complexes 7 and 8 with the longest-chain dpdp and dppt ligands show activities around or above 10⁵ g polymer mol⁻¹ h⁻¹ (Fig. 2). Even the overall activities for these complexes with MAO or with B(C₆F₅)₃/AlEt₃ are quite similar (Fig. 3) although a direct comparison should not be made in view of the different metal-to-co-catalyst ratios. For similar or even higher monomer conversions and polymerization activities the required co-catalyst quantities were much lower with B(C₆F₅)₃/AlEt₃ than with MAO (molar ratios of Pd : borane : AlEt₃ = 1 : 9 : 10 and Pd : MAO = 1 : 100). This leads to fewer co-catalyst residues in

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time/min</th>
<th>Conversion (%)</th>
<th>Activity [g poly/mol·h⁻¹]</th>
<th>Mₘ/g mol⁻¹</th>
<th>Mₜ/g mol⁻¹</th>
<th>Q = Mₘ/Mₜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/MAO</td>
<td>5</td>
<td>2.0</td>
<td>2.1 × 10⁴</td>
<td>1.0 × 10⁶</td>
<td>2.7 × 10⁶</td>
<td>1.7</td>
</tr>
<tr>
<td>2/MAO</td>
<td>5</td>
<td>3.7</td>
<td>4.2 × 10⁴</td>
<td>1.3 × 10⁶</td>
<td>2.6 × 10⁶</td>
<td>1.9</td>
</tr>
<tr>
<td>3/MAO</td>
<td>5</td>
<td>18.4</td>
<td>2.1 × 10⁴</td>
<td>7.1 × 10⁴</td>
<td>1.7 × 10⁶</td>
<td>2.4</td>
</tr>
<tr>
<td>4/MAO</td>
<td>5</td>
<td>36.0</td>
<td>4.1 × 10⁴</td>
<td>1.8 × 10⁵</td>
<td>7.9 × 10⁵</td>
<td>4.4</td>
</tr>
<tr>
<td>5/MAO</td>
<td>5</td>
<td>3.3</td>
<td>3.7 × 10⁴</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>6/MAO</td>
<td>5</td>
<td>0.1</td>
<td>1.1 × 10⁴</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>7/MAO</td>
<td>60</td>
<td>1.8</td>
<td>1.7 × 10⁴</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>8/MAO</td>
<td>60</td>
<td>9.0</td>
<td>9.1 × 10⁴</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>9/MAO</td>
<td>60</td>
<td>0.4</td>
<td>4.0 × 10²</td>
<td>7.2 × 10³</td>
<td>1.4 × 10⁵</td>
<td>1.9</td>
</tr>
<tr>
<td>10/MAO</td>
<td>60</td>
<td>1.7</td>
<td>1.6 × 10⁴</td>
<td>5.7 × 10⁴</td>
<td>1.4 × 10⁵</td>
<td>2.4</td>
</tr>
<tr>
<td>11/MAO</td>
<td>60</td>
<td>0.3</td>
<td>3.0 × 10²</td>
<td>2.8 × 10⁴</td>
<td>6.9 × 10⁵</td>
<td>2.6</td>
</tr>
<tr>
<td>12/MAO</td>
<td>60</td>
<td>0.6</td>
<td>5.8 × 10²</td>
<td>1.5 × 10⁵</td>
<td>4.4 × 10⁵</td>
<td>2.9</td>
</tr>
<tr>
<td>1–12/MAO</td>
<td>0</td>
<td>0</td>
<td>No activity observed</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>


Fig. 1 Activities of 1–12 with MAO as co-catalyst in the polymerization of norbornene. Detailed conditions are given in Table 2.

![Graph](image-url)
the polymer which should be highly advantageous for the prospective optical applications of poly(norbornene).

Thus, the activity correlates with the length of the alkylgroup of the bidentate phosphane ligand, that is the chelate ring size appears to be independent of the co-catalytic system which is used to activate the nickel- or palladium-pre-catalysts (Fig. 3). In the case of nickel the increase in chain length results in a steady increase in the polymerization activity. Whereas for the palladium complexes the polymerization activities dropped significantly when going from \( n = 2 \) to \( 3 \) that is from a five- to a six-membered chelate ring and then increased again. Similar activity trends for the nickel- or palladium-series with chelate ring size may be the result of a similar polymerization mechanism or activation process when using MAO or \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3 \) as a co-catalyst. Still, 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 \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3 \)-activated Ni- or Pd-complexes are not well known. Some investigations to be discussed below were aimed at increasing the understanding of the activation process of these pre-catalysts to supplement our recent mechanistic study on the activation of palladium(n) salts containing \( [\text{PdCl}_2\text{F}]^2- \) and \( \text{Br}_3\text{Cl}_2 \) ions with evidence for the \emph{in situ} formation of \( \text{PdCl}_3 \).

An exception upon \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3 \)-activation is the palladium–dppe complex 5. The reproducible and extremely high activity of 5 of the order of \( 10^6 \text{ g}_{\text{polymer}} \text{ mol}_{\text{Pd}}^{-1} \text{ h}^{-1} \) is noteworthy (Fig. 2 and 3). A conversion of 50% was reached after a polymerization time of 10 s. This may already point to a different activation mechanism and active species compared to the other complexes (see below). Furthermore, we note that only the nickel pre-catalysts 3 and 4 which contain a six- or seven-membered dpbb and dpddp ligand, respectively, could be activated with \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} \) alone for the vinyl polymerization of norbornene, albeit with low activity. The GPC data of the nickel/borane catalyzed poly(norbornene) correspond closely to the data of the polymer samples obtained with MAO as co-catalyst. All polymers displayed a monomodal and narrow molar mass distribution around \( Q = 2 \). The average chain length lies between 1,300 \( (4/\text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3) \) and 12,000 \( (3/\text{B}(\text{C}_6\text{F}_5)\text{Cl}) \) monomer units corresponding to a number-average molar mass \( M_n \) between 1.2 \( \times 10^5 \) and 1.1 \( \times 10^6 \) g mol\(^{-1}\).

The influence of the halogen ligand was investigated and the nickel–dppe complexes 1 and 13 with chloro and bromo ligands were tested in combination with the two co-catalytic systems MAO and \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3 \) (Table 4 and Fig. 4). The polymerization activity can be increased considerably when changing the halogen ligand in the nickel–dppe complexes from chloro to bromo. These effects may be explained by the weaker Ni–Br bond strength.

For the palladium(II) pre-catalysts 5 and 6 we investigated the influence of the molar ratio of \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} \) on the polymerization activity (see Table 5 and Fig. 5). The \( \text{Pd} – \text{dppe} \) complex 5 and the dpdp-analog 6 had shown dramatic differences in the polymerization activities with \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3 \) as co-catalysts.

Both palladium pre-catalysts 5 and 6 show the same activity trends when varying the molar ratio of \( \text{Pd} / \text{B}(\text{C}_6\text{F}_5)\text{Cl} \) in the polymerization of norbornene. A decrease of the amount of \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} \) from \( \text{Pd} : \text{B}(\text{C}_6\text{F}_5)\text{Cl} / \text{AlEt}_3 \) = 1 : 9 to 1 : 2 : 10 led to a steady decrease in polymerization activity. Yet, even at a

---

**Table 3** Polymerization of norbornene (NB) with complexes 1 to 8 and 10 in combination with \( \text{B}(\text{C}_6\text{F}_5)\text{Cl} \) and triethylaluminium (AlEt\(_3\))

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time/min</th>
<th>Conversion (%)</th>
<th>Activity/g(<em>{\text{polymer}}) mol(</em>{\text{metal}}^{-1}) h(^{-1})</th>
<th>( M_g)/g mol(^{-1})</th>
<th>( M_w)/g mol(^{-1})</th>
<th>( Q = M_w/M_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>4.1</td>
<td>3.8 ( \times 10^3 )</td>
<td>4.1 ( \times 10^6 )</td>
<td>1.0 ( \times 10^6 )</td>
<td>2.5</td>
</tr>
<tr>
<td>2/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>9.0</td>
<td>8.6 ( \times 10^3 )</td>
<td>3.4 ( \times 10^6 )</td>
<td>8.1 ( \times 10^6 )</td>
<td>2.4</td>
</tr>
<tr>
<td>3/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>5</td>
<td>9.0</td>
<td>1.0 ( \times 10^4 )</td>
<td>3.9 ( \times 10^6 )</td>
<td>8.4 ( \times 10^6 )</td>
<td>2.2</td>
</tr>
<tr>
<td>4/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>5</td>
<td>14.8</td>
<td>1.7 ( \times 10^4 )</td>
<td>1.2 ( \times 10^6 )</td>
<td>4.2 ( \times 10^6 )</td>
<td>3.4</td>
</tr>
<tr>
<td>5/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>1/6</td>
<td>54.3</td>
<td>1.9 ( \times 10^4 )</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>6/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>3.1</td>
<td>3.0 ( \times 10^4 )</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>7/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>5</td>
<td>8.1</td>
<td>9.2 ( \times 10^4 )</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>8/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>1</td>
<td>17.4</td>
<td>9.9 ( \times 10^4 )</td>
<td>Not soluble</td>
<td>Not soluble</td>
<td>Not soluble</td>
</tr>
<tr>
<td>10/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>0.6</td>
<td>5.7 ( \times 10^4 )</td>
<td>6.5 ( \times 10^6 )</td>
<td>1.2 ( \times 10^6 )</td>
<td>1.8</td>
</tr>
<tr>
<td>1/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>0</td>
<td>No activity observed</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>15.0</td>
<td>1.4 ( \times 10^5 )</td>
<td>1.1 ( \times 10^6 )</td>
<td>2.1 ( \times 10^6 )</td>
<td>1.9</td>
</tr>
<tr>
<td>4/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>11.1</td>
<td>1.0 ( \times 10^5 )</td>
<td>9.5 ( \times 10^6 )</td>
<td>1.5 ( \times 10^6 )</td>
<td>1.6</td>
</tr>
<tr>
<td>1.25/8/(\text{B}(\text{C}_6\text{F}_5)\text{Cl})/\text{AlEt}_3 )</td>
<td>60</td>
<td>0</td>
<td>No activity observed</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Conditions: room temperature; toluene/methylene chloride solution.\(^a\) 30.1 mmol NB, \([\text{M}] : [\text{NB}] = 1 : 1000, [\text{M}] : [\text{Al}] = 1 : 9 \), total volume 40.0 mL.\(^b\) 30.1 mmol NB, \([\text{M}] : [\text{NB}] = 1 : 1000, [\text{M}] : [\text{Al}] = 1 : 10\), total volume 40.0 mL.\(^c\) Table 3.
Table 4  Polymerization of norbornene (NB) with the Ni–dppe complexes 1 (Cl ligand) and 13 (Br ligand)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time/min</th>
<th>Conversion (%)</th>
<th>Activity/(\text{g}<em>{\text{polymer}} \times \text{mol}</em>{\text{N}}^{-1} \times \text{h}^{-1})</th>
<th>(M_2/\text{g}) mol(^{-1})</th>
<th>(M_2/\text{g}) mol(^{-1})</th>
<th>(Q = M_2/\text{M}_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/MAO(^{-})</td>
<td>5</td>
<td>2.0</td>
<td>(2.1 \times 10^4)</td>
<td>(1.6 \times 10^6)</td>
<td>(2.7 \times 10^6)</td>
<td>1.7</td>
</tr>
<tr>
<td>13/MAO(^{-})</td>
<td>5</td>
<td>3.8</td>
<td>(4.3 \times 10^4)</td>
<td>(5.1 \times 10^6)</td>
<td>(9.5 \times 10^6)</td>
<td>1.9</td>
</tr>
<tr>
<td>B(C(_3)F(_8))/AlEt(_3)</td>
<td>60</td>
<td>4.1</td>
<td>(3.8 \times 10^4)</td>
<td>(4.1 \times 10^6)</td>
<td>(1.0 \times 10^6)</td>
<td>2.5</td>
</tr>
<tr>
<td>B(C(_3)F(_8))/AlEt(_3)</td>
<td>5</td>
<td>19.2</td>
<td>(2.2 \times 10^4)</td>
<td>(1.1 \times 10^6)</td>
<td>(3.1 \times 10^6)</td>
<td>2.8</td>
</tr>
<tr>
<td>1,13/AlEt(_3)</td>
<td>60</td>
<td>0</td>
<td>No activity observed</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>1,13/B(C(_3)F(_8))(^{-})</td>
<td>60</td>
<td>0</td>
<td>No activity observed</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Conditions: room temperature; toluene/methylene chloride solution; \(10.6 \text{ mmol NB, [Ni]} : \text{[NB]} = 1 : 1000, [Ni] \times \text{[Al]} = 1 : 100, \text{total volume 40.0 mL.}\)

Table 5  Polymerization of norbornene (NB) with the PdCl\(_2\) complexes 5 (dppe) and 6 (dppp) and varying ratios of borane in B(C\(_3\)F\(_8\))/AlEt\(_3\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Molar ratio Pd : B : Al Time/min</th>
<th>Conversion (%)</th>
<th>Activity/(\text{g}<em>{\text{polymer}} \times \text{mol}</em>{\text{N}}^{-1} \times \text{h}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1 : 9 : 0</td>
<td>1/6</td>
<td>54.3</td>
</tr>
<tr>
<td>5</td>
<td>1 : 7 : 10</td>
<td>1/6</td>
<td>24.0</td>
</tr>
<tr>
<td>5</td>
<td>1 : 5 : 10</td>
<td>1/6</td>
<td>12.5</td>
</tr>
<tr>
<td>5</td>
<td>1 : 3 : 10</td>
<td>1/6</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>1 : 2 : 10</td>
<td>1/6</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>1 : 1 : 10</td>
<td>1/6</td>
<td>0.0</td>
</tr>
<tr>
<td>6</td>
<td>1 : 9 : 10</td>
<td>60</td>
<td>3.1</td>
</tr>
<tr>
<td>6</td>
<td>1 : 5 : 10</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>1 : 2 : 10</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>1 : 1 : 10</td>
<td>60</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Conditions: room temperature; toluene/methylene chloride solution; \(30.1 \text{ mmol NB, [Ni]} : \text{[NB]} = 1 : 1000, \text{[Al]} = 1 : 9, \text{total volume 40.0 mL.}\)

complete loss in polymerization activity. No activity could be detected within a 1 h reaction time. Hence, activation of the metal–phosphane pre-catalysts 5 and 6 necessitates the presence of at least two equivalents of B(C\(_3\)F\(_8\)). This is different from the results of an analogous study on the activation of bis-(diphenylglyoximato)nickel with B(C\(_3\)F\(_8\))/AlEt\(_3\) where a high activity down to a molar ratio of Ni : B : Al = 1 : 1 : 10 was found.\(^{29}\)

In addition, it is known that B(C\(_3\)F\(_8\)) with trimethylaluminium, AlEt\(_3\)\(^{5,6,8}\), or with AlEt\(_3\)\(^{25}\) gives an aryl/alkyl group exchange (eqn. (1))

\[
2 \text{B(C}_3\text{F}_8\text{)} + 2 \text{AlEt}_3 \rightarrow 2 \text{AlEt}_3 \cdot (\text{C}_3\text{F}_8\text{)}_2 + 2 \text{B(C}_3\text{F}_8\text{)} \cdot \text{Et}_3 \quad (1)
\]

which results in the formation of AlEt\(_3\) \cdot (C\(_3\)F\(_8\)) \(_2\) and B(C\(_3\)F\(_8\)) \cdot \text{Et}_3 with Al(C\(_3\)F\(_8\)) as the main product for a molar B : Al ratio of about 1 : 1. Furthermore, aluminium organyls can work as halide abstracting agents.\(^{31,6,8}\) Hence, AlEt\(_3\) \cdot (C\(_3\)F\(_8\)) will then react with the pre-catalysts and can abstract the two chloride atoms to presumably form the polymerization active species (eqn. (2)).

\[
\text{M(L)}\text{Cl}_2 + 2 \text{AlEt}_3 \cdot (\text{C}_3\text{F}_8\text{)}_2 \rightarrow [\text{M(L)}^2]^+ + 2 \text{Cl}^{-} + \text{AlEt}_3 \cdot (\text{C}_3\text{F}_8\text{)}_2^{-} \quad (2)
\]

The bidentate phosphane ligand remains bound to palladium.

It was ascertained in separate experiments that neither B(C\(_3\)F\(_8\)) nor AlEt\(_3\) alone acted as a co-catalyst towards the palladium complexes 5 and 6. Thus, the presence and interaction of both components, B(C\(_3\)F\(_8\)) and AlEt\(_3\), is necessary for activation of 5 and 6. The high Lewis acidity of B(C\(_3\)F\(_8\)) 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\(_3\)H\(_8\)) led to no polymerization activity.\(^{16}\)

NMR studies

The activation hypothesis put forward in eqn. (2) was further tested by multinuclear \(\text{(^1H, ^19F, and ^31P)}\) NMR investigations.
Instead of MAO the better defined co-catalytic system B(C$_3$F$_7$)$_2$/
AlEt$_3$ was used for the NMR studies. The fluorine atoms in
$\text{C}_3\text{F}_5$ and the phosphate ligands on palladium provide for $^{19}$F
and $^{31}$P NMR probes, in addition to $^1$H, to investigate the activ-
ation process. Detailed multinuclear NMR data of the com-
plexes 5 and 6 and the phosphate ligands dppe and dppp in
combination with different amounts of the Lewis acid B(C$_3$F$_7$)$_2$
is available as ESI.†

The spectral changes in the $^1$H NMR are indicative of a reac-
tion between dppe and dppp and B(C$_3$F$_7$)$_2$ and also between 5
and 6 and B(C$_3$F$_7$)$_2$. However, in the latter reaction mixture they
do not allow one to distinguish between phosphorus co-
ordination to Pd or to B. This is best elucidated by using $^{31}$P
NMR. The $^{31}$P signals and their interpretation are provided in
Scheme 3. The $^{31}$P signals of the dppe or dppp ligands in
combination with B(C$_3$F$_7$)$_2$ are shifted with respect to the signals
of the pure ligands, hence indicating a possible P–B coordination.
We ascribe the one signal for dppe/B(C$_3$F$_7$)$_2$ to a 1 : 1 adduct
between the reactants together with a fast equilibrium (on the
NMR time scale) between the two phosphorus donor atoms
(see Scheme 3). For dppp/B(C$_3$F$_7$)$_2$ two signals are observed
which we assign to a 1 : 1 and a 1 : 2 adduct. The 1 : 2 adduct
becomes possible in the case of dppe because of the wider sep-
raration of the two phosphorus donor atoms by the longer alkyl
chain. Similar results were observed in the 1 : 9-spectrum of 1,4-
bis(diphenylphosphino)butane (dpbb) in combination with
B(C$_3$F$_7$)$_2$. The signal of the dpbb ligand at $-16.1$ ppm (CDCl$_3$
RT) were low-field broadened by the addition of B(C$_3$F$_7$)$_2$, and three
new signals appeared at $9.6$ ppm, $13.9$ ppm and $14.5$ ppm, with
the latter two signals significantly broadened (CDCl$_3$, RT).
Again, the signal at $9.6$ ppm can be assigned to a 1 : 2-adduct
and the two broad signals at $13.9$ ppm and $14.5$ ppm should be
the result of the formation of the 1 : 1 adduct mentioned above
(similar chemical shifts compared to the signals of dpbb/
B(C$_3$F$_7$)$_2$). The appearance of two signals in the case of dpbb/
B(C$_3$F$_7$)$_2$ may be explained by a slow equilibrium between the
two phosphorus donor atoms.

Yet, the chemical shifts of the ligand–B(C$_3$F$_7$)$_2$ adducts are
quite different from those seen from the reaction of 5 or 6 with
B(C$_3$F$_7$)$_2$. The $^{31}$P signals for 5 or 6 and B(C$_3$F$_7$)$_2$ are slightly
shifted compared to the $^{31}$P signal of the complexes as a result
of a (necessary) solvent change and the coordination or
abstraction of the chloride atoms by B(C$_3$F$_7$)$_2$. In the case
of 5/B(C$_3$F$_7$)$_2$, the signal at $+56.9$ ppm is assigned to [Pd(dppe)]$^{2+}$
from a ligand redistribution of the unstable [Pd(dppe)]$^{2+}$ (see
below). The NMR chemical shift is close to the one observed for
[Pd(dppe)]$^{2+}$ (58.7 ppm in CD$_2$OD) (see also Scheme 7). For
6/B(C$_3$F$_7$)$_2$, the $^{31}$P NMR signal at $+16.0$ ppm assigned to
[Pd(dpbb)]$^{2+}$ can be compared to the structurally elu-
cidated cation [Pd(dpbb)–Cl–C$_3$F$_7$]$_2$ in 16 (see below) which
resonates at $+17.9$ ppm.

The $^{19}$F NMR spectrum supports the interaction of dppe and
dppp with B(C$_3$F$_7$)$_2$. Two sets of ortho, meta and para signals
are observed in the case of a 1 : 9 molar ratio with the more
intense one corresponding to the free borane. The second set is
assigned to the P–B interaction (Scheme 4). The smaller inten-
sity ratio between free and coordinated borane of 2.4 : 1 in the
case of dpbb/B(C$_3$F$_7$)$_2$ versus 3.9 : 1 for dppe/B(C$_3$F$_7$)$_2$ is in
accord with the interpretation of a 1 : 2 dppp–borane adduct
in addition to the 1 : 1 adduct (see above). Furthermore, chloride
abstraction from 5 and 6 can be deduced from the $^{19}$F NMR
data. The addition of various equivalents of B(C$_3$F$_7$)$_2$ to
the palladium complexes 5 and 6 gives the same spectral features
(see Fig. 6 and Scheme 4). Two sets of ortho, meta and para
signals are again observed. It is a coincidence that the set
labelled with an asterisk (*) appears to have the same chemical
shifts as the set assigned to the P–B interaction from dppe and
dppp (Scheme 4). Alternatively, also the chloride-bridged adduct
([F$_3$C$_6$H$_2$B–Cl–B(C$_3$F$_7$)$_2$])$_2$ from Et$_4$N$^+$Cl$^-$ and B(C$_3$F$_7$)$_2$,
at a 1 : 9 ratio shows the same chemical shifts. The $^{19}$F NMR
chemical shifts of B(C$_3$F$_7$)$_2$ are not very sensitive to the type
of donor atom (here P or Cl) bound to boron. Together with the
above $^{31}$P NMR results, the features in the $^{19}$F NMR from the
reaction of 5 or 6 and B(C$_3$F$_7$)$_2$ (Fig. 6) have to be explained by
a fast equilibrium on the NMR time scale between free borane
and a 1 : 1 boron–chloride adduct, [Cl–B(C$_3$F$_7$)$_2$]$^-$, together
with an additional 2 : 1 boron–chloride adduct, [F$_3$C$_6$H$_2$B–Cl–
B(C$_3$F$_7$)$_2$]$^-$, as depicted in Scheme 4. The averaged signals for

\[ \text{Scheme 3: } ^{31}\text{P NMR data of the interaction between dppe, dppp, dpbb, 5 and 6 with B(C}_3\text{F}_7\text{)}_2\text{ (solvent CD}_2\text{Cl}_2\text{, except for 5 and 6 alone in d}_6\text{-DMSO}\]
the fast equilibrium between free borane and \([\text{Cl} – \text{B}(\text{C}_3\text{F}_5)]\) is shifted towards the signals for pure \(\text{B}(\text{C}_3\text{F}_5)\), with increasing borane ratio. The signals for \([\text{F}(\text{C}_3\text{F}_5)]\text{B} – \text{Cl} – \text{B}(\text{C}_3\text{F}_5)\) remain nearly constant. There may also be an equilibrium between components. Concerning the system \(\text{dppp}/10\text{AlEt}_3\text{Al}(\text{C}_6\text{F}_5)\) from \(\text{borane}\) ratio. The signals for \([\text{F}(\text{C}_3\text{F}_5)]\text{B} – \text{Cl} – \text{B}(\text{C}_3\text{F}_5)\)/free borane which is, however, slow on the NMR time scale. The assignment and the formation of a boron–chloride adduct was verified by an independent investigation of tetraethylammonium chloride, \(\text{Et}_4\text{N}^+\text{Cl}^-\) with \(\text{B}(\text{C}_3\text{F}_5)\), where the same signal pattern could be observed (Scheme 4).22

Still, the pre-catalysts 5 and 6 could not be activated with \(\text{B}(\text{C}_3\text{F}_5)\) alone and triethylaluminium (\(\text{AlEt}_3\)) had to be applied simultaneously for activation. The \(^{31}\text{P}\) signals of the ternary system and their interpretation are provided in Scheme 5. The \(^{31}\text{P}\) signals of dppe or dppp in combination with \(\text{B}(\text{C}_3\text{F}_5)\) show remarkable di

normal NMR characteristics, the formation of a paramagnetic palladium center can be excluded and the broadening of the \(^{31}\text{P}\) NMR signals should be the result of some fast exchange reaction of the dppe ligand. Still, no signals were found at positions seen in the dppe/\(\text{B}(\text{C}_3\text{F}_5)\)/\(\text{AlEt}_3\) mixture, so that a complete ligand abstraction by \(\text{AlEt}_3\), \(\text{B}(\text{C}_3\text{F}_5)\), can be excluded. Intramolecular phosphate exchange pathways responsible for spin loss and signal coalescence were observed in the \(\text{Pd}(0)\) complexes \(\text{PdL}_2\) with \(\text{L} = \text{Pr}(\text{CH}_2)_2\text{P} \text{PrCl}_2\) for \(n = 3\) and 4 (but not \(n = 2\)). Besides, \(\text{Pd}[\text{Pr}(\text{CH}_2)_2\text{P} \text{PrCl}_2]\) for \(n = 3\) and 4 (but not \(n = 2\)) are coordinatively unsaturated trigonal complexes which are in equilibrium with the binuclear complexes \(\text{L} = \text{Pd}(\text{CH}_2)_2\text{P} \text{PrCl}_2\). In summary, as for \(\text{B}(\text{C}_3\text{F}_5)\), the \(^{31}\text{P}\) NMR spectra also excluded the dppe or dppe ligand abstraction from 5 or 6 by the \(\text{B}(\text{C}_3\text{F}_5)/\text{AlEt}_3\) components.

The \(^{31}\text{P}\) NMR spectra of the ternary mixture of the palladium complexes 5 or 6 in combination with different equivalents of \(\text{B}(\text{C}_3\text{F}_5)\) and ten equivalents of \(\text{AlEt}_3\) are depicted in Fig. 7. Their analysis requires an understanding of the interactions between \(\text{B}(\text{C}_3\text{F}_5)\) and \(\text{AlEt}_3\) or between \(\text{Cl}^-\), \(\text{B}(\text{C}_3\text{F}_5)\), and \(\text{AlEt}_3\). As mentioned above, \(\text{B}(\text{C}_3\text{F}_5)\) and \(\text{AlEt}_3\) lead to a facile ary/alkyl group exchange which results in the formation of \(\text{Al}(\text{C}_3\text{F}_5)\) as the main product when using a \(\text{B}(\text{C}_3\text{F}_5)\) : \(\text{AlEt}_3\) ratio of about 1 : 1 (see eqn. (1)). Lower amounts of \(\text{B}(\text{C}_3\text{F}_5)\) or \(\text{vice versa}\) higher amounts of \(\text{AlEt}_3\).
given in ppm). See ESI for complete spectroscopic details.

The spectra were measured in CD$_2$Cl$_2$ or CD$_3$OD (solvent CD$_3$OD was used, room temperature, data given in ppm). See ESI for complete spectroscopic details.

Scheme 5 $^3$P NMR data of the interaction between dppe, dppp and 5 with AlEt$_3$ and different amounts of B(C$_6$F$_5$)$_3$ and 10 equivalents of AlEt$_3$. The following abbreviations were used: $^3$P = signals of the anionic species [EtB(C$_6$F$_5$)$_3$] at $-132.98$ (d, 23.7 Hz, $o$-F), $-165.87$ (t, 20.3 Hz, $p$-F) and $-168.38$ (t, 18.7 Hz, m-F), free = chloride-free aluminium species of the type AlEt$_{3-n}$(C$_6$F$_5$)$_n$, $n=1$–3, CP = 1 : 1 aluminium-chloride adduct of the type [Cl-AlEt$_3$]. $n=1$–3 together with the corresponding 2 : 1 aluminium-chloride adduct. See Fig. 7 for corresponding $^3$P NMR spectra.

Scheme 6 $^{19}$F NMR data of the interaction between Cl$^-$/B(C$_6$F$_5$)$_3$ and AlEt$_3$ (CD$_2$Cl$_2$, room temperature, data given in ppm). See ESI for complete spectroscopic details.

The $^{19}$F NMR spectra of the palladium pre-catalysts 5 and 6 in combination with different equivalents of B(C$_6$F$_5$)$_3$ and ten equivalents of AlEt$_3$ showed remarkable differences (Fig. 7). With regard to the differences in the polymerization activities of the palladium pre-catalysts 5 (1.9 × 10$^4$ g polymer/mol h$^{-1}$) and 6 (3.0 × 10$^4$ g polymer/mol h$^{-1}$) it was important to concentrate on the signals which contain information about the removal of the chloride atoms of the complexes. Beside the known signals of the anionic boron-species [EtB(C$_6$F$_5$)$_3$] at $-132.98$ (d, 23.7 Hz, $o$-F), $-165.87$ (t, 20.3 Hz, $p$-F) and $-168.38$ (t, 18.7 Hz, m-F) at low B(C$_6$F$_5$)$_3$ concentrations, the $^{19}$F NMR spectra were dominated by the signals of monomeric respectively dimeric aluminium or aluminium-chloride adducts with different numbers of C$_6$F$_5$-groups. Unfortunately, an assignment of individual signals cannot be done with high certainty. In case of the m-F-atoms (ca. $-161$ to $-165$ ppm) and the p-F-atoms (ca. $-151$ to $-160$ ppm) it was possible to distinguish between the signals of aluminium or aluminium-chloride species and to extract quantitative information about the chloride-abstraction from the pre-catalysts 5 and 6 by B(C$_6$F$_5$)$_3$/AlEt$_3$. Using this information it was obvious that in the case of the highly-active pre-catalyst 5 the signals of the aluminium-chloride species were more intense than in the case of the low-active pre-catalyst 6. Taking the absence of $^{19}$F NMR signals into account (Scheme 5), the interactions between 6 and B(C$_6$F$_5$)$_3$/AlEt$_3$ result only in minor chloride abstractions and enter instead into fast exchange reactions between B(C$_6$F$_5$)$_3$/AlEt$_3$ and the dppp ligand. A direct correlation between the intensities of the $^{19}$F NMR signals and the differences in the polymerization activities of the palladium pre-catalysts 5 and 6 is difficult and may lead to incomplete assumptions for the activation process with B(C$_6$F$_5$)$_3$/AlEt$_3$ as will be outlined below.

During the NMR experiments we became aware of the formation of a fine, black precipitate following the addition of B(C$_6$F$_5$)$_3$/AlEt$_3$ to the palladium pre-catalyst 5. This precipitate was identified as elemental palladium and its formation may
play an important role in the activation process (see below). The following experiment proved the formation of elemental palladium after the addition of $\text{B(C}_6\text{F}_5\text{)}_3/\text{AlEt}_3$ (Scheme 7).

Under an inert gas atmosphere $0.3 \text{ mmol } 5$ and $0.9 \text{ mmol } \text{B(C}_6\text{F}_5\text{)}_3$ were dissolved in $25 \text{ mL}$ dried $\text{CH}_2\text{Cl}_2$ and $3.0 \text{ mmol } \text{AlEt}_3$ ($1 \text{ mol} \text{ L}^{-1}$ in hexane) were added (molar ratio $5 : \text{B(C}_6\text{F}_5\text{)}_3 : \text{AlEt}_3 = 1 : 3 : 10$). After two days the black precipitate, which started to form directly after the addition of $\text{AlEt}_3$ was centrifuged, washed with $\text{CH}_2\text{Cl}_2$ and redissolved in $\text{HNO}_3/\text{HCl}$ ($\nu/\nu = 1/3$). After the removal of $\text{HNO}_3$ via evaporation, a solution of dimethylglyoxime in ethanol was added to the HCl/water solution. The yellow precipitate was clearly identified as bis(dimethylglyoxime)/palladium(ii) by IR. A mass balance of bis(dimethylglyoxime)/palladium(ii) showed a reduction of about $38\%$ of the palladium(ii) after addition of $\text{B(C}_6\text{F}_5\text{)}_3/\text{AlEt}_3$. After the removal of elemental palladium (after two days) the remaining clear, red-brown $\text{CH}_2\text{Cl}_2$ solution showed one singlet at $58.6 \text{ ppm}$ in its $^{13}\text{P NMR}$ which proved the coordination of the dppe-ligand to palladium(ii) (cf. Scheme 5) presumably as $[\text{Pd(dppe)}]^{2+}$ (see below). The NMR chemical shift is close to the one observed for $[\text{Pd(dppe)}]^{2+}$ in combination with $\text{B(C}_6\text{F}_5\text{)}_3$ after several months. Under the same conditions a crystallization starting from complex and carborane with diethyl ether.

X-Ray structure determinations

To further understand the activity differences of the palladium complexes 5 and 6 we tried to isolate crystalline products from the interaction between the complexes and the Lewis acid $\text{B(C}_6\text{F}_5\text{)}_3$. We are aware, of course, that isolable crystalline products may have little to do with the polymerization-active solution species, hence, any structural results have to be interpreted with caution towards the catalytic observations.

Complexes 5 or 6 and $\text{B(C}_6\text{F}_5\text{)}_3$ (molar ratios $5 : \text{B(C}_6\text{F}_5\text{)}_3 = 1 : 2$) were dissolved in a mixture of toluene and methylene chloride ($\nu/\nu = 1 : 2$) and it was only possible to obtain extremely air-sensitive crystals starting from $5/\text{B(C}_6\text{F}_5\text{)}_3$ after several months. Under the same conditions a crystallization starting from complex 6 was not possible. Structure analysis revealed the formation of a $[\text{Pd(dppe)}]^{2+}$ fragment $^{88,89,92}$ with $\text{B(C}_6\text{F}_5\text{)}_3$ in $[\text{Pd(dppe)}]^{2+}$ and the mono-chelate as the thermodynamic product. The carborane counterion to $[\text{Pd(dppe)}]^{2+}$ has picked up a chloride atom (probably from $\text{CH}_2\text{Cl}_2$) and become $[\text{closo-Cl}_2\text{B}_12\text{H}_{11}\text{Cl}]^{-}$. The phenyl rings on the opposing dppe ligands in the $[\text{Pd(dppe)}]^{2+}$ cations in 14 and 15 are too far apart for a meaningful $\pi-\pi$ interaction, different from the situation in the $[\text{Ni(dppe)}]^{2+}$ cation.

![Scheme 7](image)

From $[\text{Pd(dppe)}]^{2+}$ due to the absence of nucleophilic counter anions as the opposite occurs in the presence of such coordinating counter anions with the bis-chelate as the kinetic product and the mono-chelate as the thermodynamic product.

In order to provide a more stabilizing anion for the potential $[\text{Pd(L)}]^{2+}$ cation we reacted the monocarba-closo-dodecaborane(12) anion, $[\text{closo-Cl}_2\text{B}_12\text{H}_{11}\text{Cl}]^{-}$ as its silver salt with the palladium complexes 5 and 6. In both cases suitable crystals were obtained after several days by overlaying a filtered methylene chloride solution of complex and carborane with diethyl ether.

Starting from the palladium–dppe complex 5, the $[\text{Pd(dppe)}]^{2+}$ cation $^{88}$ is again found in the crystal structure of $[\text{Pd(dppe)}][\text{CB}_6\text{H}_4\text{Cl}_2]/\text{CH}_2\text{Cl}_2$ (15, Fig. 9). Thus, the instability of mono-ligated $[\text{Pd(dppe)}]^{2+}$ and the reaction given in eqn. (3) must be invoked again. The carborane counterion to $[\text{Pd(dppe)}]^{2+}$ has picked up a chloride atom (probably from $\text{CH}_2\text{Cl}_2$) and become $[\text{closo-Cl}_2\text{B}_12\text{H}_{11}\text{Cl}]^{-}$. The phenyl rings on the opposing dppe ligands in the $[\text{Pd(dppe)}]^{2+}$ cations in 14 and 15 are too far apart for a meaningful $\pi-\pi$ interaction, different from the situation in the $[\text{Ni(dppe)}]^{2+}$ cation.

![Fig. 8](image)

![Fig. 9](image)
In contrast, the crystals derived from the palladium–dpdp complex 6 and Ag[closo-1-CB$_3$H$_4$] showed the expected formation of the mono-ligated [Pd(dpdp)]$^+$ species in the structure of [Pd(dpdp)(CB$_9$H$_6$)]$_2$[CB$_6$H$_12$] (16). Here the cation was stabilized by coordination to one of the carborane anions as an exo-(diphsophane)palladium-closo-monocarborane complex [Pd(dpdp)(closo-CB$_9$H$_6$)]$^+$ (Fig. 10). This complex cation crystallizes with a second carborane equivalent [CB$_6$H$_12$] as the counter ion. In the structure of 16 about 22% of the carborane counter anions were found to contain a hydroxy group (introduced most likely by traces of water in the solvent) and hence be of formula [CB$_6$H$_12$](OH)$^-$ as the counter ion. In the structure of 16, the P–Pd–P and B(C$_6$)–P2 formation of [Pd(L)]$^+$ (L = dppe, dppp) as shown in solution from 6 and B(C$_6$)$_3$F$_3$ (see Scheme 3). Similar structures with [CB$_6$H$_12$] ligated to a metal in a bidentate mode have already been described with platinum or rhodium.

Comparison of the crystal data of the pre-catalysts 5 and 6 in combination with B(C$_6$)$_3$F$_3$ and B(C$_6$)$_3$AlEt$_3$ with the structural features of the complexes 14, 15 and 16, the activation process of the pre-catalysts may be formulated in the following way (Scheme 8). (1) Addition of B(C$_6$)$_3$F$_3$ or B(C$_6$)$_3$AlEt$_3$ to the pre-catalysts 5 and 6 resulted at least in partial chloride abstraction and in the formation of [Pd(L)]$^+$ fragments (L = dppe, dppp) as shown by the multinuclear NMR experiments. These [Pd(L)]$^+$ species exhibit however only a low to medium polymerization activity. (2) In case of 5, the [Pd(dppe)]$^+$ cations are unstable and react in a ligand redistribution reaction to form a [Pd(dppe)]$^{2+}$ cation and “naked” Pd$^{2+}$ (demonstrated by the $^{31}$P NMR experiments and the formation of elemental palladium under non-polymerization-conditions and indirectly by the crystal data of 14 and 15). “Naked” Pd$^{2+}$ cations are supposed to be the highly-active species for the polymerization of norbornene. The in-situ formation of “naked” Pd$^{2+}$ appears to be the key to the high activity which is not seen when applying Pd(II) salts, such as PdCl$_2$ in bulk. The chloride abstraction and the ligand redistribution should be a fast two-step-reaction for pre-catalyst 5 – as shown by the short polymerization time (54% conversion in 10 s) and the immediate precipitation of elemental palladium under non-polymerization-conditions. (3) No ligand redistribution but fast exchange reactions between B(C$_6$)$_3$F$_3$/AlEt$_3$ and the dppp ligand were observed in the case of 6/B(C$_6$)$_3$AlEt$_3$, the crystal data of compound 16 and the missing precipitation of elemental palladium after the addition of B(C$_6$)$_3$F$_3$/AlEt$_3$ to pre-catalyst 6.

The possibility to undergo a ligand redistribution reaction and thereby to form “naked” Pd$^{2+}$ as a highly-active species for the polymerization of norbornene could be the result of the steric features in the [Pd(L)]$^+$ fragments with L = dppe and dppp and in the resulting square-planar [Pd(L)$_2$]$^{2+}$ complexes. Comparison of the crystal data of the pre-catalysts 5 and 6 or compounds 14–16 showed the expected smaller bite angle on Pd for the five-membered ring formed with dppe. The bite angle with dpdp in a six-membered chelate ring is larger by about 5$\degree$ (Scheme 9, argument 1).

Combining the results of the multinuclear NMR investigations with the pre-catalysts 5 and 6 in combination with B(C$_6$)$_3$F$_3$ and B(C$_6$)$_3$AlEt$_3$, the activation process of the pre-catalysts may be formulated in the following way (Scheme 8). (1) Addition of B(C$_6$)$_3$F$_3$ or B(C$_6$)$_3$AlEt$_3$ to the pre-catalysts 5 and 6 resulted at least in partial chloride abstraction and in the formation of [Pd(L)]$^+$ fragments (L = dppe, dppp) as shown by the multinuclear NMR experiments. These [Pd(L)]$^+$ species exhibit however only a low to medium polymerization activity. (2) In case of 5, the [Pd(dppe)]$^+$ cations are unstable and react in a ligand redistribution reaction to form a [Pd(dppe)]$^{2+}$ cation and “naked” Pd$^{2+}$ (demonstrated by the $^{31}$P NMR experiments and the formation of elemental palladium under non-polymerization-conditions and indirectly by the crystal data of 14 and 15). “Naked” Pd$^{2+}$ cations are supposed to be the highly-active species for the polymerization of norbornene. The in-situ formation of “naked” Pd$^{2+}$ appears to be the key to the high activity which is not seen when applying Pd(II) salts, such as PdCl$_2$ in bulk. The chloride abstraction and the ligand redistribution should be a fast two-step-reaction for pre-catalyst 5 – as shown by the short polymerization time (54% conversion in 10 s) and the immediate precipitation of elemental palladium under non-polymerization-conditions. (3) No ligand redistribution but fast exchange reactions between B(C$_6$)$_3$F$_3$/AlEt$_3$ and the dppp ligand were observed in the case of 6/B(C$_6$)$_3$AlEt$_3$, the crystal data of compound 16 and the missing precipitation of elemental palladium after the addition of B(C$_6$)$_3$F$_3$/AlEt$_3$ to pre-catalyst 6.

The possibility to undergo a ligand redistribution reaction and thereby to form “naked” Pd$^{2+}$ as a highly-active species for the polymerization of norbornene could be the result of the steric features in the [Pd(L)]$^+$ fragments with L = dppe and dppp and in the resulting square-planar [Pd(L)$_2$]$^{2+}$ complexes. Comparison of the crystal data of the pre-catalysts 5 and 6 or compounds 14–16 showed the expected smaller bite angle on Pd for the five-membered ring formed with dppe. The bite angle with dpdp in a six-membered chelate ring is larger by about 5$\degree$ (Scheme 9, argument 1).

Combining the results of the multinuclear NMR investigations with the pre-catalysts 5 and 6 in combination with B(C$_6$)$_3$F$_3$ and B(C$_6$)$_3$AlEt$_3$, the activation process of the pre-catalysts may be formulated in the following way (Scheme 8). (1) Addition of B(C$_6$)$_3$F$_3$ or B(C$_6$)$_3$AlEt$_3$ to the pre-catalysts 5 and 6 resulted at least in partial chloride abstraction and in the formation of [Pd(L)]$^+$ fragments (L = dppe, dppp) as shown by the multinuclear NMR experiments. These [Pd(L)]$^+$ species exhibit however only a low to medium polymerization activity. (2) In case of 5, the [Pd(dppe)]$^+$ cations are unstable and react in a ligand redistribution reaction to form a [Pd(dppe)]$^{2+}$ cation and “naked” Pd$^{2+}$ (demonstrated by the $^{31}$P NMR experiments and the formation of elemental palladium under non-polymerization-conditions and indirectly by the crystal data of 14 and 15). “Naked” Pd$^{2+}$ cations are supposed to be the highly-active species for the polymerization of norbornene. The in-situ formation of “naked” Pd$^{2+}$ appears to be the key to the high activity which is not seen when applying Pd(II) salts, such as PdCl$_2$ in bulk. The chloride abstraction and the ligand redistribution should be a fast two-step-reaction for pre-catalyst 5 – as shown by the short polymerization time (54% conversion in 10 s) and the immediate precipitation of elemental palladium under non-polymerization-conditions. (3) No ligand redistribution but fast exchange reactions between B(C$_6$)$_3$F$_3$/AlEt$_3$ and the dppp ligand were observed in the case of 6/B(C$_6$)$_3$AlEt$_3$, the crystal data of compound 16 and the missing precipitation of elemental palladium after the addition of B(C$_6$)$_3$F$_3$/AlEt$_3$ to pre-catalyst 6.

The possibility to undergo a ligand redistribution reaction and thereby to form “naked” Pd$^{2+}$ as a highly-active species for the polymerization of norbornene could be the result of the steric features in the [Pd(L)]$^+$ fragments with L = dppe and dppp and in the resulting square-planar [Pd(L)$_2$]$^{2+}$ complexes. Comparison of the crystal data of the pre-catalysts 5 and 6 or compounds 14–16 showed the expected smaller bite angle on Pd for the five-membered ring formed with dppe. The bite angle with dpdp in a six-membered chelate ring is larger by about 5$\degree$ (Scheme 9, argument 1).

![Fig. 10](image-url) Molecular structure of [Pd(dpdp)(CB$_9$H$_6$)]$_2$[CB$_6$H$_12$] (16). Selected distances (Å) and angles (°): Pd–P1 2.257(1), Pd–P2 2.253(1), Pd–B7a 2.406(4), Pd–H7a 1.945, Pd–B12a 2.406(4), Pd–H11a 1.929, Pd–P–Pd 1.948(3), P1–Pd–B7a 113.3(1), P2–Pd–B7a 155.6(1), P1–Pd–B12a 154.8(1), P2–Pd–B12a 114.0(1).

It is obvious that in the case of the dpdp-ligand the larger P–Pd–P angle will increase the steric interaction between two coordinated dpdp-ligands which may explain the not-observed formation of the [Pd(dpdp)]$^{2+}$ complex. No ligand redistribution means no formation of “naked” Pd$^{2+}$. A palladium(0) species of formula [Pd(dpdp)]$^{2+}$ is described in the literature. The formation of the zero-valent species is the result of the distorted tetrahedral coordination sphere around the palladium(0) center which was also found in the corresponding [Pd(dpdp)]$^{2+}$ species. There are reports on the failed synthesis of [Pd(dpdp)]$^{2+}$ together with a recent paper on the
preparation of [Pd(dppe)]Cl₂ (without any structural proof on the formation of a bis-chelate complex, however).  

We note again that the Pd(t) complexes PdCl₂(L = Pr₃P(CHR₂)₂PPr₃) for n = 3 and 4 (but not n = 2) were described as coordinatively unsaturated trigonal complexes (one P-atom is dangling free) which are in equilibrium with the binuclear complexes LPd-dppp. This appears to be a principle difference in the stability (and structure?) of [Pd(dppe)]Cl₂ and [Pd(dppe)Cl₃]. The former has been found to be inactive in CO/ethene copolymerization while the latter exhibits an appreciable activity and can react with CO/Hz. The possible formation of [Pd(dppe)Cl₂] as an intermediate is also seen in the formation of a dimeric, unsaturated palladium(t) species of the type ([dppe]Pd)Cl₂. In the case of the pre-catalyst 5 the ligand redistribution reaction and the formation of “naked” Pd²⁺ as a highly-active species should be the result of a smaller P–Pd–P angle which reduces the steric interaction between the two dppe-ligands (Scheme 9, argument 1). For the smaller nickel ion the formation of [Ni(dppe)]Cl₂ and [Ni(dppe)Cl₃] is also possible.  

In addition to the formation of “naked” Pd²⁺ the difference in the bite angle in the Pd(L)²⁻−fragments with L = dppe and dppt follows the trend for the polymerization activity (Scheme 3, see Scheme 9, argument 2). Ligand dppe is described as a narrowing ligand towards Pd because of its P-Al interaction as noted above for the formation of AlEt₃ and PdCl₂ 6 in the absence of the norbornene monomer the formation of Pd metal is observed for 5/B(C₆F₅)₃/AlEt₃ but not for 6/B(C₆F₅)₃/AlEt₃. The finding of “simple” unligated species upon activation in cycloolefin polymerization agrees with our recent observation on the in situ formation of PdCl₃ from palladium(II) salts containing [PdCl₂]⁻ and [PdCl₃]⁻ ions.  

Acknowledgements

The research was supported by the Fonds der Chemischen Industrie. We appreciate a gift of PdCl₂ by Degussa-Hüls AG and a gift of MAO by Witco GmbH. We thank the referees who provided helpful comments.

References and notes

5 G. Sartori, F. C. Ciampelli and N. Cameli, Chim. Ind. (Milano), 1963, 45, 1478.

Conclusions

Norbornene undergoes a vinyl/αddition polymerization using activated phosphate-chelated metal(t) halide complexes of the general type [M₂(dpP(CH₂CH₃)PPh₂)X₃] with n = 2 (dppe), 3 (dppt) and 4 (dpptt) M = Co, Ni and Pd, X = Cl, Br. The nickel(t) and palladium complexes gave polymerization activities of about 10⁻¹¹ g polymer/mol metal⁻¹ h⁻¹ when activated with methylalumoxane (MAO) or with a combination of tristetrafluorophenyl)borane/triethylaluminium [B(C₆F₅)₃/AlEt₃]. It was also possible to activate the nickel complexes Ni(dppt)Cl₂ and Ni(dpptt)Cl₂ with the Lewis acid B(C₆F₅)₃ alone. Bromine complexes gave a somewhat higher activity than the analogous chloride compounds, apparently due to the weaker Ni–Br bond. The increase in the alkyl-chain length resulted for the nickel complexes in a steady increase in the polymerization activity whereas for the palladium complexes the polymerization activities dropped first from dppe to dppt and then increased subsequently. Multinuclear (¹³P and ¹⁹F) NMR investigations on the complexes Pd(dpP)Cl₃ and Pd(dppt)Cl₂ in combination with B(C₆F₅)₃ and B(C₆F₅)₃/AlEt₃ suggest the formation of [Pd(L)]⁺ cations in the activation process. E(C₆F₅)₃ (E = B, Al) reacts with the pre-catalysts [M₂(dpP(CH₂CH₃)PPh₂)X₃] under abstraction of the two halide atoms. The anions detected were the species [C≡E(C₆F₅)₃]⁻ and [E(C₆F₅)₃-E=C≡E(C₆F₅)₃] with E = B when using B(C₆F₅)₃ alone, E = Al when employing B(C₆F₅)₃/AlEt₃. B(C₆F₅)₃ and AlEt₃ lead to an alky/aryl group exchange which results in the formation of AlEt₃-(C₆F₅)₂ and B(C₆F₅)₃-Et, with Al(C₆F₅)₃ and B(C₆F₅)₃ being the main products for an about equimolar ratio of B(C₆F₅)₃ and AlEt₃. The extremely high polymerization rate of the complex Pd(dppt)Cl₂ (5, 1.0 × 10⁻⁸ g polymer/mol h⁻¹), for example in comparison to Pd(dppe)Cl₂ (5, 3.0 × 10⁻⁹ g polymer/mol h⁻¹), upon activation with B(C₆F₅)₃/AlEt₃ is explained by the formation of highly active “naked” Pd²⁺ through a ligand redistribution of the unstable [Pd(dppe)]⁺ cation to yield [Pd(dppe)]²⁺ and Pd²⁺ together with the lower coordinating ability of the anionic adduct [C≡Al(C₆F₅)₃]⁻ in comparison to [C≡E(C₆F₅)₃]⁻. [Pd(dppe)]⁺ cations were found in crystalline solids derived from 5 and B(C₆F₅)₃ or Ag[close-1-CB₆H₃]. In the absence of the norbornene monomer the formation of Pd metal is observed for 5/B(C₆F₅)₃/AlEt₃ but not for 6/B(C₆F₅)₃/AlEt₃. The finding of “simple” unligated species upon activation in cycloolefin polymerization agrees with our recent observation on the in situ formation of PdCl₃ from palladium(II) salts containing [PdCl₂]⁻ and [PdCl₃]⁻ ions.
99 [Ni(dppe)$_2$](NO$_3$)$_2$ and - (ClO$_4$)$_2$; A. F. Williams, Acta Crystallogr., Sect. C, 1989, 45, 1002–1005.