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Dihalogeno(diphosphane)metal(II) complexes (metal = Co, Ni, Pd) as pre-catalysts for the vinyl/addition polymerization of norbornene – elucidation of the activation process with $B(C_6F_5)_3$/$AlEt_3$ or Ag[*closo*-1-$CB_{11}H_{12}$] and evidence for the *in situ* formation of "naked" Pd^{2+} as a highly active species †

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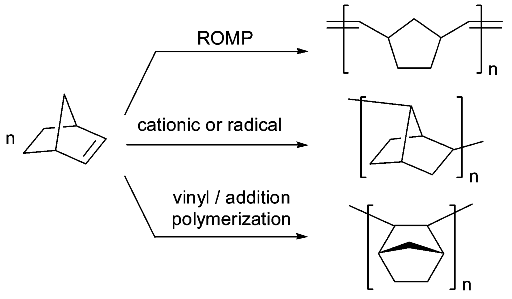
Dihalogenometal(II) complexes with bidentate phosphane ligands of the general type $[M\{Ph_2P(CH_2)_nPPh_2\}X_2]$ with $n = 2$ to 5, X = Cl or Br and M = Co, Ni or Pd have been utilized as catalysts for the vinyl/addition polymerization of norbornene. These complexes can be activated with the Lewis-acids methylalumoxane (MAO) or tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ in combination with triethylaluminium ($AlEt_3$). The nickel(II) and palladium(II) complexes show very high polymerization activities up to 10^7 $g_{polymer}$ mol_{metal}^{-1} h^{-1}. Yet, the complexes $Pd(dppe)Cl_2$ (**5**, 1.9×10^7 $g_{polymer}$ mol_{Pd}^{-1} h^{-1}) and $Pd(dppp)Cl_2$ (**6**, 3.0×10^3 $g_{polymer}$ mol_{Pd}^{-1} h^{-1}) demonstrated that small changes in the ligand structure could have great effects on the polymerization activity [dppe = 1,2-bis(diphenylphosphino)ethane, $Ph_2P(CH_2)_2PPh_2$; dppp = 1,3-bis(diphenylphosphino)propane, $Ph_2P(CH_2)_3PPh_2$]. The activation process of the pre-catalysts **5** and **6** in combination with $B(C_6F_5)_3$/$AlEt_3$ was followed by multinuclear (^1H, ^{19}F, and ^{31}P) NMR investigations and by reaction with $B(C_6F_5)_3$ and Ag[*closo*-1-$CB_{11}H_{12}$]. The reaction of $B(C_6F_5)_3$ and $AlEt_3$ leads to an aryl/alkyl group exchange resulting in the formation of $AlEt_{3-n}(C_6F_5)_n$ and $B(C_6F_5)_{3-n}Et_n$ with $Al(C_6F_5)_3$ and BEt_3 as main products for an about equimolar ratio. $AlEt_{3-n}(C_6F_5)_n$ will then react with the pre-catalysts and abstract the chloride atoms to form $[M\{Ph_2P(CH_2)_nPPh_2\}]^{2+}$ as the active species for the polymerization. The higher polymerization activity of **5**/$B(C_6F_5)_3$/$AlEt_3$ compared to **6**/$B(C_6F_5)_3$/$AlEt_3$ can be explained by a ligand redistribution reaction of unstable $[Pd^{II}(dppe)]^{2+}$ to give inactive and isolable $[Pd^{II}(dppe)_2]^{2+}$ and highly active, "naked" Pd^{2+} cations together with the lower coordinating ability of the anionic adduct $[Cl–Al(C_6F_5)_3]^-$ in comparison to $[Cl–B(C_6F_5)_3]^-$. The Lewis-acid $Al(C_6F_5)_3$ is much more activating than $B(C_6F_5)_3$. The $[Pd(dppe)_2]^{2+}$ cation from the ligand redistribution was isolated in the (X-ray) structurally elucidated compounds $[Pd^{II}(dppe)_2]$-$[ClB(C_6F_5)_3]_2 \cdot 4CH_2Cl_2$ and $[Pd^{II}(dppe)_2][CB_{11}H_{11}Cl]_2 \cdot 3CH_2Cl_2$. The stable $[Pd(dppp)]^{2+}$ cation from **6** could be crystallized as $[Pd^{II}(dppp)(CB_{11}H_{12})][CB_{11}H_{12}]$ ($CB_{11}H_{12}$ = mono-anionic carborane [*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).



Scheme 1

Polymers produced *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.[1–3] Only a few reports describe the formation of low molar mass oligomeric material with 2,7-connectivity of the monomer from the cationic or radical homopolymerization of norbornene.[4] Finally, the vinyl or addition polymerization of norbornene yields saturated 2,3-inserted rotationally constrained polymers in which the bicyclic structural unit remains intact and only the double bond of the π-component is opened. Catalysts containing the metals titanium,[5,6] zirconium,[7–11] chromium,[12] and currently the late transition-metals cobalt,[13–15] nickel[16–31] and palladium[29,32–48] are described in the literature for the vinyl/addition polymerization of norbornene.[49–56] The late transition-metal complexes are commonly activated with methylalumoxane (MAO),[17–20,34,49] except for the cationic palladium-complexes $[Pd(NCR)_4]^{2+}2A^-$ (NCR weakly bound nitrile-ligand; A = "non"-coordinating counter ion).[35–45] Another co-catalytic system for the activation of metal complexes is the organo-Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ 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[57–65] and was recently also applied to the activation of late transition-metal complexes for the (co)polymerization of cyclopentene,[66] ethene,[67] norbornene and norbornene derivatives.[16,32,31,50–56]

Previously, we have communicated initial polymerization results of nickel(II) and palladium(II) dihalogeno complexes bearing bidentate phosphane ligands as pre-catalysts for the

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† Electronic supplementary information (ESI) available: Full ^1H, ^{19}F and ^{31}P NMR data of compounds **5** and **6** in combination with different amounts of $B(C_6F_5)_3$/$AlEt_3$. See http://www.rsc.org/suppdata/dt/b3/b302937a/

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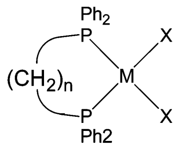
vinyl polymerization of norbonene.[32] These complexes can be activated with MAO as well as with $B(C_6F_5)_3$ in combination with $AlEt_3$ and showed remarkable polymerization activities up to 2.0×10^7 $g_{polymer}$ mol_{metal}^{-1} h^{-1}. In this paper, we wish to present the polymerization results of the complete series of cobalt(II), nickel(II) and palladium(II) complexes of the general type $[M\{Ph_2P(CH_2)_nPPh_2\}Cl_2]$ with n = 2 to 5 and M = 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 $B(C_6F_5)_3$ and $AlEt_3$ by using multinuclear (^1H, ^{19}F, and ^{31}P) NMR investigations and crystallization of reaction products with $B(C_6F_5)$ or the *closo*-carborane anion $[CB_{11}H_{12}]^-$.



1 n = 2, M = Ni, X = Cl, Ni(dppe)Cl_2
2 n = 3, M = Ni, X = Cl, Ni(dppp)Cl_2
3 n = 4, M = Ni, X = Cl, Ni(dppb)Cl_2
4 n = 5, M = Ni, X = Br, Ni(dpppt)Br_2
5 n = 2, M = Pd, X = Cl, Pd(dppe)Cl_2
6 n = 3, M = Pd, X = Cl, Pd(dppp)Cl_2
7 n = 4, M = Pd, X = Cl, Pd(dppb)Cl_2
8 n = 5, M = Pd, X = Cl, Pd(dpppt)Cl_2
9 n = 2, M = Co, X = Cl, Co(dppe)Cl_2
10 n = 3, M = Co, X = Cl, Co(dppp)Cl_2
11 n = 4, M = Co, X = Cl, Co(dppb)Cl_2
12 n = 5, M = Co, X = Cl, Co(dpppt)Cl_2
13 n = 2, M = Ni, X = Br, Ni(dppe)Br_2

dppe = 1,2-bis(diphenylphosphino)ethane
dppp = 1,3-bis(diphenylphosphino)propane
dppb = 1,4-bis(diphenylphosphino)butane
dpppt = 1,5-bis(diphenylphosphino)pentane

Scheme 2

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.[49,68]

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 Optik IFS 25. NMR spectra were recorded with a Bruker Avance DPX 200 at 300 K and 200 MHz (^1H NMR), 81 MHz (^{31}P NMR, calibration against an external standard of 85% H_3PO_4) and 188 MHz (^{19}F NMR, calibration against an external standard of $CDFCl_2$). ^1H NMR spectra were calibrated against the solvent signal (CD_2Cl_2 5.32 ppm). The NMR spectra for compound $[Pd(dppp)(CB_{11}H_{12})][CB_{11}H_{12}]$ (**16**) were recorded with a Bruker Avance 500 at 300 K and 500 MHz (^1H NMR) and 202 MHz (^{31}P 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_2Cl_2 as solvent. Elemental analysis were obtained on a VarioEL from Elementaranalysensysteme 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,[69] data reduction with SAINT.[69] An experimental absorption correction was performed with SADABS.[70] The structures were solved by direct methods (SHELXS-97)[71]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite.[71] 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_3, HFIX 23 for CH_2, HFIX 153 for CH and BH in the carborane, HFIX 83 for OH) and isotropic temperature factors of U(H) = 1.2 U_{eq}(BH, CH and CH_2) or U(H) = 1.5 U_{eq}(CH_3, O). One of the chlorine atoms in each of the two independent CH_2Cl_2 solvent molecules of crystallization in the structure of $[Pd(dppe)_2][ClB(C_6F_5)_3]_2 \cdot 4CH_2Cl_2$ (**14**) was found to be disordered. One of the CH_2Cl_2 solvent molecules in $[Pd(dppe)_2][CB_{11}H_{11}Cl]_2 \cdot 3CH_2Cl_2$ (**15**) is disordered around a crystallographic glide plane. In the structure of $[Pd(dppp)(CB_{11}H_{12})][CB_{11}H_{12}]$ (**16**) about 22% of the carborane counter anions were found to contain a hydroxy group, and hence to be of formula $[CB_{11}H_{11}(OH)]^-$. The OH-group may have been introduced by the solvent diethyl ether which contained traces of water.[72] Thus, the crystal structure would have to be correctly formulated as $[Pd(dppp)(CB_{11}H_{12})][CB_{11}H_{11.78}(OH)_{0.22}]$. The carbon atom in $CB_{11}H_{11}Cl$ in **15** and in the bound and free cage of $CB_{11}H_{12}$ [or $CB_{11}H_{12}(O_{0.22})$] in **16** were located as their B–C bond lengths are slightly shorter than those for B–B. For **15** B–C = 1.701(6)–1.728(8) 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 $CB_{11}H_{11}(OH)$, since the carbon atom was not found opposite to the hydroxide-bound boron (B10) atom. In the anion $CB_{11}H_{11}Cl$ 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.[73] Also, the carbon atom was found opposite to one of the BH 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.[74,75] Details of the X-ray structure determinations and refinements are provided in Table 1. Graphics were obtained with ORTEP 3 for Windows.[76] 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.rsc.org/suppdata/dt/b3/b302937a/ for crystallographic data in CIF or other electronic format.

Materials

Cobalt(II) chloride (Aldrich), nickel(II) chloride (Aldrich), nickel(II) chloride hexahydrate (Acros), nickel(II) bromide (Aldrich), palladium(II) chloride (Merck-Schuchardt), 1,2-bis(diphenylphosphino)ethane (dppe, Aldrich), 1,3-bis(diphenylphosphino)propane (dppp, Strem Chemicals), potassium diphenylphosphide ($(C_6H_5)_2PK$, 0.5 M solution in tetrahydrofuran), 1,4-dichlorobutane (Aldrich), 1,5-dichloropentane (Aldrich), methylalumoxane (10 wt% solution in toluene, Witco), tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, Aldrich), and triethylaluminium ($AlEt_3$, 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. Norbornene (bicyclo[2.2.1]hept-2-ene, Aldrich) was purified by distillation and used as a solution in toluene. 1,4-Bis(diphenylphosphino)butane (dppb),[77] 1,5-bis(diphenylphosphino)pentane[77] (dpppt) and $Ag[CB_{11}H_{12}]$[78] were synthesized by the published literature procedures.

Preparation of the pre-catalysts

The nickel(II) complexes Ni(dppe)Cl_2 (**1**) and Ni(dppp)Cl_2 (**2**) were synthesized by addition of the ligand in CH_2Cl_2 to a solu-

Table 1 Crystal data for the palladium complexes $[Pd^{II}(dppe)_2][ClB(C_6F_5)_3]_2 \cdot 4CH_2Cl_2$ (**14**), $[Pd^{II}(dppe)_2][CB_{11}H_{11}Cl]_2 \cdot 3CH_2Cl_2$ (**15**) and $[Pd^{II}(dppp)(CB_{11}H_{12})][CB_{11}H_{12}]$ (**16**)

Compound	**14**	**15**	**16**
Formula	$C_{92}H_{56}B_2Cl_{10}F_{30}P_4Pd$	$C_{57}H_{75}B_{22}Cl_8P_4Pd$	$C_{29}H_{50}B_{22}O_{0.22}P_2Pd$
M	2337.77	1511.89	808.37
Crystal size/mm	0.23 × 0.09 × 0.08	0.18 × 0.10 × 0.10	0.16 × 0.12 × 0.08
Crystal description	Isometric, colorless	Isometric, brown	Isometric, yellow
T/K	213(2)	213(2)	213(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/m$	$P\bar{1}$
a/Å	10.909(3)	19.750(2)	10.9600(8)
b/Å	14.192(3)	16.029(1)	11.4034(9)
c/Å	16.104(4)	13.770(1)	18.4232(14)
α/°	103.811(4)	90.00	102.192(1)
β/°	104.192(4)	119.159(1)	98.503(1)
γ/°	91.833(4)	90.00	107.025(1)
V/Å^3	2336.2(9)	3806.8(5)	2097.1(3)
Z	1	2	2
D/g cm^{-3}	1.662	1.319	1.280
$F(000)$	1164	1538	824
μ/mm^{-1}	0.661	0.645	0.543
Measured reflections	18052	11893	19180
Unique reflections (R_{int})	8734 (0.0365)	4726 (0.0182)	9809 (0.0416)
Obs. reflections [$I>2\sigma(I)$]	5827	3808	5954
Max/min $\Delta\rho^a$/e Å^{-3}	0.954/−0.847	0.483/−0.469	1.152/−1.241
$R1/wR2$ [$I>2\sigma(I)$]^b	0.0454/0.0995	0.0418/0.1181	0.0522/0.0933
$R1/wR2$ (all data)^b	0.0769/0.1135	0.0549/0.1274	0.0971/0.1090
Goodness-of-fit on $F^{2\,c}$	0.979	1.042	1.038

[a] Largest difference peak and hole. [b] $R1 = [\Sigma(||F_o| - |F_c||)/\Sigma|F_o|]$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] Goodness-of-fit $= [\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$.

tion of $NiCl_2 \cdot 6H_2O$ in ethanol according to a procedure given by Busby *et al.*[79] The palladium(II) complexes $Pd(dppe)Cl_2$ (**5**), $Pd(dppp)Cl_2$ (**6**), $Pd(dppb)Cl_2$ (**7**) and $Pd(dpppt)Cl_2$ (**8**) were synthesized by combining a solution of $PdCl_2$ in hot concentrated HCl and ethanol or 1-butanol with a solution of the appropiate ligand in CH_2Cl_2 or 1-butanol.[32] The nickel(II) complexes $Ni(dppb)Cl_2$ (**3**), $Ni(dpppt)Br_2$ (**4**), $Ni(dppe)Br_2$ (**13**) and the cobalt(II) complexes $Co(dppe)Cl_2$ (**9**), $Co(dppp)Cl_2$ (**10**), $Co(dppb)Cl_2$ (**11**) and $Co(dpppt)Cl_2$ (**12**) were synthesized according to a modified procedure given by Sacconi and Gelsomini.[77] The yields were in the range of 70 to 97% and the purities were checked by CHN-analysis.

Synthesis of $[Pd^{II}(dppe)_2][ClB(C_6F_5)_3]_2 \cdot 4CH_2Cl_2$ (14). $Pd(dppe)Cl_2$ (0.115 g, 0.2 mmol) and $B(C_6F_5)_3$ (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 $[Pd^{II}(dppe)_2][CB_{11}H_{11}Cl]_2 \cdot 3CH_2Cl_2$ (15). $Ag[CB_{11}H_{12}]$ (0.075 g, 0.30 mmol) was placed under an inert-gas atmosphere into a Schlenk-flask which was covered with aluminium foil to protect the silver salt from light. $Pd(dppe)Cl_2$ (0.086 g, 0.15 mmol) was suspended in freshly dried CH_2Cl_2 (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 CH_2Cl_2 and the solvent was removed *in vacuo* to a volume of 5 mL. Some crystals suitable for X-ray diffraction were grown within several days after overlaying the CH_2Cl_2 solution with diethyl ether at room temperature. Single-crystal X-ray analysis yielded a compound with the formula of the title compound. The small amount of crystalline material available (~10 mg) precluded any further analyses.

Synthesis of $[Pd^{II}(dppp)(CB_{11}H_{12})][CB_{11}H_{12}]$ (16). $Ag[CB_{11}H_{12}]$ (0.075 g, 0.30 mmol) was placed under an inert-gas atmosphere into a Schlenk-flask which was covered with aluminium foil to protect the silver salt from light. $Pd(dppp)Cl_2$ (0.089 g, 0.15 mmol) was dissolved in freshly dried CH_2Cl_2 (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 CH_2Cl_2 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). $C_{29}H_{50}B_{22}P_2Pd$ (804.93): calcd. C 43.27, H 6.26; found C 44.09, H 6.49%. ^1H NMR (500 MHz, CD_2Cl_2): δ = 1.0–2.5 (br, 22H, $CHB_{11}H_{11}$), 2.54 (s, br, 2H, $CHB_{11}H_{11}$), 2.75 (t, br, 4H, P–CH_2–CH_2–CH_2–P), 2.83 (s, br, 2H, P–CH_2–CH_2–CH_2–P), 7.30–7.70 (m, 20H, aromatic H-atoms); ^{31}P NMR (202 MHz, CD_2Cl_2): δ = 17.9. Crystals suitable for X-ray diffraction were grown within several days after redissolving the solid product in a minimum of methylene chloride and overlayering 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 carborane counter anions that were found to contain a hydroxy group, and hence to be of formula $[CB_{11}H_{11}(OH)]^-$.

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)s 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

Table 2 Polymerization of norbornene (NB) with complexes **1** to **12** in combination with methylalumoxane (MAO)

Catalyst[a]	Time/min	Conversion (%)	Activity/$g_{polymer}$ mol_{metal}^{-1} h^{-1}	M_n/g mol^{-1}	M_w/g mol^{-1}	$Q = M_w/M_n$
1/MAO	5	2.0	2.1×10^4	1.6×10^6	2.7×10^6	1.7
2/MAO	5	3.7	4.2×10^4	1.3×10^6	2.6×10^6	1.9
3/MAO	5	18.4	2.1×10^5	7.1×10^5	1.7×10^6	2.4
4/MAO	5	36.0	4.1×10^5	1.8×10^5	7.9×10^5	4.4
5/MAO	5	3.3	3.7×10^4		Not soluble	
6/MAO	5	0.1	1.1×10^3		Not soluble	
7/MAO	60	1.8	1.7×10^3		Not soluble	
8/MAO	5	8.0	9.1×10^4		Not soluble	
9/MAO	60	0.4	4.0×10^2	7.2×10^5	1.4×10^6	1.9
10/MAO	60	1.7	1.6×10^3	5.7×10^5	1.4×10^6	2.4
11/MAO	60	0.3	3.0×10^2	2.8×10^5	6.9×10^5	2.5
12/MAO	60	0.6	5.8×10^2	1.5×10^5	4.4×10^5	2.9
1–12/–[b]	60	0	No activity observed	–	–	–

Conditions: room temperature; toluene/methylene chloride solution.[a] 10.6 mmol NB, [M] : [NB] = 1 : 1000, [M] : [Al] = 1 : 100, total volume 10.0 mL. [b] 10.6 mmol NB, [M] : [NB] = 1 : 1000, total volume 10.0 mL.

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 $B(C_6F_5)_3/AlEt_3$ 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 [$B(C_6F_5)_3$ and $AlEt_3$] 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 $B(C_6F_5)_3/AlEt_3$, we conclude that the combination of $B(C_6F_5)_3/AlEt_3$ alone is not polymerization active.

Results and discussion

Norbornene polymerization

Nickel(II), palladium(II) and cobalt(II) complexes of the general type $[M\{Ph_2P(CH_2)_nPPh_2\}X_2]$ 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 methylalumoxane (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 3.0×10^2 (**11**/MAO) to 4.1×10^5 $g_{polymer}$ mol_{metal}^{-1} h^{-1} (**4**/MAO). Only the nickel complexes **3** and **4** and perhaps the palladium complex **8** exhibit activities around or above 10^5 $g_{polymer}$ mol_{metal}^{-1} h^{-1}. These complexes contain the six- or seven-membered dppb and dpppt 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.[15] 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(norbornene)s were insoluble in common solvents as expected from the literature.[16,29,31–37,49,50] The soluble polymer samples displayed a monomodal and narrow molar mass distribution with $Q = M_w/M_n$ close to a value of 2 (except for the highly active **4**/MAO with $Q = 4.4$). The number-average molar mass (M_n) was found between 1.5×10^5 and 1.6×10^6 g mol^{-1}. Thus, the average chain length for the polymers lies between 1,600 (**12**) and 17,000 (**1**) monomer units ($M_{norbornene} = 94.16$ 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.[80] A dispersity of $Q \approx 2$ indicates a single-site character, *i.e.* a highly homogeneous structure for the active catalyst species.

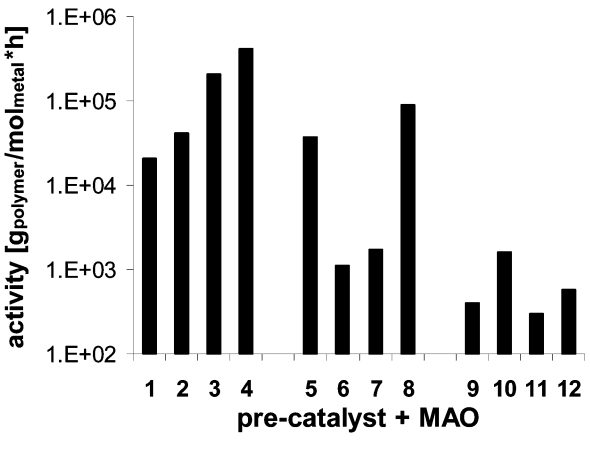


Fig. 1 Activities of **1**–**12** with MAO as co-catalyst in the polymerization of norbornene. Detailed conditions are given in Table 2.

In order to gain additional information about the activation process the activator was changed from MAO to the better defined co-catalyst $B(C_6F_5)_3$ with or without triethylaluminium ($AlEt_3$). Mechanistic investigations with MAO as a co-catalyst are difficult since the exact composition and structure of MAO is still not entirely clear.[61,65,81–84] The results of the polymerization of norbornene with the pre-catalysts **1** to **8** and **10** in combination with $B(C_6F_5)_3/AlEt_3$ or with $B(C_6F_5)_3$ 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 $B(C_6F_5)_3/AlEt_3$. 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 dppb and dpppt ligands show activities around or above 10^5 $g_{polymer}$ mol_{metal}^{-1} h^{-1} (Fig. 2). Even the overall activities for these complexes with MAO or with $B(C_6F_5)_3/AlEt_3$ 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 $B(C_6F_5)_3/AlEt_3$ than with MAO (molar ratios of Pd : borane : $AlEt_3$ = 1 : 9 : 10 and Pd : MAO = 1 : 100). This leads to fewer co-catalyst residues in

Table 3 Polymerization of norbornene (NB) with complexes **1** to **8** and **10** in combination with $B(C_6F_5)_3$ and triethylaluminium ($AlEt_3$)

Catalyst	Time/min	Conversion (%)	Activity/$g_{polymer}$ mol_{metal}^{-1} h^{-1}	M_n/g mol^{-1}	M_w/g mol^{-1}	$Q = M_w/M_n$
1/$B(C_6F_5)_3/AlEt_3$ [a]	60	4.1	3.8×10^3	4.1×10^5	1.0×10^6	2.5
2/$B(C_6F_5)_3/AlEt_3$ [a]	60	9.0	8.6×10^3	3.4×10^5	8.1×10^5	2.4
3/$B(C_6F_5)_3/AlEt_3$ [a]	5	9.0	1.0×10^5	3.9×10^5	8.4×10^5	2.2
4/$B(C_6F_5)_3/AlEt_3$ [a]	5	14.8	1.7×10^5	1.2×10^5	4.2×10^5	3.4
5/$B(C_6F_5)_3/AlEt_3$ [a]	1/6	54.3	1.9×10^7		Not soluble	
6/$B(C_6F_5)_3/AlEt_3$ [a]	60	3.1	3.0×10^3		Not soluble	
7/$B(C_6F_5)_3/AlEt_3$ [a]	5	8.1	9.2×10^4		Not soluble	
8/$B(C_6F_5)_3/AlEt_3$ [a]	1	17.4	9.9×10^5		Not soluble	
10/$B(C_6F_5)_3/AlEt_3$ [a]	60	0.6	5.7×10^2	6.5×10^5	1.2×10^6	1.8
1–**8**/$AlEt_3$ [b]	60	0	No activity observed	–	–	–
3/$B(C_6F_5)_3$ [c]	60	15.0	1.4×10^4	1.1×10^6	2.1×10^6	1.9
4/$B(C_6F_5)_3$ [c]	60	11.1	1.0×10^4	9.5×10^5	1.5×10^6	1.6
1,**2**,**5**–**8**/$B(C_6F_5)_3$ [c]	60	0	No activity observed	–	–	–

Conditions: room temperature; toluene/methylene chloride solution. [a] 30.1 mmol NB, [M] : [NB] = 1 : 1000, [M] : [B] : [Al] = 1 : 9 : 10, total volume 40.0 mL. [b] 30.1 mmol NB, [M] : [NB] = 1 : 1000, [M] : [Al] = 1 : 10, total volume 40.0 mL. [c] 30.1 mmol NB, [M] : [NB] = 1 : 1000, [M] : [B] = 1 : 9, total volume 40.0 mL.

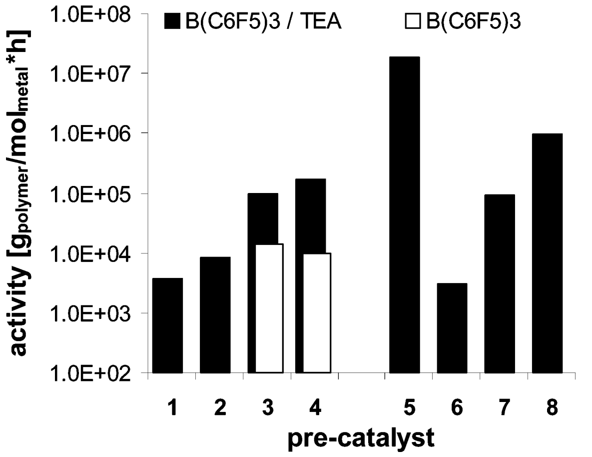


Fig. 2 Activities of **1**–**8** with $B(C_6F_5)_3/AlEt_3$ or $B(C_6F_5)_3$ alone as co-catalyst in the polymerization of norbornene. Detailed conditions are given in Table 3.

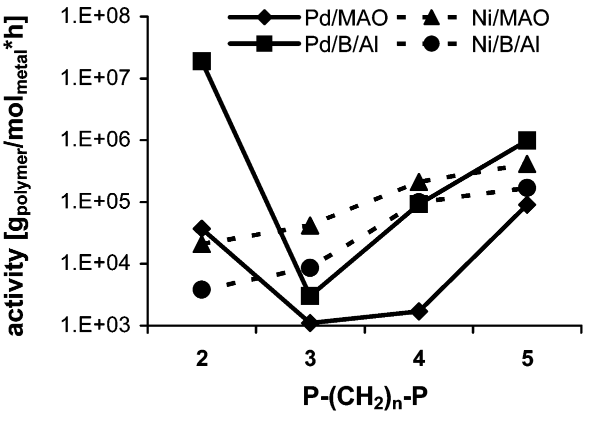


Fig. 3 Polymerization activities of the metal–phopshine chelate complexes $[M\{Ph_2P(CH_2)_nPPh_2\}Cl_2]$ **1**–**8** as a function of the chelate size n (n=2 to 5); activation with MAO or B/Al (= $B(C_6F_5)_3/AlEt_3$). Detailed conditions are given in Tables 2 and 3.

the polymer which should be highly advantageous for the prospective optical applications of poly(norbornene).

Thus, the activity correlates with the length of the alkyl-group 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 $B(C_6F_5)_3/AlEt_3$ 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 $B(C_6F_5)_3/AlEt_3$-activated Ni- or Pd-complexes are not well known.[49] 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(II) salts containing $[PdCl_4]^{2-}$ and $[Pd_2Cl_6]^{2-}$ ions with evidence for the *in situ* formation of $PdCl_2$.[32]

An exception upon $B(C_6F_5)_3/AlEt_3$-activation is the palladium–dppe complex **5**. The reproducible and extremely high activity of **5** of the order of 10^7 $g_{polymer}$ mol_{Pd}^{-1} 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 dppb and dpppt ligand, respectively, could be activated with $B(C_6F_5)_3$ alone for the vinyl polymerization of norbornene, albeit with low activity. The GPC data of the nickel/borane catalyzed poly(norbornene)s 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**/$B(C_6F_5)_3/AlEt_3$) and 12,000 (**3**/$B(C_6F_5)_3$) monomer units corresponding to a number-average molar mass (M_n) between 1.2×10^5 and 1.1×10^6 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 $B(C_6F_5)_3/AlEt_3$ (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 $B(C_6F_5)_3$ on the polymerization activity (see Table 5 and Fig. 5). The Pd–dppe complex **5** and the dppp-analog **6** had shown dramatic differences in the polymerization activities with $B(C_6F_5)_3/AlEt_3$ as co-catalysts.

Both palladium pre-catalysts **5** and **6** show the same activity trends when varying the molar ratio of Pd : $B(C_6F_5)_3$ in the polymerization of norbornene. A decrease of the amount of $B(C_6F_5)_3$ from Pd : $B(C_6F_5)_3$: Al = 1 : 9 : 10 down to 1 : 2 : 10 led to a steady decrease in polymerization activity. Yet, even at a

Table 4 Polymerization of norbornene (NB) with the Ni–dppe complexes **1** (Cl ligand) and **13** (Br ligand)

Catalyst	Time/min	Conversion (%)	Activity/$g_{polymer}$ mol_{Ni}^{-1} h^{-1}	M_n/g mol^{-1}	M_w/g mol^{-1}	$Q = M_w/M_n$
1/MAO[a]	5	2.0	2.1×10^4	1.6×10^6	2.7×10^6	1.7
13/MAO[a]	5	3.8	4.3×10^4	5.1×10^5	9.5×10^5	1.9
1/$B(C_6F_5)_3/AlEt_3$[b]	60	4.1	3.8×10^3	4.1×10^5	1.0×10^6	2.5
13/$B(C_6F_5)_3/AlEt_3$[b]	5	19.2	2.2×10^5	1.1×10^5	3.1×10^5	2.8
1,13/$AlEt_3$[c]	60	0	No activity observed	–	–	–
1,13/$B(C_6F_5)_3$[d]	60	0		–	–	–

Conditions: room temperature; toluene/methylene chloride solution.[a] 10.6 mmol NB, [Ni] : [NB] = 1 : 1000, [Ni] : [Al] = 1 : 100, total volume 10.0 mL. [b] 30.1 mmol NB, [Ni] : [NB] = 1 : 1000, [Ni] : [B] : [Al] = 1 : 9 : 10, total volume 40.0 mL. [c] 30.1 mmol NB, [Ni] : [NB] = 1 : 1000, [Ni] : [Al] = 1 : 10, total volume 40.0 mL. [d] 30.1 mmol NB, [Ni] : [NB] = 1 : 1000, [Ni] : [B] = 1 : 9, 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 $B(C_6F_5)_3/AlEt_3$

Catalyst	Molar ratio Pd : B : Al	Time/min	Conversion (%)	Activity/$g_{polymer}$ mol_{Pd}^{-1} h^{-1}
5	1 : 9 : 0	1/6	54.3	1.9×10^7
5	1 : 7 : 10	1/6	24.0	8.1×10^6
5	1 : 5 : 10	1/6	12.5	4.3×10^6
5	1 : 3 : 10	1/6	4.5	1.5×10^6
5	1 : 2 : 10	1/6	2.1	7.1×10^5
6	1 : 9 : 10	60	3.1	3.0×10^3
6	1 : 5 : 10	60	1.0	9.0×10^2
6	1 : 2 : 10	60	1.0	9.5×10^2
5, 6	1 : 1 : 10	60	0	–
5, 6	1 : 0 : 10	60	0	–

Conditions: room temperature; toluene/methylene chloride solution, 30 mmol NB, [Pd] : [NB] = 1 : 1000, total volume 40.0 mL.

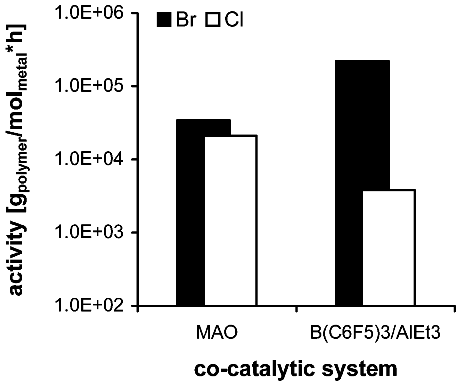


Fig. 4 Polymerization activities of the nickel–dppe complexes **1** and **13** with chloro or bromo ligands; activation with MAO or $B(C_6F_5)_3/AlEt_3$. Detailed conditions are given in Table 4.

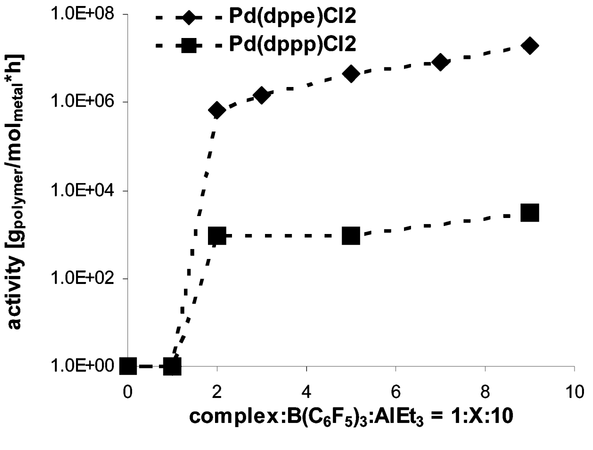


Fig. 5 Polymerization activities of the Pd complexes **5** and **6** with dppe or dppp ligands as a function of the borane ratio; activation with $B(C_6F_5)_3/AlEt_3$. Detailed conditions are given in Table 5.

ratio of Pd : $B(C_6F_5)_3$: Al = 1 : 2 : 10 the activity could be considered (very) high for **5**. However, a further decrease in the amount of $B(C_6F_5)_3$, below a ratio of Pd : B = 1 : 2 resulted in a 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 $B(C_6F_5)_3$. This is different from the results of an analogous study on the activation of bis(diphenylglyoximato)nickel with $B(C_6F_5)_3/AlEt_3$ 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 $B(C_6F_5)_3$ with trimethylaluminium, $AlMe_3$[85,86] or with $AlEt_3$[29] gives an aryl/alkyl group exchange (eqn. (1))

$$2\,B(C_6F_5)_3 + 2\,AlEt_3 \longrightarrow 2\,AlEt_{3-n}(C_6F_5)_n + 2\,B(C_6F_5)_{3-n}Et_n \qquad (1)$$

which results in the formation of $AlEt_{3-n}(C_6F_5)_n$ and $B(C_6F_5)_{3-n}Et_n$ with $Al(C_6F_5)_3$ as the main product for a molar B : Al ratio of about 1 : 1. Furthermore, aluminium organyls can work as halide abstracting agents.[61,65,87] Hence, $AlEt_{3-n}(C_6F_5)_n$ will then react with the pre-catalysts and can abstract the two chloride atoms to presumably form the polymerization active species (eqn. (2)).

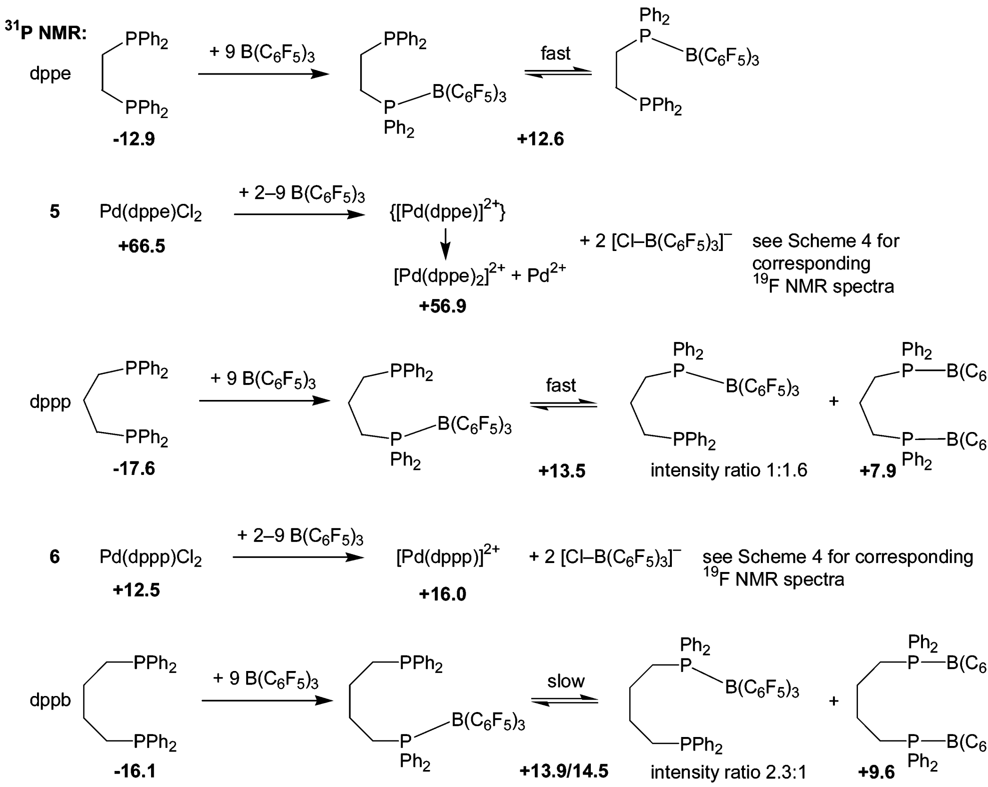
$$M(L)Cl_2 + 2\,AlEt_{3-n}(C_6F_5)_n \longrightarrow [M(L)]^{2+} + 2\,[Cl\text{–}AlEt_{3-n}(C_6F_5)_n]^- \qquad (2)$$

The bidentate phosphane ligand remains bound to palladium.

It was ascertained in separate experiments that neither $B(C_6F_5)_3$ nor $AlEt_3$ alone acted as a co-catalyst towards the palladium complexes **5** and **6**. Thus, the presence and interaction of both components, $B(C_6F_5)_3$ and $AlEt_3$, is necessary for activation of **5** and **6**. The high Lewis acidity of $B(C_6F_5)_3$ 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 $B(C_6H_5)_3$ led to no polymerization activity.[16]

NMR studies

The activation hypothesis put forward in eqn. (2) was further tested by multinuclear (^1H, ^{19}F, and ^{31}P) NMR investigations.



Scheme 3 ^{31}P NMR data of the interaction between dppe, dppp, dppb, **5** and **6** with $B(C_6F_5)_3$ (solvent CD_2Cl_2, except for **5** and **6** alone in d_6-DMSO and dppb alone in $CDCl_3$, room temperature, data given in ppm). See ESI † for complete spectroscopic details.

Instead of MAO the better defined co-catalytic system $B(C_6F_5)_3$/$AlEt_3$ was used for the NMR studies. The fluorine atoms in $-C_6F_5$ and the phosphane ligands on palladium provide for ^{19}F and ^{31}P NMR probes, in addition to ^{1}H, to investigate the activation process. Detailed multinuclear NMR data of the complexes **5** and **6** and the phosphane ligands dppe and dppp in combination with different amounts of the Lewis acid $B(C_6F_5)_3$ is available as ESI. †

The spectral changes in the ^{1}H NMR are indicative of a reaction between dppe and dppp and $B(C_6F_5)_3$ and also between **5** and **6** and $B(C_6F_5)_3$. However, in the latter reaction mixture they do not allow one to distinguish between phosphane coordination 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 $B(C_6F_5)_3$ 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/$B(C_6F_5)_3$ 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/$B(C_6F_5)_3$ 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 dppp because of the wider separation 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 (dppb) in combination with $B(C_6F_5)_3$. The signal of the dppb ligand at −16.1 ppm ($CDCl_3$, RT) were low-field shifted by the addition of $B(C_6F_5)_3$ and three new signals appeared at 9.6 ppm, 13.9 ppm and 14.5 ppm, with the latter two signals significantly broadened (CD_2Cl_2, 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 dppp/$B(C_6F_5)_3$). The appearance of two signals in the case of dppb/$B(C_6F_5)_3$ may be explained by a slow equilibrium between the two phosphorus donor atoms.

Yet, the chemical shifts of the ligand–$B(C_6F_5)_3$ adducts are quite different from those seen from the reaction of **5** or **6** with $B(C_6F_5)_3$. The ^{31}P signals for **5** or **6** and $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$. In the case of **5**/$B(C_6F_5)_3$ the signal at +56.9 ppm is assigned to $[Pd(dppe)_2]^{2+}$ from a ligand redistribution of the unstable $[Pd(dppe)]^{2+}$ (see below). The NMR chemical shift is close to the one observed for $[Pd(dppe)_2](OAc)$ (58.7 ppm in CD_3OD) (see also Scheme 7).[88,89] For **6**/$B(C_6F_5)_3$, the ^{31}P NMR signal at +16.0 ppm assigned to $[Pd(dppp)]^{2+}$ can be compared to the structurally elucidated cation [Pd(dppp)(*closo*-$CB_{11}H_{12}$)]$^+$ in **16** (see below) which resonates at +17.9 ppm.

The ^{19}F NMR data supports the interaction of dppe and dppp with $B(C_6F_5)_3$. 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 intensity ratio between free and coordinated borane of 2.4 : 1 in the case of dppp/$B(C_6F_5)_3$ *versus* 3.9 : 1 for dppe/$B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ 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 $[(F_5C_6)_3B–Cl–B(C_6F_5)_3]^-$ from $Et_4N^+Cl^-$ and $B(C_6F_5)_3$ at a 1 : 9 ratio shows the same chemical shifts. The ^{19}F NMR chemical shifts in $B(C_6F_5)_3$ 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 $B(C_6F_5)_3$ (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, $[Cl–B(C_6F_5)_3]^-$, together with an additional 2 : 1 boron–chloride adduct, $[(F_5C_6)_3B–Cl–B(C_6F_5)_3]^-$, as depicted in Scheme 4. The averaged signals for

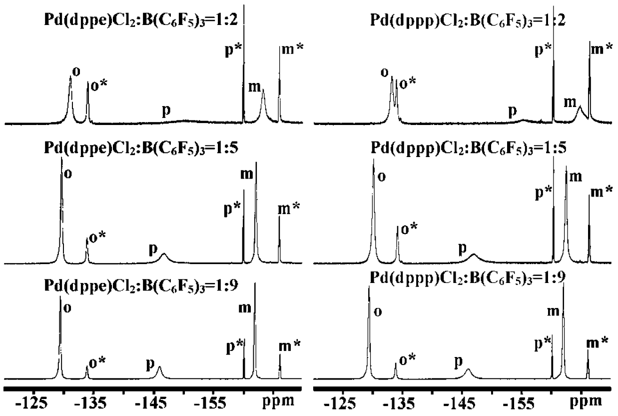
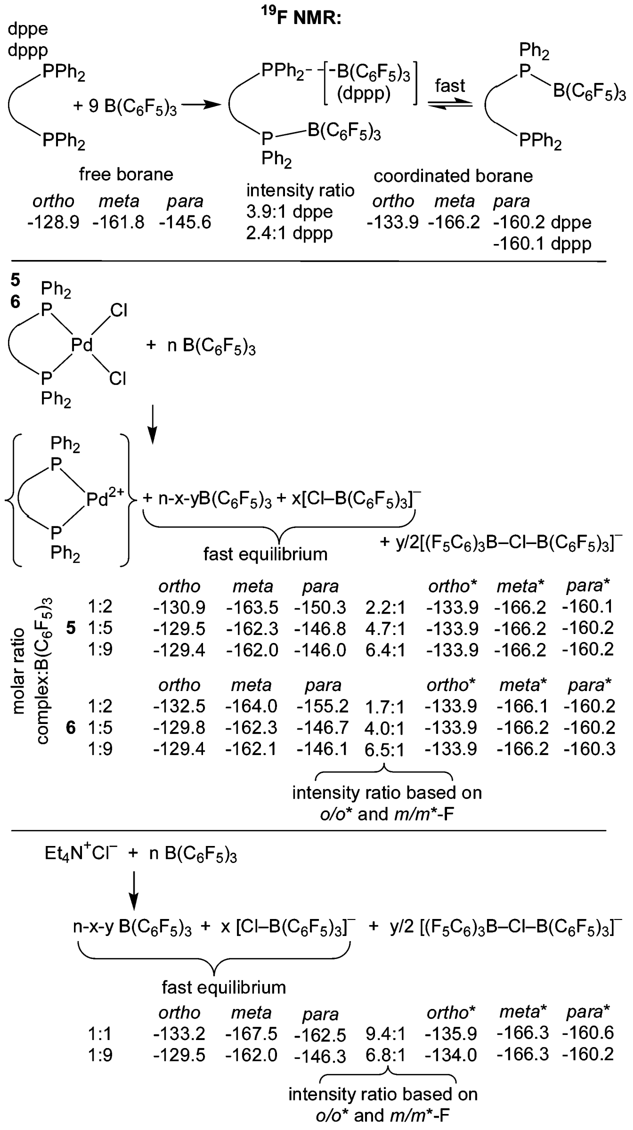


Fig. 6 ^{19}F NMR spectra of $Pd(dppe)Cl_2$ (**5**) and $Pd(dppp)Cl_2$ (**6**) in combination with different amounts of $B(C_6F_5)_3$. The letters *o*, *m*, *p* indicate the *ortho*, *meta*, and *para* fluorine atoms in the fast equilibrium between $B(C_6F_5)_3$ and $[Cl–B(C_6F_5)_3]^-$. The letters *o**, *m**, *p** indicate the *ortho*, *meta*, and *para* fluorine atoms in the $[(F_5C_6)_3B–Cl–B(C_6F_5)_3]^-$ species (Scheme 4). The spectra were measured in CD_2Cl_2 (0.6 mL) at room temperature; 7 μmol palladium complex and the corresponding amount of $B(C_6F_5)_3$. See ESI † for signal multiplicity, FF coupling constants and further details.



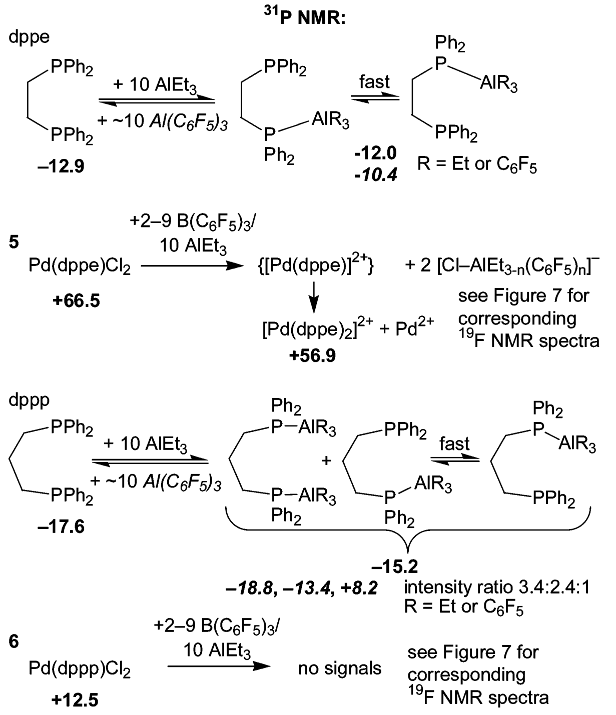
Scheme 4 ^{19}F NMR data of the interaction between dppe, dppp and Cl^- (from **5**, **6** or Et_4NCl) and $B(C_6F_5)_3$ (CD_2Cl_2, room temperature, data given in ppm). See ESI † for signal multiplicity, FF coupling constants and further details.

the fast equilibrium between free borane and $[Cl–B(C_6F_5)_3]^-$ are shifted towards the signals for pure $B(C_6F_5)_3$ with increasing borane ratio. The signals for $[(F_5C_6)_3B–Cl–B(C_6F_5)_3]^-$ remain nearly constant. There may also be an equilibrium between $[(F_5C_6)_3B–Cl–B(C_6F_5)_3]^-$ and $[Cl–B(C_6F_5)_3]^-$/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, $Et_4N^+Cl^-$ with $B(C_6F_5)_3$ where the same signal pattern could be observed (Scheme 4).[32]

Still, the pre-catalysts **5** and **6** could not be activated with $B(C_6F_5)_3$ alone and triethylaluminium ($AlEt_3$) had to be applied simultaneously for activation. The ^{31}P signals of the ternary system and their interpretation are provided in Scheme 5. The ^{31}P signals of dppe or dppp in combination with $B(C_6F_5)_3/AlEt_3$ are only very little shifted with respect to the signals of the pure ligands. Such small shifts are in agreement, however, with changes in ^{31}P chemical shifts found in trimethylaluminium–phosphane complexes.[90,91] Thus, the shifts indicate a P–Al adduct, possibly as part of a fast equilibrium between the free components. Concerning the system dppp/10$AlEt_3$ just one single ^{31}P resonance is observed. Possibly also the 1 : 2 complex $(dppp)(AlEt_3)_2$ is part of the fast equilibrium between the 1 : 1 adducts or no 1 : 2 adduct is formed from $AlEt_3$ alone but only with $Al(C_6F_5)_3$. The addition of ten equivalents of $AlEt_3$ to the complexes **5** and **6** in combination with different amounts of $B(C_6F_5)_3$ showed remarkable differences in the ^{31}P NMR spectra. In the case of **5**/$B(C_6F_5)_3$/$AlEt_3$ the ^{31}P NMR spectrum was the same as observed before for **5**/$B(C_6F_5)_3$ (see Scheme 3), that is the signal did not change when adding the $AlEt_3$ to a solution of **5** and $B(C_6F_5)_3$. The species with a signal at 56.9 ppm in Schemes 3 and 5 is assigned to $[Pd(dppe)_2]^{2+}$ which is derived from a ligand redistribution of the unstable $[Pd(dppe)]^{2+}$ (see also below).[88,89,92] The redistribution also gives rise to a Pd^{2+} cation. However, the reaction mixture from **5**/$B(C_6F_5)_3$ and also **6**/$B(C_6F_5)_3$ is inactive towards polymerization. We explain this fact by a stronger, deactivating coordination of $[Cl–B(C_6F_5)_3]^-$ to the cations. The adduct $[Cl–Al(C_6F_5)_3]$ is suggested to be less coordinating. In other words, the Lewis-acid $Al(C_6F_5)_3$ appears to be more activating than $B(C_6F_5)_3$.

Upon addition of $AlEt_3$ to a solution of **6** and $B(C_6F_5)_3$ the ^{31}P NMR signal broadened strongly which we can explain either by formation of a paramagnetic palladium center or by some fast exchange reaction involving the dppp ligand. Taking into account that the ^{1}H NMR and ^{19}F NMR spectra showed normal NMR characteristics, the formation of a paramagnetic palladium center can be excluded and the broadening of the ^{31}P NMR signals should be the result of some fast exchange reaction of the dppp ligand. Still, no signals were found at positions seen in the dppp/$B(C_6F_5)_3$/$AlEt_3$ mixture, so that a complete ligand abstraction by $AlEt_{3-n}(C_6F_5)_n$ can be excluded. Intramolecular phosphane exchange pathways responsible for spin loss and signal coalescence were observed in the Pd(0) complexes PdL_2 with $L = {}^iPr_2P(CH_2)_nP^iPr_2$ for $n = 3$ and 4 (but not $n = 2$). Besides, $[Pd({}^iPr_2P(CH_2)_nP^iPr_2)_2]$ for $n = 3$ and 4 (but not $n = 2$) are coordinatively unsaturated trigonal complexes which are in equilibrium with the binuclear complexes $LPd(\eta^2\text{-}L)\text{-}PdL$.[93] In summary, as for $B(C_6F_5)_3$ the ^{31}P NMR spectra also excluded the dppe or dppp ligand abstraction from **5** or **6** by the $B(C_6F_5)_3$/$AlEt_3$ components.

The ^{19}F NMR spectra of the ternary mixture of the palladium complexes **5** or **6** in combination with different equivalents of $B(C_6F_5)_3$ and ten equivalents of $AlEt_3$ are depicted in Fig. 7. Their analysis requires an understanding of the interactions between $B(C_6F_5)_3$ and $AlEt_3$ or between Cl^-, $B(C_6F_5)_3$ and $AlEt_3$. As mentioned above, $B(C_6F_5)_3$ and $AlEt_3$ lead to a facile aryl/alkyl group exchange which results in the formation of $Al(C_6F_5)_3$ as the main product when using a $B(C_6F_5)_3$: $AlEt_3$ ratio of about 1 : 1 (see eqn. (1)). Lower amounts of $B(C_6F_5)_3$ or *vice versa* higher amounts of $AlEt_3$



Scheme 5 ^{31}P NMR data of the interaction between dppe, dppp, **5** and **6** with $AlEt_3$ and different amounts of $B(C_6F_5)_3$. *$Al(C_6F_5)_3$* is derived from the nearly equimolar (9 : 10) reaction of $B(C_6F_5)_3$ and $AlEt_3$ (resulting chemical shifts given in *italics*) (solvent CD_2Cl_2, except for **5** and **6** alone where d_6-DMSO was used, room temperature, data given in ppm). See ESI† for complete spectroscopic details.

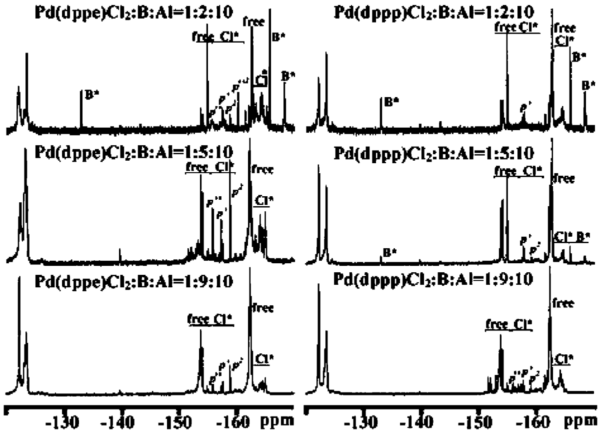
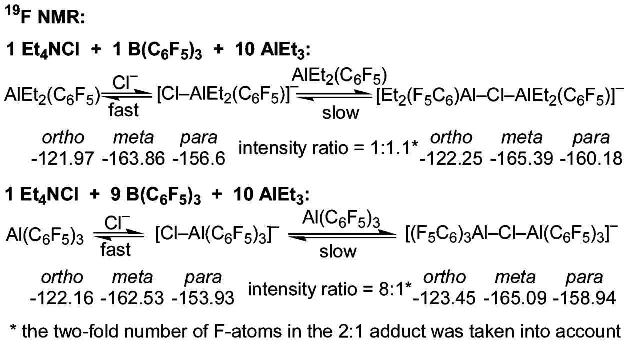


Fig. 7 ^{19}F NMR spectra of $Pd(dppe)Cl_2$ (**5**) and $Pd(dppp)Cl_2$ (**6**) in combination with different amounts of $B(C_6F_5)_3$ and 10 equivalents of $AlEt_3$. The following abbreviations were used: **B***=signals of the anionic species $[EtB(C_6F_5)_3]^-$ at −132.98 (d, 23.7 Hz, *o*-F), −165.87 (t, 20.3 Hz, *p*-F) and −168.38 (t, 18.7 Hz, *m*-F),[95] **free** = chloride-free aluminium species of the type $AlEt_{3-n}(C_6F_5)_n$, n=1–3, **Cl***=1 : 1 aluminium–chloride adduct of the type $[Cl–AlEt_{3-n}(C_6F_5)_n]^-$, n=1–3 together with the corresponding 2 : 1 aluminium–chloride adduct. Signals are assigned based on $Et_4N^+Cl^-/B(C_6F_5)_3/AlEt_3$; only the *para*-fluorine atoms are indicated for clarity: p''=$[Cl–AlEt_2(C_6F_5)]^-$ at −155.83 (t, 19.2 Hz, *p*-F), p''^2=$[Et_2(F_5C_6)Al–Cl–AlEt_2(C_6F_5)]^-$ at −160.24 (t, 19.4 Hz, *p*-F), p^2=$[(F_5C_6)_3Al–Cl–Al(C_6F_5)_3]^-$ at −158.96 (t, 19.2 Hz, *p*-F), p'=$[Cl–AlEt(C_6F_5)_2]^-$ or $[Et(F_5C_6)_2Al–Cl–AlEt(C_6F_5)_2]^-$ at −157.41 (t, 19.4 Hz, *p*-F) or −157.73 (t, 19.2 Hz, *p*-F), respectively. The spectra were measured in CD_2Cl_2 (0.6 mL) at room temperature (7 μmol palladium complex, 70 μmol $AlEt_3$ and the corresponding amount of $B(C_6F_5)_3$).

indicate a stepwise aryl/alkyl group exchange and show the formation of $AlEt(C_6F_5)_2$ or $AlEt_2(C_6F_5)$ as main products, depending on the $B(C_6F_5)_3$: $AlEt_3$ ratio (see Fig. 7).[85,94] The interactions between Cl^-, $B(C_6F_5)_3$ and $AlEt_3$ were investigated by the addition of one equivalent of $Et_4N^+Cl^-$ to a 1 : 10 and a 9 : 10 mixture of $B(C_6F_5)_3$ and $AlEt_3$ using ^{19}F NMR spectroscopy (Scheme 6). In the 1 : 1 : 10 spectrum of $Et_4N^+Cl^-$: $B(C_6F_5)_3$: $AlEt_3$ three different groups of signals were found and according to the intensity ratios and in comparison to the spectra of $B(C_6F_5)_3/AlEt_3$ with different molar ratios, the signals can be attributed to the formation of $Et_2Al(Et)_2AlEt(C_6F_5)$ (weak signals), $AlEt_2(C_6F_5)/[Cl–AlEt_2(C_6F_5)]^-$ (broad signals) and $[Et_2(F_5C_6)Al–Cl–AlEt_2(C_6F_5)]^-$. The broad signals are due to fast equilibrium on the NMR time scale between free $AlEt_2(C_6F_5)$ and $[Cl–AlEt_2(C_6F_5)]^-$.

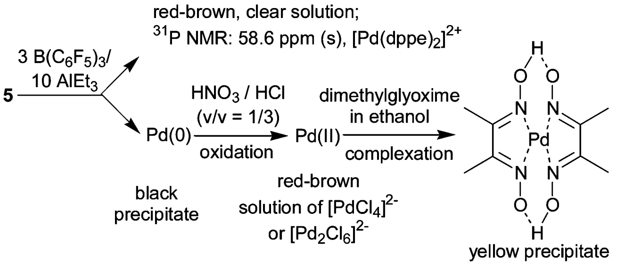


Scheme 6 ^{19}F NMR data of the interaction between Cl^-, $B(C_6F_5)_3$ and $AlEt_3$ (CD_2Cl_2, room temperature, data given in ppm). See ESI† for signal multiplicity, FF coupling constants and further details.

Addition of one equivalent of $Et_4N^+Cl^-$ to a 9 : 10 mixture of $B(C_6F_5)_3/AlEt_3$ resulted in a ^{19}F NMR spectrum which can also be explained by a fast equilibrium between free $Al(C_6F_5)_3$ and the 1 : 1 aluminium–chloride adduct together with an additional 2 : 1 aluminium–chloride adduct (Scheme 6).

The ^{19}F NMR spectra of the palladium pre-catalysts **5** and **6** in combination with different equivalents of $B(C_6F_5)_3$ 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** (1.9×10^7 $g_{polymer}$ mol_{Pd}^{-1} h^{-1}) and **6** (3.0×10^3 $g_{polymer}$ mol_{Pd}^{-1} 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 $[EtB(C_6F_5)_3]^-$ 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)[95] at low $B(C_6F_5)_3$ 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_6F_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 $B(C_6F_5)_3/AlEt_3$. 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 ^{31}P NMR signals into account (Scheme 5), the interactions between **6** and $B(C_6F_5)_3/AlEt_3$ result only in minor chloride abstractions and enter instead into fast exchange reactions between $B(C_6F_5)_3/AlEt_3$ 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 $B(C_6F_5)_3/AlEt_3$ as will be outlined below.

During the NMR experiments we became aware of the formation of a fine, black precipitate following the addition of $B(C_6F_5)_3/AlEt_3$ 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 $B(C_6F_5)_3/AlEt_3$ (Scheme 7).



Scheme 7

Under an inert-gas atmosphere 0.3 mmol **5** and 0.9 mmol $B(C_6F_5)_3$ were dissolved in 25 mL dried CH_2Cl_2 and 3.0 mmol $AlEt_3$ (1 mol L^{-1} in hexane) were added (molar ratio **5** : $B(C_6F_5)_3$: $AlEt_3$ = 1 : 3 : 10). After two days the black precipitate, which started to form directly after the addition of $AlEt_3$ was centrifuged, washed with CH_2Cl_2 and redissolved in HNO_3/HCl (v/v = 1/3). After the removal of 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 $B(C_6F_5)_3/AlEt_3$. After the removal of elemental palladium (after two days!) the remaining clear, red-brown CH_2Cl_2 solution showed one singlet at 58.6 ppm in its ^{31}P NMR which proved the coordination of the dppe-ligand to palladium(II) (*cf.* Scheme 5) presumably as $[Pd(dppe)_2]^{2+}$ (see below). The NMR chemical shift is close to the one observed for $[Pd(dppe)_2](OAc)$ (58.7 ppm in CD_3OD).[88,89] In the case of the low-active pre-catalyst **6** in combination with $B(C_6F_5)_3/AlEt_3$ no precipitation with respect to the reduction of palladium(II) was observed over a period of several hours.

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 $B(C_6F_5)_3$. 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 $B(C_6F_5)_3$ (molar ratios = 1 : 3) were dissolved in a mixture of toluene and methylene chloride (v/v = 1 : 2) and it was only possible to obtain extremely air-sensitive crystals starting from **5**/$B(C_6F_5)_3$ after several months. Under the same conditions a crystallization starting from complex **6** was not possible. Structure analysis revealed the formation of a $[Pd(dppe)_2]^{2+}$ fragment[96] with $[ClB(C_6F_5)_3]^-$ anions in $[Pd^{II}(dppe)_2][ClB(C_6F_5)_3]_2{\cdot}4CH_2Cl_2$ (**14**) from **5**/$B(C_6F_5)_3$ (Fig. 8). The isolation of $[ClB(C_6F_5)_3]^-$ supports the chloride abstracting functionality of $B(C_6F_5)_3$ which was outlined above. The formation of $[Pd(dppe)_2]^{2+}$ must be explained by a ligand redistribution reaction between two $[Pd(dppe)]^{2+}$ moieties (eqn. (3)).

$$2\,[Pd(dppe)]^{2+} \longrightarrow [Pd(dppe)_2]^{2+} + Pd^{2+} \qquad (3)$$

The latter cations are apparently unstable in the absence of stabilizing anions (see below).

The same ligand redistribution reaction between two $[Pd(dppe)]^{2+}$ moieties was formulated in the NMR studies and catalytic activation reactions of **5** with $B(C_6F_5)_3$ or $B(C_6F_5)_3/AlEt_3$ (see Schemes 3 and 5). The concomittant formation of elemental palladium was demonstrated in Scheme 7. It has been suggested that the formation of $[Pd(dppe)_2]^{2+}$ from $[Pd(dppe)]^{2+}$ is 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.[88,89,92]

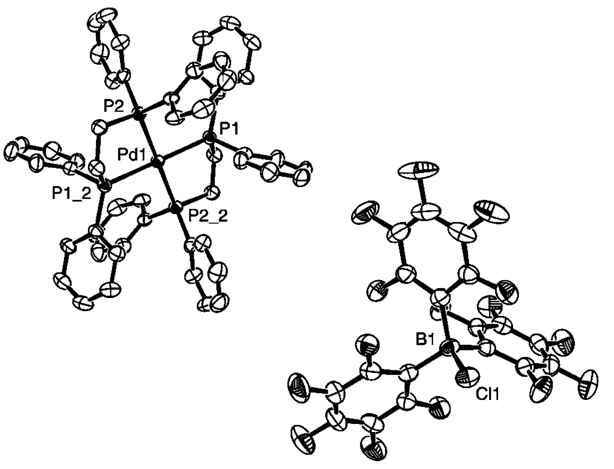


Fig. 8 Molecular structure of $[Pd(dppe)_2][ClB(C_6F_5)_3]_2{\cdot}4CH_2Cl_2$ (**14**); only one of the symmetry related anions is shown for clarity. Selected distances (Å) and angles (°): Pd–P1 2.3412(10), Pd–P2 2.3582(9), B–Cl1 1.925(4), B–C 1.626(6)–1.644(5); P1–Pd–P2 97.31(3), P1–Pd–P2_2 82.68(3), Cl–B–C 102.2(3)–112.3(3), C–B–C 107.7(3)–114.2(3); symmetry operation _2 = −x + 1, −y, −z − 1. CH_2Cl_2 molecules of crystallization are omitted for clarity.

In order to provide a more stabilizing anion for the potential $[Pd(L)]^{2+}$ cation we reacted the monocarba-*closo*-dodecaborane(12) anion, [*closo*-1-$CB_{11}H_{12}]^-$ as its silver salt with the palladium complexes **5** and **6**. In both cases suitable crystals were obtained after several days by overlayering a filtered methylene chloride solution of complex and carborane with diethyl ether.[97] Starting from the palladium–dppe complex **5**, the $[Pd(dppe)_2]^{2+}$ cation[96] is again found in the crystal structure of $[Pd^{II}(dppe)_2][CB_{11}H_{11}Cl]_2{\cdot}3CH_2Cl_2$ (**15**, Fig. 9). Thus, the instability of mono-ligated $[Pd(dppe)]^{2+}$ and the reaction given in eqn. (3) must be invoked again. The carborane counterion to $[Pd(dppe)_2]^{2+}$ has picked up a chlorine atom (probably from CH_2Cl_2) and become [*closo*-$CB_{11}H_{11}Cl]^-$.[97] The phenyl rings on the opposing dppe ligands in the $[Pd(dppe)_2]^{2+}$ cations in **14** and **15** are too far apart for a meaningful π–π interaction,[98] different from the situation in the $[Ni(dppe)_2]^{2+}$ cation.[99]

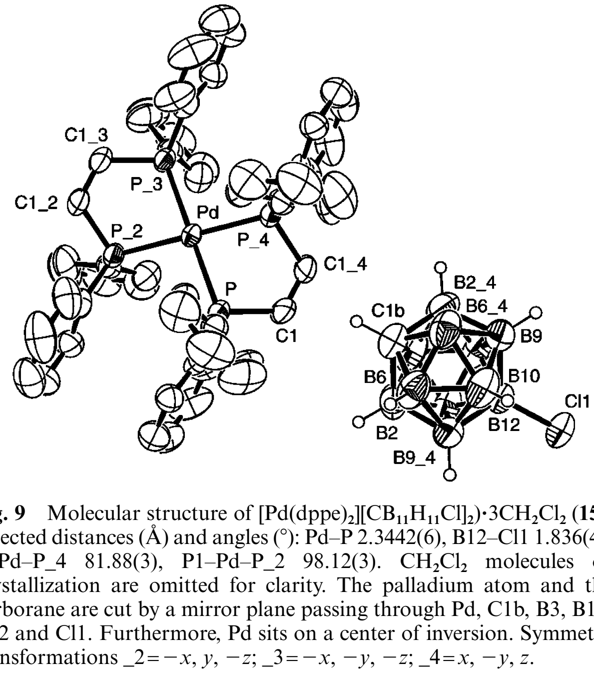


Fig. 9 Molecular structure of $[Pd(dppe)_2][CB_{11}H_{11}Cl]_2){\cdot}3CH_2Cl_2$ (**15**). Selected distances (Å) and angles (°): Pd–P 2.3442(6), B12–Cl1 1.836(4); P–Pd–P_4 81.88(3), P1–Pd–P_2 98.12(3). CH_2Cl_2 molecules of crystallization are omitted for clarity. The palladium atom and the carborane are cut by a mirror plane passing through Pd, C1b, B3, B10, B12 and Cl1. Furthermore, Pd sits on a center of inversion. Symmetry transformations _2 = −x, y, −z; _3 = −x, −y, −z; _4 = x, −y, z.

In contrast, the crystals derived from the palladium–dppp complex **6** and Ag[*closo*-1-$CB_{11}H_{12}$] showed the expected formation of the mono-ligated [Pd(dppp)]$^{2+}$ species in the structure of [Pd^{II}(dppp)($CB_{11}H_{12}$)][$CB_{11}H_{12}$] (**16**). Here the cation was stabilized by coordination to one of the carborane anions as an *exo*-(diphosphane)palladium-*closo*-monocarborane complex [Pd(dppp)(*closo*-$CB_{11}H_{12}$]$^+$ (Fig. 10). This complex cation crystallizes with a second carborane equivalent [$CB_{11}H_{12}$]$^-$ 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 [$CB_{11}H_{11}$(OH)]$^-$. The ^{31}P NMR signal of the cation is observed at +17.9 ppm, close to the +16.0 ppm of the proposed species [Pd(dppp)]$^{2+}$ formed in solution from **6** and $B(C_6F_5)_3$ (see Scheme 3). Similar structures with [$CB_{11}H_{12}$] ligated to a metal in a bidentate mode have already been described with platinum[74] or rhodium.[75,100]

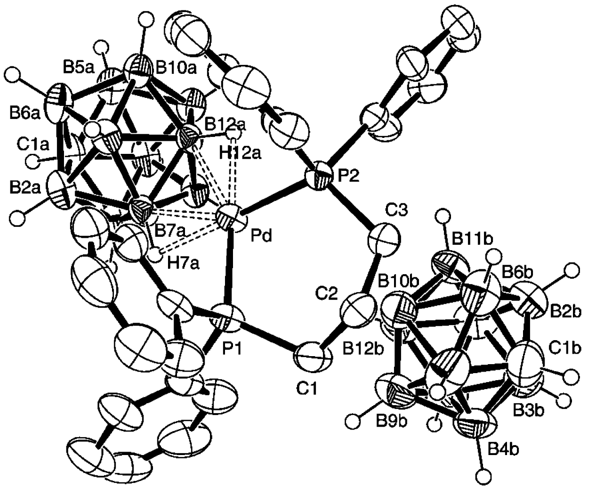
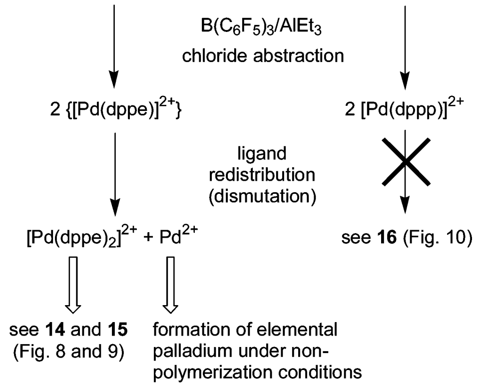


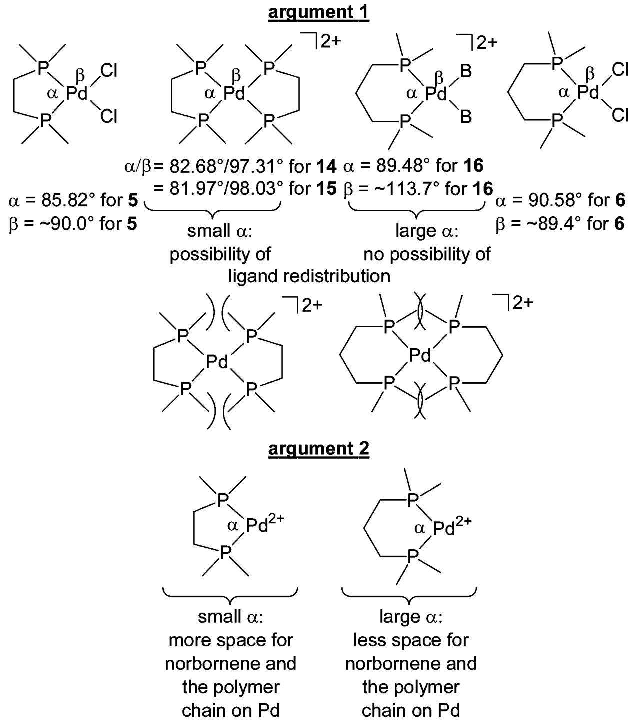
Fig. 10 Molecular structure of [Pd(dppp)($CB_{11}H_{12}$)][$CB_{11}H_{12}$] (**16**). Selected distances (Å) and angles (°): Pd–P1 2.257(1), Pd–P2 2.253(1), Pd–B7a 2.401(4), Pd–H7a 1.945, Pd–B12a 2.406(4), Pd–H12a 1.929; P2–Pd–P1 89.48(3), P1–Pd–B7a 113.3(1), P2–Pd–B7a 155.6(1), P1–Pd–B12a 154.8(1), P2–Pd–B12a 114.0(1).

Combining the results of the multinuclear NMR investigations with the pre-catalysts **5** and **6** in combination with $B(C_6F_5)_3$ and $B(C_6F_5)_3/AlEt_3$ with the structural features of the compounds **14**, **15** and **16**, the activation process of the pre-catalysts may be formulated in the following way (Scheme 8). (1) Addition of $B(C_6F_5)_3$ or $B(C_6F_5)_3/AlEt_3$ to the pre-catalysts **5** and **6** resulted at least in partial chloride abstraction and in the formation of [Pd(L)]$^{2+}$ fragments (L = dppe, dppp) as shown by the multinuclear NMR experiments. These [Pd(L)]$^{2+}$ species exhibit however only a low to medium polymerization activity. (2) In case of **5**, the [Pd(dppe)]$^{2+}$ cations are unstable and react in a ligand redistribution reaction to form a [Pd(dppe)$_2$]$^{2+}$ 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.[32] 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 $B(C_6F_5)_3/AlEt_3$ and the dppp ligand were observed in the case of **6**/$B(C_6F_5)_3/AlEt_3$. This was indentified by the absence of ^{31}P NMR signals in the spectra of **6**/$B(C_6F_5)_3/AlEt_3$, by the crystal data of compound **16** and the missing precipitation of elemental palladium after the addition of $B(C_6F_5)_3/AlEt_3$ to pre-catalyst **6**.



Scheme 8

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)]$^{2+}$ 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** [101,102] or compounds **14**–**16** showed the expected smaller bite angle on Pd for the five-membered ring formed with dppe. The bite angle with dppp in a six-membered chelate ring is larger by about 5° (Scheme 9, argument 1).



Scheme 9

It is obvious that in the case of the dppp-ligand the larger P–Pd–P-angle will increase the steric interaction between two coordinated dppp-ligands which may explain the not-observed formation of the [Pd^{II}(dppp)$_2$]$^{2+}$ complex. No ligand redistribution means no formation of "naked" Pd^{2+}. A palladium(0) species of formula [Pd^0(dppp)$_2$] 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^0(dppe)$_2$] species.[103] There are reports on the failed synthesis of [Pd(dppp)$_2$]$^{2+}$ [93,103] together with a recent paper on the preparation of $[Pd(dppp)_2]^{2+}$ (without any structural proof on the formation of a bis-chelate complex, however).[104] We note again that the Pd(0) complexes PdL_2 with L = $^iPr_2P(CH_2)_nP^iPr_2)_2$ 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-(η^2-L)PdL.[93] There appears to be a principle difference in the stability (and structure?) of $[Pd(dppe)_2]^{2+}$ and $[Pd(dppp)_2]^{2+}$. The former has been found to be inactive in CO/ethene co-polymerization while the latter exhibits an appreciable activity and can react with CO/H_2O.[89,92] The possible formation of $[Pd(dppp)]^{2+}$ as an intermediate is also seen in the formation of a dimeric, unsaturated palladium(I) species of the type $[(dppp)Pd^I]_2^{2+}$.[105] In the case of the pre-catalyst **5** the ligand redistribution reaction and the formation of "naked" Pd^{2+} 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 $[Ni^{II}(dppe)_2]^{2+}$ and $[Ni^0(dppe)_2]$ is also possible.[99,106]

In addition to the formation of "naked" Pd^{2+} the difference in bite angle in the $[Pd(L)]^{2+}$-fragments with L = dppe and dppp follows the trend for the polymerization activity (Scheme 3, see Scheme 9, argument 2). Ligand dppe is described as a "narrow-bite" ligand towards Pd because of its P–Pd–P-angle.[107] After chloride-abstraction a smaller bite angle offers more space on the metal center for incoming norbornene units and the growing polymer chain. In contrast to this a "wide-bite" ligand like dppp will provide less space and larger steric hindrance for an insertion-polymerization of norbornene and therefore decrease the polymerization activity. This argument also holds for the smaller nickel atom, where the bite angle increases from dppe[108] to dppp.[109] As an opposing trend towards the increase in bite angle, the observed rise in activity towards the larger dppb and dpppt ligands (Scheme 3) can be explained by the lessened chelate effect which will lead to an easier and more frequent opening of the chelate ring. This ring opening may be helped by a P–Al interaction as noted above for **6**/$B(C_6F_5)_3$/$AlEt_3$ (to explain the absence of ^{31}P NMR signals).

The probably necessary formation of a metal–organyl starting group for the insertion polymerization of norbornene is suggested to occur *via* C_6F_5 transfer from $B(C_6F_5)_3\cdot H_2O$[110–112] and $Al(C_6F_5)_3$[113] respectively to the metal center or by alkylation of the metal center from the known alkyl transfer agents BEt_3 or $AlEt_3$.[87]

Conclusions

Norbornene undergoes a vinyl/addition polymerization using activated phosphane-chelated metal(II) halide complexes of the general type $[M\{Ph_2P(CH_2)_nPPh_2\}X_2]$ with $n = 2$ (dppe), 3 (dppp), 4 (dppb) and 5 (dpppt), M = Co, Ni and Pd, X = Cl, Br. The nickel(II) and palladium(II) complexes gave polymerization activities of about 10^3–10^7 $g_{polymer}$ mol_{metal}^{-1} h^{-1} when activated with methylalumoxane (MAO) or with a combination of tris(pentafluorophenyl)borane/triethylaluminium [$B(C_6F_5)_3$/$AlEt_3$]. It was also possible to activate the nickel complexes $Ni(dppb)Cl_2$ and $Ni(dpppt)Cl_2$ with the Lewis acid $B(C_6F_5)_3$ alone. Bromine complexes gave a somewhat higher activity than the analogous chlorine 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 the dppp complex and then increased subsequently. Multinuclear (^{31}P and ^{19}F) NMR investigations on the complexes $Pd(dppe)Cl_2$ and $Pd(dppp)Cl_2$ in combination with $B(C_6F_5)_3$ and $B(C_6F_5)_3$/$AlEt_3$ suggest the formation of $[Pd(L)]^{2+}$ cations in the activation process. $E(C_6F_5)_3$ (E = B, Al) reacts with the pre-catalysts $[M\{Ph_2P(CH_2)_nPPh_2\}X_2]$ under abstraction of the two halide atoms. The anions detected were the species $[Cl–E(C_6F_5)_3]^-$ and $[(F_5C_6)_3E–Cl–E(C_6F_5)_3]^-$ with E = B when using $B(C_6F_5)_3$ alone, E = Al when employing $B(C_6F_5)_3$/$AlEt_3$. $B(C_6F_5)_3$ and $AlEt_3$ lead to an aryl/alkyl group exchange which results in the formation of $AlEt_{3-n}(C_6F_5)_n$ and $B(C_6F_5)_{3-n}Et_n$ with $Al(C_6F_5)_3$ and BEt_3 being the main products for an about equimolar ratio of $B(C_6F_5)_3$ and $AlEt_3$. The extremely high polymerization activity of the complex $Pd(dppe)Cl_2$ (**5**, 1.9×10^7 $g_{polymer}$ mol_{Pd}^{-1} h^{-1}), for example in comparison to $Pd(dppp)Cl_2$ (**6**, 3.0×10^3 $g_{polymer}$ mol_{Pd}^{-1} h^{-1}), upon activation with $B(C_6F_5)_3$/$AlEt_3$ is explained by the formation of highly active "naked" Pd^{2+} through a ligand redistribution of the unstable $[Pd(dppe)]^{2+}$ cation to yield $[Pd(dppe)_2]^{2+}$ and Pd^{2+} together with the lower coordinating ability of the anionic adduct $[Cl–Al(C_6F_5)_3]^-$ in comparison to $[Cl–B(C_6F_5)_3]^-$. $[Pd(dppe)_2]^{2+}$ cations were found in crystalline solids derived from **5** and $B(C_6F_5)_3$ or Ag[*closo*-1-$CB_{11}H_{12}$]. In the absence of the norbornene monomer the formation of Pd metal is observed for **5**/$B(C_6F_5)_3$/$AlEt_3$ but not for **6**/$B(C_6F_5)_3$/$AlEt_3$. The finding of "simple" unligated species upon activation in cyclo-olefin polymerization agrees with our recent observation on the *in situ* formation of $PdCl_2$ from palladium(II) salts containing $[PdCl_4]^{2-}$ and $[Pd_2Cl_6]^{2-}$ ions.[32]

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