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η^5-Cyclopentadienylpalladium(II) complexes: Synthesis, characterization and use for the vinyl addition polymerization of norbornene and the copolymerization with 5-vinyl-2-norbornene or 5-ethylidene-2-norbornene

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In memoriam to Prof. Herbert Schumann and his seminal contributions, among others, to the chemistry of cyclopentadienyl–metal complexes.

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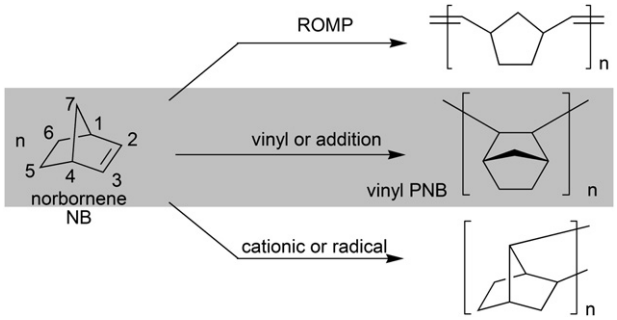
ABSTRACT

Dinuclear complexes of palladium(II), containing two bridging halogen (Cl or Br) ligands, $[N^nBu_4]_2[(X_5C_6)_2Pd(\mu\text{-}Cl)_2Pd(C_6X_5)_2]$ and $[(X_5C_6)(L)Pd(\mu\text{-}Y)_2Pd(C_6X_5)(L)]$ (X = F, Cl; Y = Cl, Br), readily react with cyclopentadienylthallium, C_5H_5Tl, to give the corresponding air stable half-sandwich, pseudo-trigonal η^5-cyclopentadienylpalladium complexes, $[N^nBu_4][(\eta^5\text{-}C_5H_5)Pd(C_6X_5)_2]$ (X = F **1**, Cl **2**) and $(\eta^5\text{-}C_5H_5)Pd(C_6X_5)(L)$ (X = F, L = $CNBu^t$ **3**, PPh_3 **4**, PMe_2Ph **5**, PEt_3 **6**, $AsPh_3$ **7**, $SbPh_3$ **8**; X = Cl, L = PMe_2Ph **9**, PEt_3 **10**), respectively. With tetraphenylcyclopentadienylthallium, C_5Ph_4HTl or pentabenzylcyclopentadienylthallium, C_5Bn_5Tl (Bn = CH_2Ph) the air stable half-sandwich complexes $(\eta^5\text{-}C_5Ph_4H)Pd(C_6F_5)(AsPh_3)$, **12** and $(\eta^5\text{-}C_5Bn_5)Pd(C_6F_5)(AsPh_3)$, **13** are synthesized accordingly. The molecular structures were verified by NMR-spectroscopy, X-ray crystallography (**7**, **12**, **13**) and electron impact-mass spectrometry (EI-MS). The precatalysts **4** and **7** can be activated with methylalumoxane (MAO) for the homopolymerization of norbornene (NB) and 5-ethylidene-2-norbornene (ENB) and for the copolymerization of NB with 5-vinyl-2-norbornene (VNB) or ENB with activities of more than 10^6 $g_{PNB}/(mol_{Pd}\cdot h)$. The higher activity of **7**/MAO over **4**/MAO towards NB homopolymerization was reversed when the olefin-substituted VNB or ENB were added. Then, the more strongly bound PPh_3 ligand of **4** (versus $AsPh_3$ of **7**) can compete with the olefin functionality of VNB or ENB and assume a directing role for the insertion of the ring double bond. As a consequence **4**/MAO shows almost the same activity in NB and ENB homopolymerization.

1. Introduction

Norbornene (NB, bicyclo[2.2.1]hept-2-ene) can be polymerized by three different ways, each leading to its own polymer type (Scheme 1) [1–3]. Of special interest is the vinyl or addition polymerization of NB. In this case, the bicyclic structure of the monomer remains intact, and only the double bond of the π component is opened [4].

Vinyl PNB is of interest due to its good mechanical strength, heat resistivity, and optical transparency for deep ultraviolet (193 nm) photoresist binder resins in lithographic processes [5], interlevel dielectrics in microelectronics applications, or as a cover layer for liquid-crystal displays [6,7]. Films made from norbornene vinyl polymer are excellent in transparency and heat resistance and have unchanged viscoelastic and electric characteristics to markedly high temperatures. Such a film is suitable for a condensor or an insulator [8]. Furthermore, it shows a low water uptake, a small optical birefringence and dielectric loss [9] The vinyl polymerization of NB uses catalytic systems based on titanium, chromium, iron, cobalt, copper, with recent emphasis on highly active nickel and palladium complexes [1,2,3,10].



Scheme 1. Schematic representation of the three different types of polymerization of norbornene.

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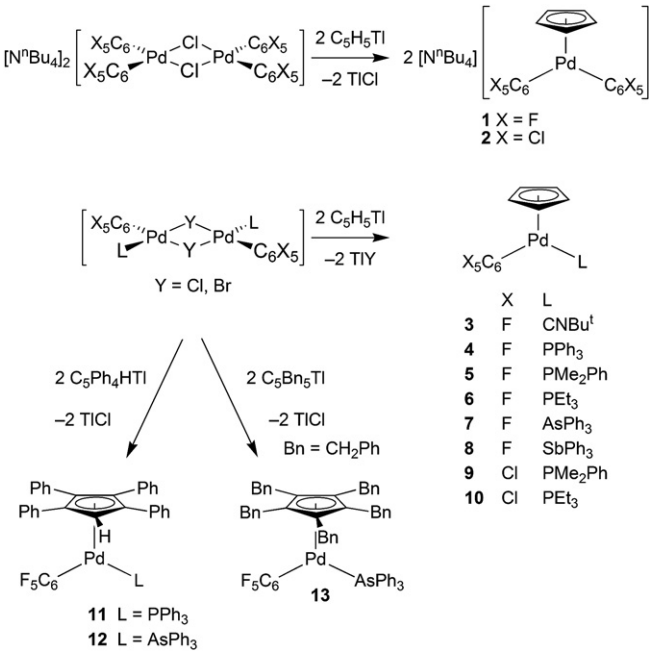
However, the poor solubility of vinyl polynorbornene (PNB) in common organic solvents and the poor adhesion are disadvantages of the homopolymer. The adhesion can be improved by attaching triethoxysilyl groups on the backbone to lower the rigidity of the system and result in higher elongation-to-break values and a decrease in residual stress [7]. A possibility to improve the solubility is to incorporate functional groups in the PNB chain. Hence, the copolymerization of norbornene with ethene [11], propene [1] or substituted NB-derivatives and the (co- and ter)polymerization of functionalized NB monomers are of current interest [12,13], because the resulting polymers can exhibit improved properties, e.g. transparency, for the above applications. Palladium and nickel catalysts in particular allow the polymerization of functionalized norbornene monomers [1,5,14].

Very few cyclopentadienyl metal complexes were reported for the application in the norbornene polymerization. Complex (η^5-C_5H_5)Pd(CH_3)(PPh_3) did not afford remarkable polymerization results for the homopolymerization of norbornene with the cocatalysts $B(C_6F_5)_3$, $[Ph_3C][B(C_6F_5)_4]$ and MMAO, whereas the catalytic system (η^5-C_5H_5)Pd(η^3-allyl)/$[Ph_3C][B(C_6F_5)_4]$ provided an activity of more than 10^5 $g_{PNB}/(mol_{Pd}\cdot h)$ [15]. Recently, the complexes [(η^5-C_5Me_5)Ir(M/E-bi-t/s)Cl]Cl {M/E-bi-t/s = 1,1′-methylene/(1,2-ethanediyl)-bis(3-methyl)-imidazole-2-thione/selone} exhibited moderate activities [$4-56\times10^3$ $g_{PNB}/(mol_{Ir}\cdot h)$] for the vinyl polymerization of norbornene [16]. The half-sandwich iridium complexes [(η^5-C_5Me_5)Ir(Cl){(C_6H_3-*i*-(R^1)$_2$-2,6)N = $CC_2H_3(CH_3)C_6H(CH_3)(R^2)$O-κ*N*,*O*}], containing hydroxyindanimine ligands produced the NB-ROMP polymer as a low-MAO catalyst, while the high-MAO catalyst initiates the vinyl-type NB polymerization according to IR, ^{1}H NMR and ^{13}C NMR studies of the polymers. Still the activity remained modest with 10^4 $g_{PNB}/(mol_{Ir}\cdot h)$ even at 2000 equivalents of MAO [17]. Also the system (η^5-C_5H_5)Ni(CH_3)(PPh_3)/$B(C_6F_5)_3$ yields polynorbornene [18].

In this work, a series of η^5-cyclopentadienylpalladium(II) complexes of the general type $[N^nBu_4][(\eta^5\text{-}C_5H_5)Pd(C_6X_5)_2]$ (**1**, **2**) and (η^5-Cp)Pd(C_6X_5)(L) (X = F, Cl; Cp = (substituted) cyclopentadienyl, L = C [isonitrile], P, As or Sb two-electron donor ligand) (**3**–**12**) were synthesized and fully characterized (Scheme 2). The precatalysts **4** and **7** were tested for the homopolymerization of NB, 5-vinyl-2-norbornene (VNB) and 5-ethylidene-2-norbornene (ENB) as well for the copolymerization of NB with VNB and ENB, respectively. Methylalumoxane, MAO was used as cocatalyst and **4**/MAO was selected for activation studies with the ^{19}F nucleus of the pentafluorophenyl group C_6F_5 as a potential probe for molecular dynamics and for precatalyst activation mechanism by ^{19}F NMR spectroscopy [19].



Scheme 2. Synthetic routes to η^5-cyclopentadienylpalladium(II) complexes **1**–**13**.

2. Experimental part

2.1. General and materials

All work involving air- and/or moisture-sensitive compounds was carried out with standard vacuum, Schlenk, or drybox techniques. Flasks were conditioned by heating in high vacuum three times and filling with argon. CHN analyses were performed with a Carlo Erba model EA 1108 microanalyzer. Decomposition temperatures were determined with a Mettler TG-50 thermobalance at a heating rate of 5 °C min^{-1}. Conductance measurements were performed in acetone solution ($c \approx 5\times10^{-4}$ mol L^{-1}) with a Crison 525 conductimeter. Infrared spectra were recorded on a Perkin–Elmer 16F PC FT-IR spectrophotometer using Nujol mulls between polyethylene sheets. The ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded on a Bruker AC 200E, a Varian Unity 300 spectrometer or a Bruker Avance II 400 WB spectrometer using $SiMe_4$, $CFCl_3$ or H_3PO_4 as standards respectively. The NMR spectra were measured in NMR tubes with a screw cap to ensure an inert atmosphere. The NMR tube was filled in a Schlenk tube under argon atmosphere. Chemical ionization mass spectra (CI-MS, with NH_3 as ionizing gas) were obtained on a Thermo TSQ 700. Electron-spray ionization mass spectra (ESI-MS) were measured on a Thermo LCQ Advantage as a CH_2Cl_2/methanol solution (1:1). Palladium containing signals were assigned upon the presence of the clearly visible metal isotope pattern, arising from the distribution: ^{102}Pd (1.02%), ^{104}Pd (11.14%), ^{105}Pd (22.33%), ^{106}Pd (27.33%), ^{108}Pd (26.46%), ^{110}Pd (11.72%) [20]. Fluorine, phosphorus and arsenic are isotope-pure elements. Most intense Pd-containing mass peaks correspond to the ^{106}Pd isotope. UV/Vis-spectra were recorded on a JASCO V-570 UV/VIS spectrometer.

Toluene and dichloromethane were dried under argon with an MBraun SPS-800 system. The drying agent for toluene was activated Al_2O_3 in addition to a copper-catalyst used as an oxygen scavenger. Al_2O_3 alone was used as the drying agent for dichloromethane. Diethyl ether and acetone were dried over and distilled from molar sieve (3 Å). After the drying process the water content was determined by a Karl-Fischer titration, which showed a water mass percentage of 0.0008% for toluene, 0.0004% for dichloromethane, 0.0005% for diethyl ether. Subsequently, the solvents were stored under argon prior to use.

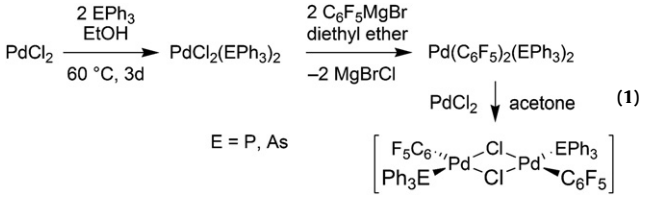
$PdCl_2$ (Applichem), PPh_3 (Acros), $AsPh_3$ (Aldrich), C_6F_5Br (Chempur), Mg turnings (Aldrich), thallium(I) ethoxide (Aldrich), thallium(I) sulfate (Fluka) and MAO (10% solution in toluene, Witco) were used as received. Norbornene (Acros), 5-vinyl-2-norbornene (Acros) and 5-ethylidene-2-norbornene (Acros) were purified by distillation under argon and used as a 7.07 mol/l solution in toluene. Cyclopentadienylthallium(I) C_5H_5Tl [21], 1,2,3,4-tetraphenylcyclopentadienylthallium(I) C_5Ph_4HTl [22], and 1,2,3,4,5-pentabenzylcyclopentadienylthallium(I) C_5Bn_5Tl [22,23] were synthesized according to literature procedures.

The starting compounds $[N^nBu_4]_2[\{Pd(C_6X_5)_2\}_2(\mu\text{-}Cl)_2]$ (X = F [24], Cl [25]), $[\{(Pd(C_6F_5)L\}_2(\mu\text{-}Y)_2]$ (L = $CNBu^t$ [26], PPh_3, $AsPh_3$ or $SbPh_3$ [27], Y = Cl; L = PMe_2Ph or PEt_3, Y = Br [28]) and $[\{(Pd(C_6Cl_5))L\}_2(\mu\text{-}Br)_2]$ (L = PMe_2Ph or PEt_3) [28] were prepared by procedures described in the indicated references. The synthesis of $[\{(Pd(C_6F_5)(AsPh_3)\}_2(\mu\text{-}Cl)_2]$ is described in the literature starting from $PdCl_2(AsPh_3)_2$ which is reacted with C_6F_5Li [27]. The PPh_3

compound $[\{(Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}Cl)_2]$ is then obtained by reacting the As-derivative with an excess of PPh_3 [27]. Because of the potentially explosive nature of C_6F_5Li above ~−70 °C we have introduced the C_6F_5 ligand with the Grignard reagent C_6F_5MgBr as described below.

2.2. Syntheses

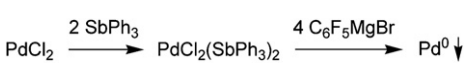
2.2.1. $[\{(Pd(C_6F_5)(EPh_3)\}\}_2(\mu\text{-}Cl)_2]$ (E = P, As) (see Eq. (1))



(1)

Magnesium turnings (525 mg, 21.6 mmol) were placed in a 100 ml Schlenk flask together with a magnetic stir bar and diethyl ether (10 ml). A solution of C_6F_5Br (5.3 g, 2.7 ml, 21.5 mmol) in diethyl ether (40 ml) was added dropwise over a period of 30 min via a syringe at room temperature. An ice bath was not necessary. The suspension was stirred for 5 h, until the Mg was completely consumed. $PdCl_2(EPh_3)_2$ (4.26 g (E = As) g, 3.79 g (E = P) 5.4 mmol), which has been prepared by the reaction of $PdCl_2$ and 2 equivalents of EPh_3, was added in an Ar counter flow and the resulting yellow suspension was heated to reflux, until it had turned into a colorless suspension of MgBrCl (10 h for $AsPh_3$ to 36 h for PPh_3). The reaction mixture was quenched with Et_2O (30 ml) and the suspension was allowed to stir in air for 2 h. After filtration, the ether was removed and the residue was extracted with toluene (3 × 30 ml), filtrated again and the organic phases were combined. After removal of the toluene, the almost colorless solids of $Pd(C_6F_5)_2(EPh_3)_2$ were dried *in vacuo* for 12 h and then dissolved in dry acetone. After the addition of 1 equivalent $PdCl_2$ the reddish suspensions were heated to reflux, until the $PdCl_2$ had completely reacted. The reactions mixtures were filtered and then reduced almost to a volume of 15 ml. The precipitation of $[\{(Pd(C_6F_5))(EPh_3)\}_2(\mu\text{-}Cl)_2]$ succeeded by the addition of hexane (E = As) and diethyl ether (E = P), respectively.

The Cl to C_6F_5 ligand substitution reaction could only be accomplished with a twofold stoichiometric excess (molar Mg:Pd ratio 4:1) of the Grignard reagent, but then delivered the dinuclear complexes $[(F_5C_6)(Ph_3E)Pd(\mu\text{-}Cl)_2Pd(C_6F_5)(EPh_3)]$ in almost quantitative yield. The synthesis of the analoguous complexes bearing a triphenylantimony ligand failed due to the *in situ* reduction of Pd (II) to metallic palladium during the ligand substitution reaction with the C_6F_5MgBr Grignard reagent (Eq. (2)).



(2)

2.2.2. Tetra-n-butylammonium cyclopentadienyl-bis (pentahalophenyl)-palladium(II), $[N^nBu_4][(C_5H_5)Pd(C_6X_5)_2]$, ***1*** *(halo, X = fluoro) and* ***2*** *(halo, X = chloro)*

To a solution of $[N^nBu_4]_2[\{Pd(C_6X_5)_2\}_2(\mu\text{-}Cl)_2]$ (X = F, Cl) (0.14 mmol) in acetone (20 ml) was added C_5H_5Tl (75.5 mg, 0.28 mmol). The mixture was stirred for 1 h at room temperature and then TlCl was removed by filtration through celite and the solution was concentrated to dryness under reduced pressure. The residue was treated with Pr^iOH-hexane yielding a redish-pink (**1**) or brown (**2**) solid, which was filtered-off and air dried.

Complex **1**: Yield 80%; m.p. 210 °C (dec.). Calcd. for $C_{33}H_{41}F_{10}NPd$: C 53.0, H 5.5, N 1.9; found C 53.3, H, 5.3, N 2.1%. Λ_M 105 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 784, 772 (Pd−C_6F_5). ^{1}H-NMR ($(CD_3)_2CO$): δ/ppm 5.62 (s, 5H, Cp), 3.43 (m, 8 H, NCH_2), 1.80 (m, 8 H, NCH_2CH_2), 1.40 (m, 8 H, $NCH_2CH_2CH_2$), 0.95 (t, 12 H, CH_3, J_{HH} = 19.8 Hz). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): δ/ppm 95.1 (s, Cp). ^{19}F-NMR ($(CD_3)_2CO$): δ/ppm −106.5 (m, $4F_o$), −166.5 (t, $2F_p$, J_{mp} = 19.8), −167.2 (m, $4F_m$).

Complex **2**: Yield 78%; m.p. 216 °C (dec.). Calcd. for $C_{33}H_{41}Cl_{10}NPd$: C 43.4, H 4.5, N 1.5; found C 43.3, H 4.3, N 1.5%. Λ_M 100 S cm^2 mol^{-1}. IR (Nujol, cm^{-1}): 830, 810 (Pd−C_6Cl_5). ^{1}H-NMR ($(CD_3)_2CO$): δ/ppm 5.65 (s, 5H, Cp), 3.43 (m, 8 H, NCH_2), 1.80 (m, 8 H, NCH_2CH_2), 1.40 (m, 8 H, $NCH_2CH_2CH_2$), 0.95 (t, 12 H, CH_3, J_{HH} = 19.8 Hz). $^{13}C\{^1H\}$-NMR ($(CD_3)_2CO$): δ/ppm 97.9 (s, Cp).

2.2.3. Cyclopentadienyl-pentafluorophenyl-(ligand L)-palladium (II), $(C_5H_5)Pd(C_6F_5)(L)$, ***3***–***8***

To a solution of $[\{(Pd(C_6F_5))(L)\}_2(\mu\text{-}Y)_2]$ (L = $CNBu^t$, PPh_3, $AsPh_3$ or $SbPh_3$, Y = Cl; L = PMe_2Ph or PEt_3, Y = Br) (0.26 mmol) in acetone (20 ml) was added C_5H_5Tl (140 mg, 0.52 mmol). The mixture was stirred for 1 h at room temperature and then TlCl was removed by filtration through celite and the solution was concentrated to dryness under reduced pressure. The residue was treated with diethyl ether-hexane (**3**, **6**, **7**, **8**) or Pr^iOH–H_2O (1:1 v:v) (**4**, **5**, also **7**) yielding a redish-pink solid, which was collected by filtration and air-dried. For complex **4** the synthesis was upscaled to 1.59 g (1.39 mmol) of $[\{(Pd(C_6F_5)(PPh_3)\}_2(\mu\text{-}Cl)_2]$ and 0.75 g, 2.78 mmol of C_5H_5Tl which were dissolved in 50 ml of acetone. For complex **7** an upscaled synthesis was carried out with 0.78 g (0.63 mmol) of $[\{(Pd(C_6F_5)(AsPh_3)\}_2(\mu\text{-}Cl)_2]$. Crystals of **4** and **7** were obtained by slow diffusion of overlayered hexane into a solution of **4** and **7**, respectively, in $CHCl_3$.

Complex **3** (L = $CNBu^t$): Yield 75%; m.p. 185 °C (dec.). Calcd. for $C_{16}H_{14}F_5NPd$: C 45.6, H 3.4, N 3.3; found C 45.6, H 3.3, N 3.2%. IR (Nujol, cm^{-1}): 2198 ν(CN), 770 (Pd−C_6F_5). ^{1}H-NMR ($CDCl_3$): δ/ppm 5.77 (s, 5H, Cp), 1.36 (s, 9H, $CNBu^t$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 96.7 (s, Cp), 30.1 (s, $CNBu^t$). ^{19}F-NMR ($CDCl_3$): δ/ppm −108.1 (m, $2F_o$), −160.6 (t, $1F_p$, J_{mp} = 19.8), −163.6 (m, $2F_m$).

Complex **4** (L = PPh_3): Yield 83% (upscaled 1.2 g, 72%); m.p. 209 °C (dec.). Calcd. for $C_{29}H_{20}F_5PPd$: C 58.0, H 3.4; found C 57.6, H, 3.4%. IR (Nujol, cm^{-1}): 770 (Pd−C_6F_5). UV (CH_2Cl_2, $c = 2.5 \cdot 10^{-5}$ mol/l): λ_{max} 510 nm (ϵ_{max} 138 l mol^{-1} cm^{-1}). ^{1}H-NMR ($CDCl_3$): δ/ppm 7.25–7.53 (m, 15H, PPh_3), 5.75 (d, 5H, Cp, J_{HP} = 2.0 Hz), $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 133.6 (d, C_o of PPh_3, J_{CP} = 12.7 Hz), 132.6 (d, C_{ipso} of PPh_3, J_{CP} = 48.2), 130.4 (d, C_p of PPh_3, J_{CP} = 2.6), 128.0 (d, C_m of PPh_3, J_{CP} = 10.8), 97.9 (d, Cp, J_{CP} 2.6). ^{19}F-NMR ($CDCl_3$): δ/ppm −108.1 (m, $2F_o$), −161.8 (t, $1F_p$, J_{mp} 20.0), −163.8 (m, $2F_m$). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ/ppm 41.1 (s). CI-MS: *m/z* (abundance, %) = 600.1 (100) $[C_5H_5Pd(C_6F_5)(PPh_3)]^+ = [M]^+$, 552.0 (7.3) $[Pd(C_6F_5)(PPh_3)(NH_3)]^+$, 535.0 (8.6) $[Pd(C_6F_5)(PPh_3)]^+$, 476.9 (very low intensity) $[C_5H_5Pd(PPh_3)(NH_3)_2]^+$, 450.0 (22.0) $[C_5H_5Pd(PPh_3)(NH_3)]^+$, 433.0 (87.8) $[C_5H_5Pd(PPh_3)]^+$, 385.0 (8.3) $[Pd(PPh_3)(NH_3)]^+$, 368.0 (10.8) $[Pd(PPh_3)]^+$, 262.1 (11.5) $[PPh_3]^+$, 232.0 (very low intensity) $[C_{11}H_5F_5]^+$, 185.1 (very low intensity) $[PPh_2]^+$, 168.0 (8.13) $[C_6F_5H]^+$.

Complex **5** (L = PMe_2Ph): Yield 87%; m.p. 173 °C (dec.). Calcd. for $C_{19}H_{16}F_5PPd$: C 47.9, H 3.4; found C 47.9, H 3.5%. IR (Nujol, cm^{-1}): 770 (Pd−C_6F_5). ^{1}H-NMR ($CDCl_3$): δ/ppm 7.59 (m, $2H_o$, PPh), 7.39 (m, $2H_m + 1H_p$, PPh), 5.64 (d, 5H, Cp, J_{HP} = 1.8 Hz), 1.53 (d, 6H, PMe_2, J_{HP} = 10.6). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 130.4 (d, C_p of PMe_2Ph,

J_{CP} = 2.6), 130.3 (d, C_o of PMe_2Ph, J_{CP} = 12.3), 128.5 (d, C_m of PMe_2Ph, J_{CP} = 10.6), 96.8 (d, Cp, J_{CP} 2.7), 19.1 (d, PMe_2, J_{CP} = 31.9). ^{19}F-NMR ($CDCl_3$): δ/ppm −108.4 (d, 2F_o, J_{om} = 29.1 Hz), −160.6 (t, 1F_p, J_{mp} = 20.0), −163.3 (m, 2F_m). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ/ppm 8.0 (s).

Complex **6** (L = PEt_3): Yield 85%; m.p. 202 °C (dec.). Calcd. for $C_{17}H_{20}F_5PPd$: C 44.7, H 4.4; found C 44.7, H 4.5%. IR (Nujol, cm^{-1}): 770 (Pd−C_6F_5). ^{1}H-NMR ($CDCl_3$): δ/ppm 5.68 (d, 5H, Cp, J_{HP} = 1.9 Hz), 1.44 (m, 6H, PCH_2), 1.01 (m, 9H, PCH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 96.1 (d, Cp, J_{CP} = 2.5 Hz), 19.5 (d, PCH_2, J_{CP} = 28.2), 7.8 (s, PCH_2CH_3). ^{19}F-NMR ($CDCl_3$): δ/ppm −107.9 (d, 2F_o, J_{om} = 26.0 Hz), −160.8 (t, 1F_p, J_{mp} = 19.8), −163.4 (m, 2F_m). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ/ppm 37.7 (s).

Complex **7** (L = $AsPh_3$): Yield 90% (upscaled 0.61 g, 75%); m.p. 177 °C (dec.). Calcd. for $C_{29}H_{20}AsF_5Pd$: C 54.0, H 3.1; found C 53.7, H 3.1%. IR (Nujol, cm^{-1}): 770 (Pd−C_6F_5). UV (CH_2Cl_2, $c = 7.4\cdot10^{-5}$ mol/l): λ_{max} 501 nm (ϵ_{max} 142 l mol^{-1} cm^{-1}). ^{1}H-NMR ($CDCl_3$): δ/ppm 7.24–7.45 (m, 15H, $AsPh_3$), 5.85 (s, 5H, Cp). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 134.2 (s, C_{ipso} of $AsPh_3$), 132.7 (s, C_o of $AsPh_3$), 130.1 (s, C_p of $AsPh_3$), 128.6 (s, C_m of $AsPh_3$), 96.9 (s, Cp). ^{19}F-NMR ($CDCl_3$): δ/ppm −107.3 (d, 2F_o, J_{om} = 25.9 Hz), −161.6 (t, 1F_p, J_{mp} = 19.8), −163.9 (m, 2F_m). CI-MS: *m/z* (abundance, %) = 644.0 (16.9) $[C_5H_5Pd(C_6F_5)(AsPh_3)]^+ = [M]^+$, 494.0 (9.4) $[C_5H_5Pd(AsPh_3)(NH_3)]^+$, 476.9 (12.5) $[C_5H_5Pd(AsPh_3)]^+$, 333.9 (2.0) $[C_6F_5{-}C_6F_5]^+$, 307.0 (100) $[HAsPh_3]^+$, 305.9 (24.7) $[AsPh_3]^+$, 244.0 (8.6) $[C_6F_5{-}C_6H_5]^+$, 168.0 (6.8) $[C_6F_5H]^+$, 77.1 (0.9) $[C_6H_5]^+$.

Complex **8** (L = $SbPh_3$): Yield 86%; m.p. 143 °C (dec.). Calcd. for $C_{29}H_{20}F_5PdSb$: C 50.4, H 2.9; found: C 50.1, H 2.8%. IR (Nujol, cm^{-1}): 770 (Pd−C_6F_5). ^{1}H-NMR ($CDCl_3$): δ/ppm 7.33 (m, 15H, $SbPh_3$), 5.91 (s, 5H, Cp). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 134.9 (s, C_o of $SbPh_3$), 131.1 (s, C_{ipso} of $SbPh_3$), 130.2 (s, C_p of $SbPh_3$), 129.1 (s, C_m of $SbPh_3$), 96.3 (s, Cp). ^{19}F-NMR ($CDCl_3$): δ/ppm −105.3 (d, 2F_o, J_{om} = 30.5 Hz), −161.0 (t, 1F_p, J_{mp} = 20.0), −163.6 (m, 2F_m).

2.2.4. Cyclopentadienyl-pentachlorophenyl-(ligand L)-palladium (II), (C_5H_5)Pd(C_6F_5)(L), **9** and **10**

To a solution of $[\{(Pd(C_6Cl_5))(L)\}_2(\mu\text{-}Br)_2]$ (L = PMe_2Ph or PEt_3) (0.18 mmol) in acetone (20 ml) was added C_5H_5Tl (97 mg, 0.36 mmol). The mixture was stirred for 1 h at room temperature and then TlCl was removed by filtration through celite and the solution was concentrated to dryness under reduced pressure. The residue was treated with MeOH yielding a brown solid, which was filtered-off and air dried.

Complex **9** (L = PMe_2Ph): Yield 78%; m.p. 179 °C (dec.). Calcd. for $C_{19}H_{16}Cl_5PPd$: C 40.8, H 2.9; found C 40.5, H 2.8%. IR (Nujol, cm^{-1}): 832 (Pd−C_6Cl_5). ^{1}H-NMR ($CDCl_3$): δ/ppm 7.58 (m, 2H_o, PPh), 7.37 (m, 2H_m + 1H_p, PPh), 5.62 (d, 5H, Cp, J_{HP} = 1.7 Hz), 1.49 (d, 6H, PMe_2, J_{HP} = 10.6). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 130.1 (d, C_p of PMe_2Ph, J_{CP} = 2.0), 130.0 (d, C_o of PMe_2Ph, J_{CP} = 12.1), 128.3 (d, C_m of PMe_2Ph, J_{CP} = 10.1), 97.6 (d, Cp, J_{CP} 2.5), 18.1 (d, PMe_2, J_{CP} = 31.9). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ/ppm 5.1 (s).

Complex **10** (L = PEt_3): Yield 80%; m.p. 180 °C (dec.). Calcd. for $C_{17}H_{20}Cl_5PPd$: C 37.9, H 3.7; found C 37.7, H 3.5%. IR (Nujol, cm^{-1}): 834 (Pd−C_6Cl_5). ^{1}H-NMR ($CDCl_3$): δ/ppm 5.68 (d, 5H, Cp, J_{HP} = 1.5 Hz), 1.45 (m, 6H, PCH_2), 1.05 (m, 9H, PCH_2CH_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ/ppm 97.2 (d, Cp, J_{CP} = 2.0 Hz), 19.0 (d, PCH_2, J_{CP} = 27.2), 7.9 (s, PCH_2CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ/ppm 32.1 (s).

2.2.5. Tetraphenylcyclopentadienyl-pentafluorophenyl-triphenylphosphane-palladium(II), (C_5Ph_4H)Pd(C_6F_5)(PPh_3), **11**

$[\{(Pd(C_6F_5)(PPh_3))\}_2(\mu\text{-}Cl)_2]$ (0.50 g, 0.44 mmol) was dissolved in dry acetone (40 ml) by gentle warming to 40 °C. The resulting yellow solution was cooled to room temperature and thalliumtetraphenylcyclopentadienide, C_5Ph_4HTl (0.50 g, 0.88 mmol) was added with caution in an Ar counter flow. The yellow solution turned into a black suspension within seconds and was stirred for an additional 6 h at room temperature. The dark suspension was filtered over Celite® to remove the precipitated TlCl and washed with acetone, until the filtrate was colorless. The greenish filtrate was concentrated under reduced pressure to a volume of 20 ml. Under stirring a H_2O/^{i}PrOH mixture (1:1 v:v, 50 ml) was added slowly and dropwise via syringe to precipitate the desired compound, which was filtered, washed with H_2O (10 ml) and ^{i}PrOH (−20 °C, 20 ml). The olive-green product was then dried in high vacuum for 6 h. The obtained air-stable complex is soluble as an olive-green solution in acetone, CH_2Cl_2, $CHCl_3$ and toluene and insoluble in unpolar solvents like n-alkanes and polar protic solvents like ^{i}PrOH or EtOH. Yield 0.24 g, 60%. ^{1}H-NMR ($CDCl_3$): δ/ppm = 6.40–7.70 (m, 35H, PPh_3 and C_5Ph_4H), 6.09 (s, 1H, C_5Ph_4H). ^{19}F-NMR ($CDCl_3$): δ/ppm = −108.5 (2F_o), −160.3 (1F_p), −162.5 (2F_m). ESI-MS: *m/z* (abundance, %) = 905.9 (15.6) $[C_5Ph_4HPd(C_6F_5)(PPh_3)]^+ = [M]^+$, 738.2 (100) $[C_5Ph_4HPd(PPh_3)]^+$.

2.2.6. Tetraphenylcyclopentadienyl-pentafluorophenyl-triphenylarsane-palladium(II), (C_5Ph_4H)Pd(C_6F_5)($AsPh_3$), **12**

Complex **12** was obtained by the same procedure as for **11** using $[\{(Pd(C_6F_5)(AsPh_3))\}_2(\mu\text{-}Cl)_2]$ (0.29 g, 0.23 mmol) and C_5Ph_4HTl (0.27 g, 0.47 mmol), instead and stirring the reaction mixture for 3 h. Crystals were obtained by slow diffusion of overlayered hexane into a solution of **12** in $CHCl_3$. Complex **12** is an air stable silver-grey solid. Yield 0.29 g, 66%. UV (CH_2Cl_2, $c = 4.3\cdot10^{-5}$ mol/l): λ_{max} 589 nm (ϵ_{max} 202 l mol^{-1} cm^{-1}). ^{1}H-NMR ($CDCl_3$): δ/ppm = 6.94–7.44 (m, 35H, $AsPh_3$ and C_5Ph_4H), 6.13 (s, 1H, C_5Ph_4H). ^{19}F-NMR ($CDCl_3$): δ/ppm = −108.5 (2F_o), −160.3 (1F_p), −162.6 (2F_m). ESI-MS: *m/z* (abundance, %) = 947.8 (100) $[C_5Ph_4HPd(C_6F_5)(AsPh_3)]^+ = [M]^+$, 769.8 (91.2) $[C_5Ph_4H{-}O{-}O{-}C_5Ph_4H]^+$, 738.2 (68.5) $[(C_5Ph_4H)_2]^+$, 642.1 (54.1) $[C_5Ph_4HPd(C_6F_5)]^+$, 323.2 $[HOAsPh_3]^+$.

2.2.7. Pentabenzylcyclopentadienyl-pentafluorophenyl-triphenylarsane-palladium(II), (C_5Bn_5)Pd(C_6F_5)($AsPh_3$), **13**

Complex **13** was obtained by the same procedure as for **11** using C_5Bn_5Tl (0.32 g, 0.44 mmol), instead. Crystals were obtained by slow diffusion of overlayered into a solution of **13** in $CHCl_3$. Complex **13** is an air stable silver-grey solid. Yield 0.29 g, 61%. UV (CH_2Cl_2, $c = 1.1\cdot10^{-4}$ mol/l): λ_{max} 576 nm (ϵ_{max} 109 l mol^{-1} cm^{-1}). ^{1}H-NMR ($CDCl_3$): δ/ppm = 6.67–7.53 (m, 40H, $AsPh_3$, $C_5(CH_2Ph)_5$), 3.52 (s, 10H, $C_5(CH_2Ph)_5$). ^{19}F-NMR ($CDCl_3$): δ/ppm = −108.8 (2F_o), −160.3 (1F_p), −162.5 (2F_m). ESI-MS: *m/z* (abundance, %) = 1093.8 (100) $[C_5Bn_5Pd(C_6F_5)(AsPh_3)]^+ = [M]^+$, 925.6 (34.5) $[C_5Bn_5Pd(AsPh_3)]^+$, 788.0 (7.4) $[C_5Bn_5Pd(C_6F_5)]^+$, 621.1 (12.6) $[C_5Bn_5Pd]^+$.

2.2.8. (Bromo/chloro)-pentafluorophenyl-bis(triphenylarsane)-palladium(II), Pd(Br/Cl)(C_6F_5)($AsPh_3$)$_2$, **14**

Compound **14** was obtained by slow diffusion of hexane into a solution of **13** in $CHCl_3$. Due to the instability of **13**, crystals of **14** were obtained as a decomposition product. The bromine impurity in the investigated crystal probably was carried over from the magnesium Grignard reagent.

2.3. X-ray structure determination

Suitable single crystals were carefully selected under a polarizing microscope. *Data Collection*: Rigaku R-axis Spider image plate detector diffractometer, temperature 173(2) K, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, double-pass method ω-scan. Data collection, cell refinement and data reduction with CrystalClear [29], empirical (multi-scan) absorption correction with ABSCOR [30].

Structure analysis and refinement: the structure was solved by direct methods (SHELXS-97) [31]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [31]. All non-hydrogen positions were refined with anisotropic temperature

factors. Hydrogen atoms for aromatic CH, were positioned geometrically (C–H = 0.94 Å) and refined using a riding model (AFIX 43) with $U_{iso}(H) = 1.2U_{eq}(CH)$. Two phenyl rings in **12** and one benzyl group in **13** is disordered (see Fig. S7 and S8 in Supplementary Material). In compound **14** a large residual electron density of 2.4 e/Å^3 was originally found within 0.3 Å from the Cl atom. Initially this residual electron density was unsuccessfully tried to refine as a disordered Cl atom position. When the occupation factor of the one Cl atom was allowed to refine, however, a value of 1.3 was obtained that indicated a heavier atom in place of the chlorine atom. Hence, in **14** a possible contamination of bromine instead of chlorine positions was considered. Allowing a partial occupancy of Br (23.3%) near the Cl atom with refinement of both occupation factors (adding up to 1) improved the *R* values, goodness-of-fit and weighting parameters considerably and lowered the otherwise large residual electron density near the chlorine atom (to 0.53 e/Å^3 within 0.8 Å from As2). Both the chlorine and bromine atom in **14** can be refined anisotropically (using the PART command). Two $AsPh_3$ phenyl rings on As2 in **14** are disordered (see Fig. S12 in Supplementary material). Crystal data and details on the structure refinement are given in Table 1. Graphics were drawn with DIAMOND [32], analyses of the Pd–Cp(centroid, ring) and on the supramolecular π–, C–H···F and C–F···π-interactions with PLATON for Windows [33]. The structural data have been deposited with the Cambridge Crystallographic Data Center (CCDC-No. 787885–787888).

2.4. Polymerizations

The polymerizations were carried out in 50 ml Schlenk flasks, which were conditioned three times by heating in high vacuum and filling with argon. All polymerization reactions were run three times to ensure reproducibility of the polymerization results. The molar Pd:Al ratio was kept constant at a value of 1:100 for all polymerization reactions. The vinyl type polymerization of norbornene was ensured by infrared spectroscopy of the PNB homopolymers which showed no absorption bands in the region of 1640 cm^{-1}, which otherwise would indicate the presence of double bonds.

2.4.1. Homopolymerization of norbornene (NB)

A solution of norbornene in toluene (7.07 mol/l, 1.5 ml, 10.6 mmol) was placed in a 50 ml Schlenk flask under inert Ar atmosphere at the chosen temperature. Toluene (3.8 ml) was added to ensure a total reaction volume of 10.0 ml. Then, a solution of MAO in toluene (0.7 ml, 1.06 mmol) was added via syringe to the norbornene solution in toluene. After 1 min the polymerization was started by addition of a solution of the precatalyst (**4** or **7**) in dichloromethane (4 ml) via syringe and the reaction mixture was stirred rapidly for the chosen time. The resulting polymer precipitated as a colorless solid and the reaction was stopped by addition of a mixture of concentrated HCl and methanol (1:1, 30 ml). The polynorbornene was filtered and washed several times with methanol and then dried in high vacuum for 6 h. Different temperatures (22 °C, 40 °C), polymerization times (0.5 min, 1 min, 2 min, 5 min) and amounts of the precatalysts **4** and **7** ($1.06 \cdot 10^{-2}$ mmol and 2.12×10^{-2} mmol) were used for the homopolymerization of norbornene. The constant amount of NB (10.6 mmol) then gave the two different molar NB:Pd ratios of 1000:1 and 500:1.

2.4.2. Copolymerization of norbornene and 5-vinyl-2-norbornene (VNB)

A solution of norbornene in toluene (7.07 mol/l, $1.5 \cdot x$ ml, $10.6 \cdot x$ mmol) and a solution of 5-vinyl-2-norbornene in toluene

Table 1
Crystal data and structure refinement for **7**, **12**, **13**, **14**.

Compound	**7**	**12**	**13**[e]	**14**
Empirical formula	$C_{29}H_{20}AsF_5Pd$	$C_{53}H_{36}AsF_5Pd$	$C_{64}H_{50}AsF_5Pd$	$C_{42}H_{30}As_2Br_{0.23}Cl_{0.77}F_5Pd$
M/g mol^{-1}	644.77	949.14	1095.36	931.69
Crystal size/mm	0.47 × 0.28 × 0.25	0.51 × 0.36 × 0.26	0.16 × 0.13 × 0.05	0.27 × 0.12 × 0.12
Crystal appearance	Block, dark-red	Isometric, grey	Plate, grey	Isometric, red
2θ range/°	6.10–54.96	6.00–54.92	6.06–54.96	6.02–50.30
completeness to 2θ/%	99.8	99.8	99.7	99.9
h; k; l range	±22; ±20; ±23	±14; ±27; ±26	±44; ±19; −26,24	±14; −29,25; ±31
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Orthorhombic
Space group	*Pbca*	$P2_1/c$	$C2/c$	*Pbca*
a/Å	17.279(4)	11.218(2)	33.936(7)	11.709(2)
b/Å	15.814(3)	21.162(4)	15.213(3)	24.260(5)
c/Å	18.096(4)	20.537(6)	20.102(4)	26.373(5)
α/°	90	90	90	90
β/°	90	120.35(2)	103.90(3)	90
γ/°	90	90	90	90
V/Å^3	4944.6(17)	4207.2(16)	10074(3)	7492(3)
Z	8	4	8	8
D_{calc}/g cm^{-3}	2.133	1.498	1.444	1.652
F(000)	2544	1912	4464	3681
μ/mm^{-1}	1.732	1.281	1.080	2.606
Max/min transmission	0.6176/0.4338	0.7319/0.5612	0.9480/0.8461	0.7450/0.5396
Reflections collected	129727	248319	127142	108733
Indep. reflections (R_{int})	5677 (0.0398)	9613 (0.0301)	11518 (0.0892)	6681 (0.0340)
Obs. reflect [$I > 2\sigma(I)$]	5028	8939	9017	5760
Parameters refined	325	633	704	580
Max./min. $\Delta\rho$[a]/e Å^{-3}	0.424/−0.381	0.414/−0.354	0.545/−0.597	0.527/−0.502
R_1/wR_2 [$I > 2\sigma(I)$][b]	0.0230/0.0556	0.0212/0.0523	0.0397/0.0804	0.0207/0.0474
R_1/wR_2 (all reflect.)[b]	0.0277/0.0573	0.0234/0.0535	0.0578/0.0867	0.0263/0.0494
Goodness-of-fit on F^2[c]	1.026	1.041	1.054	1.027
Weight. scheme w; a/b[d]	0.0266/3.9284	0.0245/2.6066	0.0313/17.9567	0.0193/5.8388

[a] Largest difference peak and hole.
[b] $R_1 = [\sum(||F_o| - |F_c||)/\sum|F_o|]$; $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.
[c] Goodness-of-fit = $[\sum[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$.
[d] $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2 \text{ or } 0) + 2F_c^2)/3$.
[e] The data set quality of **13** was lowered by the necessary fast crystallization in view of the instability of **13** in $CHCl_3$ solution.

(7.07 mol/l, $1.5\cdot(1-x)$ ml, $10.6\cdot(1-x)$ mmol) (with x set to the values of 0.8, 0.6, 0.5, 0.4, 0.2 to vary the NB:VNB ratio) were placed in a 50 ml Schlenk flask under inert Ar atmosphere. Toluene (3.8 ml) was added to ensure a total reaction volume of 10.0 ml. Then, a solution of MAO in toluene (0.7 ml, 1.06 mmol) was added via syringe to the norbornene solution in toluene. After 1 min the polymerization was started by addition of a solution of the pre-catalyst (**4** or **7**) in dichloromethane (4.0 ml) via syringe and the reaction mixture was stirred rapidly for 1 h. The resulting polymer precipitated as a colorless solid and the reaction was stopped by addition of a mixture of concentrated HCl and methanol (1:1, 30 ml). The copolymer was filtered and washed several times with methanol and then dried in high vacuum for 6 h. All copolymerizations were performed at 22 °C. The amount of the precatalysts **4** and **7** was varied (1.06×10^{-2} mmol and 2.12×10^{-2} mmol), the amount of (NB + VNB) was kept constant at 10.6 mmol leading to the different molar (NB + VNB):Pd ratios of 1000 and 500:1. The polymerization time of 1 h was fixed.

2.4.3. Copolymerization of norbornene and 5-ethylidene-2-norbornene (ENB)

A solution of norbornene in toluene (7.07 mol/l, $1.5\cdot x$ ml, $10.6\cdot x$ mmol) and a solution of 5-ethylidene-2-norbornene in toluene (7.07 mol/l, $1.5\cdot(1-x)$ ml, $10.6\cdot(1-x)$ mmol) (with x set to the values of 0.8, 0.6, 0.5, 0.4, 0.2 to vary the NB:VNB ratio) were placed in a 50 ml Schlenk flask under inert Ar atmosphere. Toluene (3.8 ml) was added to ensure a total reaction volume of 10.0 ml. Then, a solution of MAO in toluene (0.7 ml, 1.06 mmol) was added via syringe to the norbornene solution in toluene. After 1 min the polymerization was started by addition of a solution of the appropriate precatalyst (**4** or **7**) in dichloromethane (4.0 ml) via syringe and the reaction mixture was stirred rapidly for 1 h. The resulting polymer precipitated as a colorless solid and the reaction was stopped by addition of a mixture of concentrated HCl and methanol (1:1, 30 ml). The copolymer was filtered and washed several times with methanol and then dried in high vacuum for 6 h. All copolymerizations were performed at 22 °C. The amount of the precatalysts **4** and **7** was varied (1.06×10^{-2} mmol and 2.12×10^{-2} mmol), the amount of (Nb + ENB) was kept constant at 10.6 mmol leading to the different molar (NB + ENB):Pd ratios of 1000 and 500:1. A polymerization time of 1 h was chosen.

2.4.4. Homopolymerization of 5-ethylidene-2-norbornene (ENB)

A solution of 5-ethylidene-2-norbornene in toluene (7.07 mol/l, 1.5 ml, 10.6 mmol) was placed in a 50 ml schlenk flask under inert Ar atmosphere. Toluene (3.1 ml) was added to ensure a total reaction volume of 10.0 ml. Then, a solution of MAO in toluene (1.4 ml, 2.12 mmol) was added via syringe to the norbornene solution in toluene. After 1 min the polymerization was started by addition of a solution of the appropriate precatalyst (**4** or **7**, 2.12×10^{-2} mmol) in dichloromethane (4.0 ml) via syringe and the reaction mixture was stirred rapidly for the chosen time. The resulting polymer precipitated as a colorless solid and the reaction was stopped by addition of a mixture of concentrated HCl and methanol (1:1, 30 ml). The polymer was filtered and washed several times with methanol and then dried in high vacuum for 6 h. Different polymerization times for the catalytic system **4**/MAO (1 min, 2 min, 5 min, 10 min 30 min and 60 min) and **7**/MAO (1 h, 2 h, 6 h, 12 h, 24 h) were chosen. All homopolymerizations were performed at 22 °C and a molar ENB:Pd ratio of 500:1.

3. Results and discussion

3.1. Syntheses and molecular structures

The complexes $[N^nBu_4][(\eta^5\text{-}C_5H_5)Pd(C_6X_5)_2]$ (**1**, **2**) or $[(\eta^5\text{-}C_5H_5)Pd(C_6X_5)(L)]$ (**3**–**10**) (X = F or Cl, L = $CNBu^t$, PPh_3, PMe_2Ph, PEt_3, $AsPh_3$, $SbPh_3$) can easily be prepared in excellent yields by reacting the chloro- or bromo bridged organopalladium dimers $[N^nBu_4]_2[(X_5C_6)_2Pd(\mu\text{-}Cl)_2Pd(C_6X_5)_2]$ and $[(X_5C_6)(L)Pd(\mu\text{-}Y)_2Pd(C_6X_5)(L)]$ (Y = Cl, Br) with cyclopentadienylthalium (Scheme 2). The half-sandwich η^5-cyclopentadienyl complexes are air-stable, both in the solid state and in solution. They are all soluble in polar organic solvents like acetone, dichloromethane and chloroform. Good solubilities are also obtained in the aromatic solvents toluene or benzene, whereas insolubility exists in the aprotic and non-polar aliphatic solvents n-pentane or n-hexane. The new complexes have been characterized by partial elemental analyses and spectroscopic (IR and ^1H, ^{19}F, ^{13}C and ^{31}P NMR) methods. In acetone solution, complexes **1** and **2** behave as 1:1 electrolytes [34]. The IR spectra show the bands attributed to the C_6F_5 (1630, 1490, 1460, 1050, and 950 cm^{-1}) [35] or the C_6Cl_5 (1315, 1285, 1220 and 670 cm^{-1}) [36] groups. Morever, a split absorption located at *ca.* 800 cm^{-1} in the spectra of the bis(pentafluorophenyl) derivative **1** or at *ca.* 830 cm^{-1} for the bis(pentachlorophenyl)derivative **2** has been previously used for structural elucidation [37]. It is derived from the so-called halogen-sensitive mode in C_6F_5 and C_6Cl_5 halogen molecules and in square-planar MR_2L_2 (R = C_6F_5, C_6Cl_5) complexes is related to the skeletal symmetry of the entire molecule [37] and behaves like a ν(M–C) which is characteristic of the *cis*-MR_2 fragment (C_{2v} symmetry). The IR spectrum of complex **3** shows also an absorption assigned to ν(CN) of the $CNBu^t$ group at ca. 2235 cm^{-1} [38–40].

The substituted cyclopentadienyl complexes $(\eta^5\text{-Cp})Pd(C_6F_5)(EPh_3)$ (**11**–**13**) were obtained by reacting the chlorine bridged dinuclear palladium(II) complexes $[\{(Pd(C_6F_5)(EPh_3))\}_2(\mu\text{-}Cl)_2]$ [27] in acetone with two equivalents of the appropriate CpTl compound 1,2,3,4-tetraphenylcyclopentadienylthallium(I), C_5Ph_4HTl [22] for **11** (E = P), **12** (E = As) and 1,2,3,4,5-pentabenzylcyclopentadienylthallium(I), C_5Bn_5Tl [22,23] for **13** (E = As) as Cp-transfer agents [41].

The cyclopentadienyl complexes are air- and moisture-stable in the solid state. In solution complexes **1** and **10** proved to be stable over a long period of time (several weeks) in the presence of air. Complex **12** was also quite stable in solution, but decomposition occurred after several weeks, whereas complex **13** was only stable in solution for approximately 2 days even under argon. The ^{19}F NMR spectrum in $CDCl_3$ solution reveals the presence of a freely rotating pentafluorophenyl ring which gives three resonances (in the ratio 2:1:2) for the *o*-, *p*-, and *m*-fluorine atoms. CI and ESI mass spectrometric investigations show the molecular ion as the base peak for **4**, **12** and **13**. Also observed are peaks for $[CpPd(C_6F_5)]^+$ and $[CpPd(EPh_3)]^+$ (see Figs. S1–S4 in Supplementary material). The ESI mass spectra of **12** and to a lesser extent of **13** also exhibit the oxygenated Cp-ligand peaks $[Cp{-}O{-}O{-}Cp]^+$ ($Cp = C_5Ph_4H$ and C_5Bn_5) and $[C_5Bn_5OH]^+$ (Figs. S3 and S4) which may help to explain part of the instability of these two compounds in solution.

For reactive Cp–M bonds an increased inertness is typically seen in a comparison between the C_5H_5 and bulkier-Cp derivative [22,23,42–46]. However, bulky-Cp complexes can be more reactive than their less bulky analogs if a dissociative mechanism is operating for the other ligands. For example, the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the carbonyl displacement in $CpRu(CO)_2Br$ with phosphorus donor ligands increase from $Cp = C_5Ph_5$ over C_5Me_4Et to C_5H_5 with relative reaction rates of about 20:14:1, respectively. There is an enhanced lability of CO in the pentaphenyl derivative [47].

The synthesis of η^5-$CpPd(C_6F_5)(EPh_3)$ (E = P, As) with the pentaphenylcyclopentadienyl ligand has been unsuccessfully attempted a couple of times using the available C_5Ph_5Tl compound [22]. No $(C_5Ph_5)Pd$ fragment was found by NMR in the reaction mixture, although complexes with the $(\eta^5\text{-}C_5Ph_5)Pd$ moiety are known [48].

The neutral half-sandwich cyclopentadienylpalladium compounds **3**–**10** with the unsubstituted η^5-C_5H_5 ligand are redish-pink solids and also give a pink to violet solution in chloroform. Complexes **11**–**13** with the substituted tetraphenyl- or pentabenzylcyclopentadienyl ligands are olive-green (**11**) or silver-grey (**12**, **13**) in the solid state and give green to blue solutions in $CHCl_3$ (Fig. S5). The UV-spectra of the (C_5H_5)Pd complexes **4** and **7** are shown in Fig. 1. Their metal-centered d–d absorption peak appears at λ_{max} of 501 and 510 nm. The slightly stronger PPh_3 versus the $AsPh_3$ ligand yields the shorter wavelength absorption in **4** versus **7**. The d–d absorption of the (C_5Ph_4H)Pd and (C_5Bn_5)Pd complexes **12** and **13**, respectively, have a λ_{max} of 589 nm (**12**) and 576 nm (**13**), which indicates a Cp ligand field strength of the order $CpPh_4H < C_5Bn_5 < C_5H_5$.

Crystals of **4**, **7**, **12** and **13** suitable for X-ray diffraction studies were obtained by slow diffusion of overlayered hexane into a solution of the complex in $CHCl_3$. Due to the instability of **13** in solution, it was neccessary to enforce a fast crystallization within 2 days. Compounds **4**, **7**, **12** and **13** are molecular palladium(II) complexes with a pentahapto-bound (substituted) cyclopentadienyl ring, a pentafluorophenyl and a triphenylphosphine or -arsine ligand. The structure of **4** has been communicated earlier by us and shows the expected pseudo-trigonal coordination of the η^5-C_5H_5, C_6F_5 and PPh_3 ligands around the palladium atom [49]. The solid-state molecular structures of **7**, **12** and **13** with their pseudo-trigonal palladium coordination are depicted in Figs. 2–4, respectively. Cp–Pd distances (Table 2) are as expected from a comparison to related (η^5-C_5H_5)Pd-phosphine [49,50] and –stibine [51], (η^5-indenyl)Pd-phosphine [52] and –amine [53] complexes. The only other $CpPd(C_6F_5)$ derivative available is (η^5-C_5H_5)Pd(C_6F_5)(PPh_3) [49].

In **7**, **12** and **13** the Pd–C(Cp) bond length trans to the σ-pentafluorophenyl ligand is one of the shortest. A similar pattern has already been observed in a number of other structures of nickel, palladium and platinum cyclopentadienyl complexes [49,54]. Such M–C(Cp) (M = Ni, Pd, Pt) bond length differences have been rationalized in terms of the trans influence of the σ-aryl ligand. Also the variation in C–C bond lengths in the Cp rings of **7** is similar to other cyclopentadienyl complexes of nickel, platinum and especially palladium [54] and could again be attributed to the different trans influence of the σ-C_6F_5 and $AsPh_3$ ligands. The Pd–C_6F_5 bond lengths are in the range found in the literature for pentafluorophenyl–palladium complexes [55].

Compound **13** has four phenyl rings of the benzyl group situated "above" the Cp ring or away from the metal atom and one phenyl ring "below" the Cp plane approaching the other two ligands. This four versus one ratio was also seen in the decabenzylmetallocenes, $(C_5Bn_5)_2M$ of germanium, tin and lead [42] and the half-sandwich transition metal complexes $(C_5Bn_5)Co(CO)_2$ [56] and $(C_5Bn_5)Mn(CO)_3$ [57]. In the pentabenzylcyclopentadienyl-thallium, pentabenzylcyclopentadienyl-indium and pentabenzylcyclopentadienyl-potassium compound the ratio is two versus three or three versus two [23,43]. Having all five benzyl groups lying on the same side of the Cp ring is an unfavorable situation and was only observed in the structure of decabenzylferrocene, $(C_5Bn_5)_2Fe$ with all 10 phenyl rings being directed away from the metal atom. This benzyl orientation in the ferrocene derivative results from the small size of the iron atom and the close approach of the Cp ring planes (3.3 Å apart) [44].

Despite the presence of ligand π-systems in **7**, **12** and **13** there are no intermolecular π–π interactions [58] evident (vide infra). In terms of π-contacts the packing in **7**, **12** and **13** seems to be controlled by C–H···π interactions (see Supplementary material) [59]. The intermolecular C–H···π contacts start around 2.7 Å for the (C–)H···ring centroid distances. These C–H···π contacts lie at the short end of the accepted distance range for this type of contact [59,60]. In addition, a few C–H···F–C contacts can be found in **7**, **12** and **13** (see Supplementary material) [49,61].

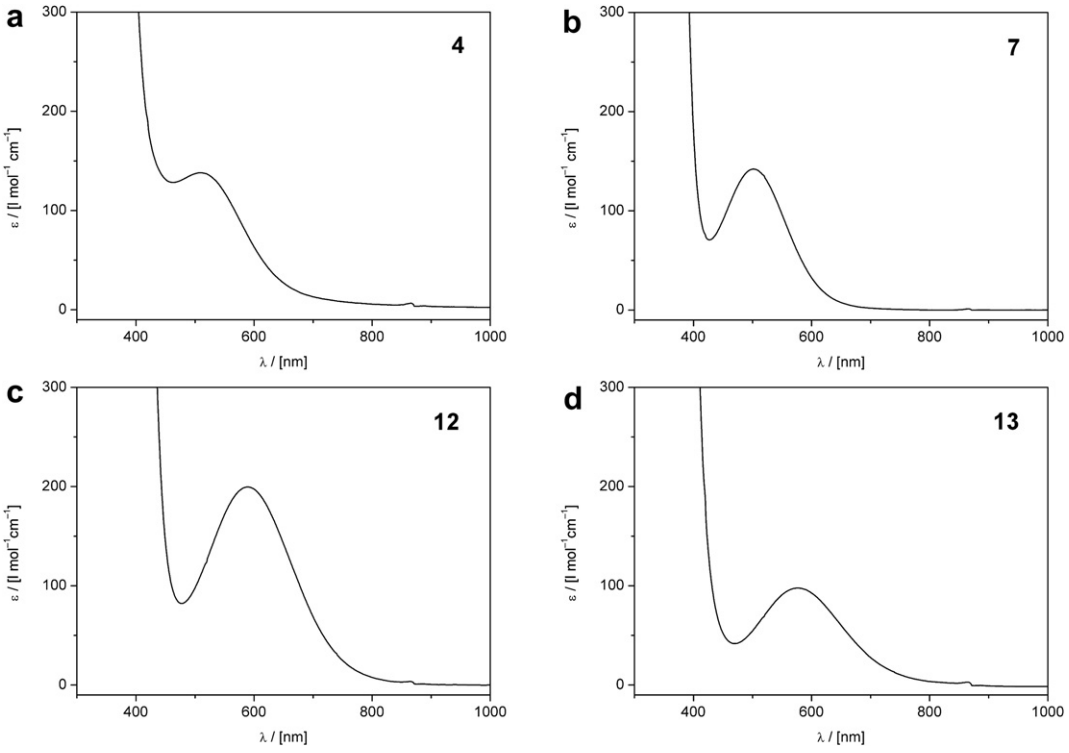


Fig. 1. UV-spectra of the $CpPd(C_6F_5)(L)$ complexes in CH_2Cl_2 (a) Cp = C_5H_5, L = PPh_3 (**4**), (b) Cp = C_5H_5, L = $AsPh_3$ (**7**), (c) Cp = C_5Ph_4H, L = $AsPh_3$ (**12**), (d) Cp = C_5Bn_5, L = $AsPh_3$ (**13**).

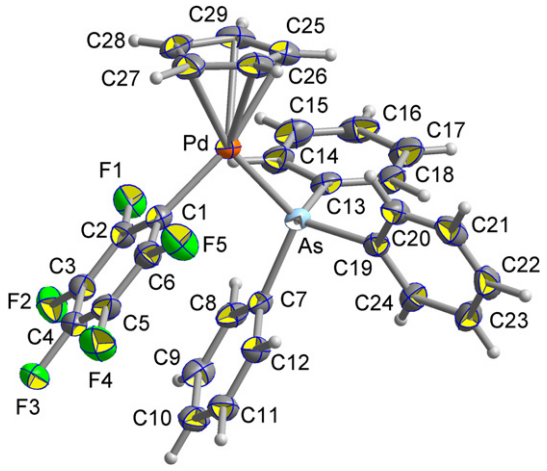


Fig. 2. Thermal ellipsoid plot (50% probability) of complex **7**; selected distances and angles in Table 2. For the intramolecular π-contact between C_6F_5 and C7–C12 see Fig. S6 in Supplementary material.

In **7** two neighboring molecules form pairs through the six-fold phenyl embrace by C–H···π contacts between the $AsPh_3$ ligands (Fig. 5) [62]. The sextuple phenyl embrace is a supramolecular attraction between Ph_3P moieties due to a concert of six attractive edge-to-face interactions between phenyl groups and has frequent occurrence in crystals, is usually centrosymmetric, and contributes an attraction of 60–85 kJ mol^{-1} [62]. Noteworthy in the structure of **4**, the PPh_3 analog to **7**, the phenyl embrace was not present (Fig. S9 in Supplementary material). Instead, in [(η^5-C_5H_5)Pd(C_6F_5)(PPh_3)], **4** there are two symmetry-independent molecules in the unit cell (also proven by solid state ^{19}F NMR) due to an intermolecular C–H···F–C contact [49]. Both **4** and **7** crystallize in the same orthorhombic space group *Pbca* with very similar *a* and *b* cell constants, but the *c* axis is doubled (35.5 Å) for **4**. Also in **12** and **13** the phenyl embrace is no longer present for the packing (Figs. S10 and S11) which indicates a dominance of C–H···phenyl(Cp) and C–H···C_6F_5 π contacts in **12** and simple van der Waals contacts in **13** besides an C–H···F–C contact in both (see supramolecular interactions in Supplementary material).

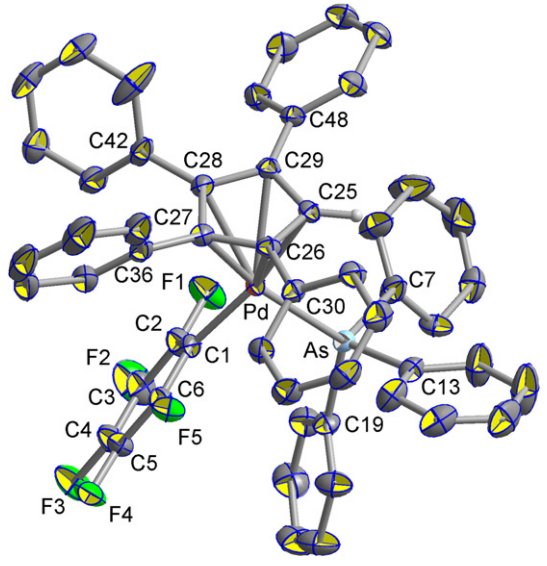


Fig. 3. Thermal ellipsoid plot (50% probability) of complex **12**; H atoms on the phenyl rings are not shown for clarity; selected distances and angles in Table 2.

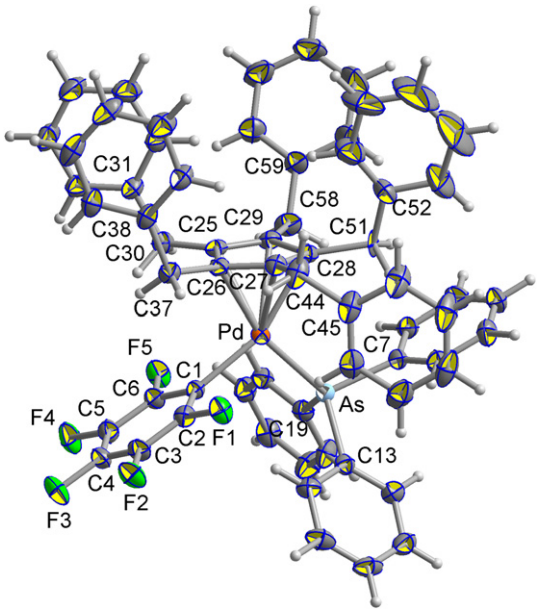


Fig. 4. Thermal ellipsoid plot (50% probability) of complex **13**; selected distances and angles in Table 2.

From the decomposition of compound **13** in $CHCl_3$ solution a square-planar, Cp-free halo-pentafluorophenyl-bis(triphenylarsane)palladium(II) complex could be isolated (Fig. 6). In the structure of compound **14** a possible contamination of bromine instead of chlorine positions had to be considered. Contamination of **14** with $PdBr(C_6F_5)(AsPh_3)_2$ may originate from the starting material C_6F_5Br, respectively the Grignard reagent C_6F_5MgBr which is reacted with $PdCl_2(AsPh_3)_2$ (Eq. (1)). Allowing a partial occupancy of Br (23.3%) near the Cl atom (76.7%) improves the R values and lowers the otherwise large residual electron density near the chlorine atom.

Table 2
Selected bond lengths (Å) and angles (°) for **7**, **12**, **13**.

Compound	**7**	**12**	**13**
Pd–C1	2.031(2)	2.0355(15)	2.057(3)
Pd–As	2.3560(4)	2.3678(5)	2.3840(9)
Pd–C25	2.281(2)[d]	2.2470(15)[d]	2.363(3)
Pd–C26	2.324(2)	2.3704(14)	2.240(3)
Pd–C27	2.254(2)	2.3641(15)	2.325(3)
Pd–C28	2.340(2)	2.3851(16)	2.308(3)[d]
Pd–C29	2.377(2)	2.4146(16)	2.405(3)
Pd–Ct[a]	1.9795(12)	2.0163(9)	1.9829(13)
Pd–Cp(plane) [b]	1.9778(2)	2.0141(1)	1.9791(2)
Ring slippage[c]	0.081	0.095	0.123
As–C7	1.947(2)	1.9376(17)	1.946(3)
As–C13	1.945(2)	1.9396(16)	1.943(3)
As–C19	1.939(2)	1.9491(16)	1.952(3)
C1–Pd–As	90.44(6)	89.02(5)	99.87(7)
C1–Pd–Ct[a]	132.89(6)	136.94(6)	125.37(8)
As–Pd–Ct[a]	136.08(2)	134.05(3)	134.00(2)
C7–As–C13	103.98(9)	103.61(7)	102.17(11)
C7–As–C19	101.95(8)	102.75(7)	101.67(11)
C13–As–C19	105.20(9)	101.23(7)	103.45(11)
Dihedral angle plane(C1–Pd–As)–Cp(plane)	86.25(12)	88.32(8)	85.68(14)

[a] Ct, ring centroid.
[b] Normal or perpendicular projection from the Pd atom onto the Cp ring plane.
[c] Distance between perpendicular projection of Pd atom on Cp ring plane and ring centroid.
[d] Carbon atom trans to the σ-C_6F_5 ligand.

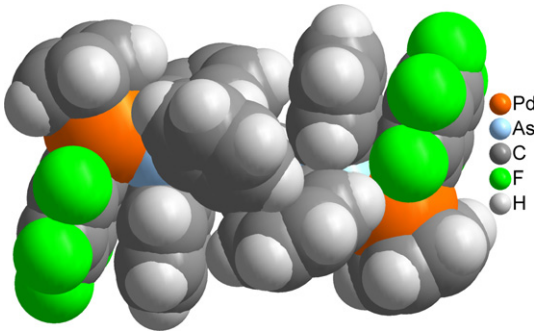
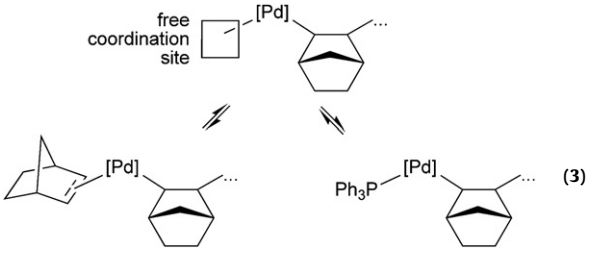


Fig. 5. Pair formation of complex **7** through the six-fold phenyl-embrace of two $AsPh_3$ ligands in space-filling mode.

Both the chlorine and bromine atom can be refined anisotropically. Such a contamination or a solid solution of two complexes would be reminiscent to the mixture of $[MoCl_2(O)(PR_3)_3]$ and $[MoCl_3(PR_3)_3]$ that was responsible for the notorious "bond-stretch isomer" problem [63]. The syntheses of $PdCl(C_6F_5)(AsPh_3)_2$ [64] and $PdBr(C_6F_5)(AsPh_3)_2$ have been described [65]. Related, structurally authenticated complexes with a *trans* Cl–Pd–C_6F_5 moiety are $[PdCl(C_6F_5)$(*N10*-9-aminoacridine)$(PPh_3)]$ [66] and $[PdCl(C_6F_5)(PPh_3)_2]$ [67]; also related are complexes $[Pd(C_6F_5)(AsR_2R')_2(NCMe)]^+$ [77] and $[PdCl(C_6H_2$-2,4,6-$(NO_2)_3)(AsPh_3)_2]$ [68].

3.2. Norbornene homopolymerization

The homopolymerization of norbornene (NB) with **4**/MAO and **7**/MAO was performed under different molar norbornene:Pd ratios (1000:1 and 500:1), polymerization times (0.5 min, 1 min, 2 min, 5 min) and temperatures (22 and 40 °C). The polymerization activities cover a range from 3.17×10^5 $g_{PNB}/(mol_{Pd} \cdot h)$ (Table S1, entry 1) to 2.07×10^6 $g_{PNB}/(mol_{Pd} \cdot h)$ (Table S1, entry 21) which can be classified as good to high [1,2]. The system **7**/MAO generally yielded higher activities than **4**/MAO. This is reasoned with a kinetic activation effect through a faster removal of the more weakly bound $AsPh_3$ ligand in **7** over the PPh_3 ligand in **4** upon reaction with MAO together with the C_6F_5 ligand to give the active Pd species (see below) [77]. The weaker $AsPh_3$ bonding is based on the longer Pd–As (~2.36 Å) over the shorter Pd–P bond (2.23 Å) [49]. Previous work has shown that upon borane or MAO activation ligands will be lost to give a coordinatively unsaturated or even a "naked" Pd^{2+} as the active species [74,75]. Hence, more weakly bound ligands which will be removed faster will lead more quickly to the active palladium catalyst. In addition, the still present and stronger coordinating PPh_3 ligand can compete in equilibrium with the NB monomer for the free metal coordination site (Eq. (3)) which, as a consequence, slows the chain growth rate [77,69]. Such a PPh_3/ethene competition is used in the Shell higher olefin process (SHOP) to control the oligomer chain length [70].



The insolubility of the obtained polynorbornenes (PNBs) as is often encountered with Pd catalysts, except for vinyl polynorbornenes from dicationic, single-component Pd complexes of the type $[Pd(NCCH_3)_4]^{2+}$ [10a], made a further characterization of the polymer molar mass and mass distribution by gel permeation chromatography (GPC) impossible. The origin of this insolubility is still not quite clear. One possibility may be chain cross-linking due to partial cationic polymerization or tacticity [1–3].

We opted to primarily compare conversions rather than activities. A comparison of activities for different reaction times can be misleading as highly reactive and sensitive catalysts with a high intrinsic activity will show a lower over-time activity at longer reaction times due to faster deactivation. Norbornene conversions increase with polymerization time and are higher for an NB:Pd ratio of 500 than for a ratio of 1000:1 for both catalysts **4**/MAO and **7**/MAO (Fig. 7 and Fig. S13).

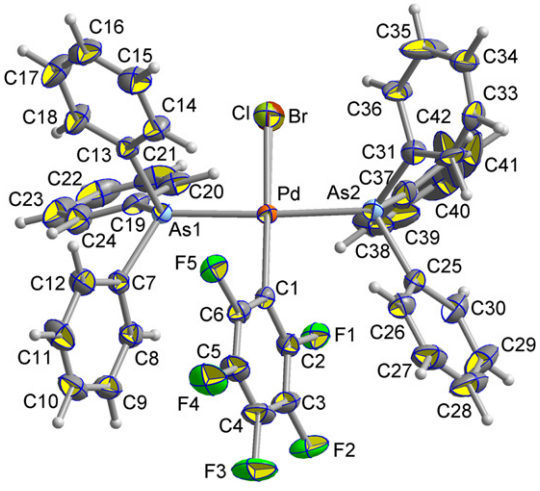


Fig. 6. Thermal ellipsoid plot (50% probability) of complex **14**. The Cl and Br atom are almost superimposed. Selected distances (Å) and angles (°): Pd–As1 2.4022(5), Pd–As2 2.4027(6), Pd–C-1 2.011(2), Pd–Cl = 2.390(4), Pd–Br 2.388(6), C-1–Pd–As1 91.73(5), C-1–Pd–As2 91.71(5), C-1–Pd–Cl 178.4(2), C-1–Pd–Br 178.1(2), Cl–Pd–As1 86.7(2), Cl–Pd–As2 89.8(2), Br–Pd–As1 88.0(2), Br–Pd–As2 88.6(2), As1–Pd–As2 176.32(1).

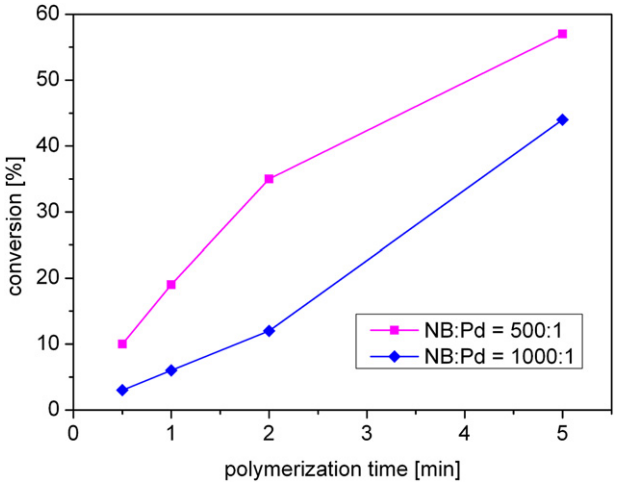


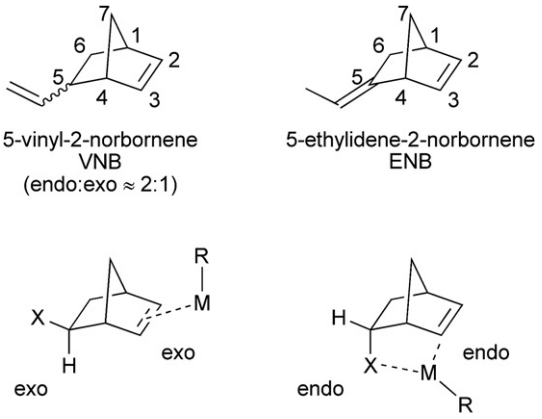
Fig. 7. Norbornene conversion-time plot for the catalytic system **4**/MAO at two different molar NB:Pd ratios; conditions: NB 10.6 mmol, molar ratio Al:Pd = 100:1, total reaction volume 10.0 ml. temperature 22 °C, see Table S1, entries 1–8.

3.3. Copolymerization of norbornene and 5-vinyl-2-norbornene (VNB)

Both catalytic systems **4**/MAO and **7**/MAO gave noticeable lower conversions in NB-VNB copolymerization than in the NB homopolymerization (Table S2). It is well established for the polymerization of norbornene derivatives that donor atoms or a donor functionality like a C=C double bond slow down the chain propagation through metal coordination [12,13]. Work on the vinyl polymerization of functionally substituted norbornenes shows that generally the *endo*-functionalized norbornenes are polymerized more slowly compared to the *exo*-analogs because of the possible coordination of the donor-containing substituent to the metal atom (Scheme 3) [12,71], which attenuates the polymerization activity. Since the synthesis of substituted norbornenes is accomplished in a Diels-Alder reaction, always a mixture of *endo*- and *exo*-isomers is obtained.

The NB/VNB copolymerization activities range from 4.64×10^3 $g_{polymer}/(mol_{Pd}\,h)$ (**7**/MAO, NB:VNB = 20:80) to 3.98×10^4 $g_{polymer}/(mol_{Pd}\,h)$ (**4**/MAO, NB:VNB = 80:20, Table S2). Activities between 10^3 and 10^5 are in same the range as found with $PdCl_2$(bisphosphane)/MAO [75]. Again, conversions are higher for an (NB + VNB):Pd ratio of 500:1 than for a ratio of 1000:1 for both catalysts **4**/MAO and **7**/MAO (Fig. 8). Different from the homopolymerization of NB, the catalytic system **4**/MAO yields higher conversions and activities in the copolymerization of NB and VNB than **7**/MAO (see below). The conversions and subsequent activities depend highly on the molar NB:VNB ratio. The activity decreases with the increase in VNB content. The highest activities are obtained for an NB:VNB ratio of 80:20, the lowest for an NB:VNB ratio of 20:80 (Fig. 8). From ^{1}H NMR the endo:exo ratio for VNB is about 2:1 (Fig. S16). As the minor exo isomer is polymerized faster this contributes to the drop in overall conversion with increasing VNB content.

The lower activities in the presence of VNB are due to its terminal α-olefin functionality. Coordination of both olefin functions of VNB can give a stable diolefin palladium complex from which the insertion polymerization is unlikely to proceed (Scheme 4; see below for support of this interpretation). The higher activity of **4**/MAO in the NB-VNB copolymerization is traced to the presence of the PPh_3 ligand in the reaction mixture. The competition of the PPh_3 and olefin coordination [69] which was disadvantageous in the NB homopolymerization (cf. Eq. (3)) now raises the activity of **4**/MAO over **7**/MAO by making the diolefin coordination more difficult (Scheme 4). The steric demand of the PPh_3 group may also play a directing role for the suggested exo–exo enchainment with the insertion of the ring double bond in the polymerization [72]. The



Scheme 3. Structure of VNB and ENB and bonding modes for functionalized norbornene derivatives (X = coordinating functionality).

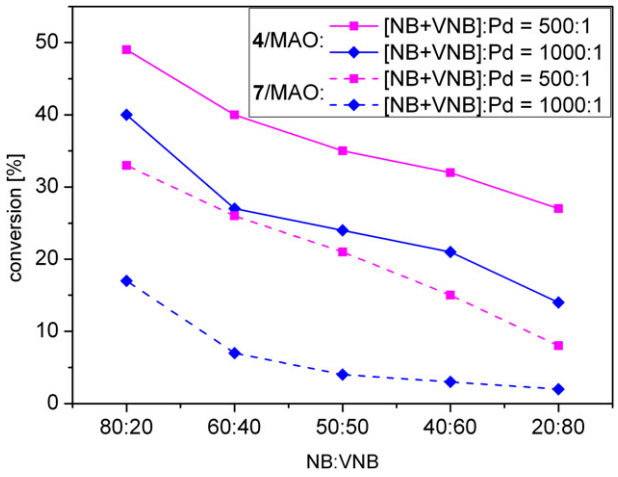


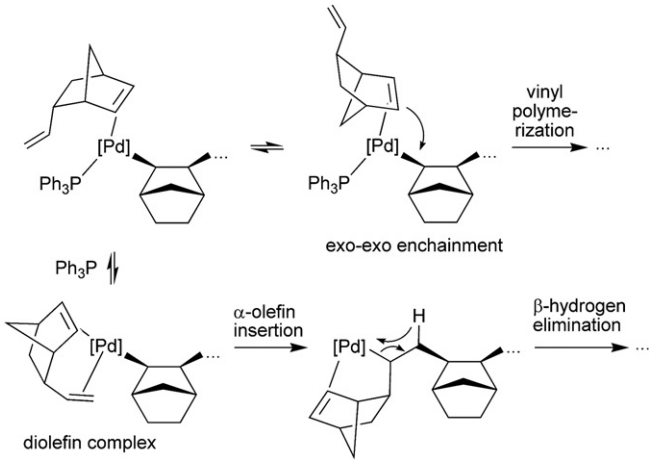
Fig. 8. Total conversion in the copolymerization of norbornene (NB) and 5-vinyl-2-norbornene (VNB) with **4**/MAO and **7**/MAO as a function of the molar NB:VNB ratio. Conditions: NB + VNB 10.6 mmol, molar ratio Al:Pd = 100:1, temperature 22 °C, reaction time 1 h, total volume 10.0 ml; see Table S2, entries 1–10 and 11–20, respectively.

NB-VNP copolymer is still insoluble, precluding a GPC characterization.

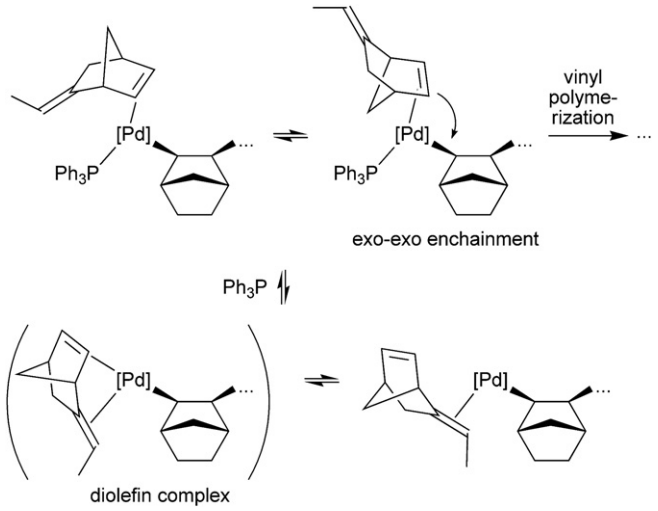
3.4. Copolymerization of norbornene and 5-ethylidene-2-norbornene (ENB)

Conversions and activities for the copolymerization of NB and ENB (Table S3) are lower than for the homopolymerization of norbornene but can be higher than for the copolymerization of NB and VNB under otherwise identical conditions (cf. Table S2). The NB/ENB copolymerization activities range from 2.17×10^3 $g_{polymer}/(mol_{Pd}\,h)$ (**7**/MAO, NB:ENB = 20:80) to 5.76×10^4 $g_{polymer}/(mol_{Pd}\,h)$ (**4**/MAO, NB:VNB = 40:60, Table S3). This supports the formation of a less active diolefin complex with VNB (Scheme 4) since the relative and rigid spatial disposition of the two olefin bonds in ENB (Scheme 5) renders an ENB-diolefin complex unlikely.

Also, the ethylidene group in ENB is a trisubstituted internal olefin whose insertion into the Pd–C bond is less likely. Still, the ethylidene group can form an inactive Pd-olefin complex so that the presence of ENB lowers the activity compared to the NB homopolymerization. Again the system **4**/MAO was more active and much less affected by an increasing molar NB:ENB ratio than



Scheme 4. Competition in the VNB-olefin and PPh_3 coordination of **4**/MAO; the formulation [Pd] indicates that additional ligands can be present. The VNB-diolefin complex may be a resting state.



Scheme 5. Competition in the ENB-olefin and PPh_3 coordination of **4**/MAO; the formulation [Pd] indicates that additional ligands can be present. The ENB-diolefin complex is less likely because of the rigid disposition of the two olefin groups. The ethylidene-Pd olefin complex may be a resting state.

7/MAO (Table S3, Fig. 9). This is again reasoned by the competition of the PPh_3 and olefin coordination (Scheme 5) [69].

The significant decrease in the conversion for the NB-ENB copolymerization with **7**/MAO compared to **4**/MAO (Fig. 9) further underscores the role of the PPh_3 ligand, as this is the only difference between **4** and **7**. The PPh_3 group can more effectively exert a structure directing role towards the exo-ENB-monoolefin-Pd coordination which is suggested for the vinyl enchainment as ENB apparently lacks the possibility for diolefin-chelate formation. In the absence of PPh_3 ($AsPh_3$ is a weaker coordinating ligand) the ENB-ethylidene-Pd olefin complex may be an effective resting state (see below for further support of this interpretation). Irrespective of the role of the phosphane it should be remembered that substituted norbornes are always less effectively incorporated into the growing polymer chain [12,13].

3.4.1. *Ethylidene-2-norbornene (ENB) – homopolymerization*

The ENB conversion is dramatically affected by the choice of the catalyst. While the catalytic system **4**/MAO gave 46% conversion to poly-ENB within 5 min of reaction time (Table S4, entry 3), **7**/MAO required 24 h for a conversion of 44% (Table S4, entry 11). This difference in catalyst activity is further evidence for the structure directing role of the PPh_3 ligand (in **4**) according to Scheme 5. The ENB homopolymer (as the above copolymers) is still insoluble in 1,2,4-trichlorobenzene even at elevated temperatures, so that a gel permeation chromatography (GPC) could not be done in order to obtain a polymer molar mass and mass distribution.

The activity of **4**/MAO in the homopolymerization of ENB was only slightly lower than in the homopolymerization of NB under identical reaction conditions (compare entries 1–3 in Table S4 with entries 6–8 in Table S1, Fig. 10). Thus, the ethylidene functionality has little effect on the polymerization activity with **4**/MAO or in the presence of PPh_3, thereby supporting the notions of Scheme 5. On the other hand, when **7**/MAO is used as the catalyst, there is a dramatic decrease in activity. Apparently in the absence of PPh_3 the ENB-ethylidene–Pd olefin complex may be an effective resting state.

4. Pre-catalyst activation

Generally, the species in *MAO-activated* Ni- or Pd-complexes and initiation steps for norbornene polymerization are not well known [1,2,3,73]. For the better defined co-catalytic system $B(C_6F_5)_3$ or $B(C_6F_5)_3/AlEt_3$ the activation process of the pre-catalyst $[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]$ was followed by multinuclear (^{1}H-, ^{13}C-, ^{19}F-, and ^{31}P-)NMR investigations and points to the formation of molecular $PdCl_2$ which may represent the active species in the polymerization process [74]. Multinuclear (^{31}P and ^{19}F) NMR investigations on $[PdCl_2(dppe)]$ and $[PdCl_2(dppp)]$ in combination with $B(C_6F_5)_3$ and $B(C_6F_5)_3/AlEt_3$ suggest the formation of $[Pd(L)]^{2+}$ cations (L = dppe, 1,2-bis(diphenylphosphino)ethane; dppp, 1,3-bis (diphenylphosphino)propane) in the activation process. $E(C_6F_5)_3$ (E = B, Al) reacts with the pre-catalysts $[MCl_2(L)]$ under abstraction of the two chloride atoms followed 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+} [75].

^{1}H-NMR and ^{19}F-NMR showed that the polynorbornene obtained in the presence of ethylene with *activator-free* (η^6-$C_6H_5CH_3$)$Ni(C_6F_5)_2$ had the end-groups $-CH{=}CH_2$ and $-C_6F_5$ [76]. The reaction of *trans*-$[Pd(C_6F_5)Br(AsRfPh_2)_2]$ (Rf = 3,5-dichloro-2,4,6-trifluorophenyl,$C_6Cl_2F_3$) and $[Pd(C_6F_5)(NCMe)(bipy)]BF_4$ with an excess of norbornene but *no cocatalyst* was monitored by ^{19}F-NMR and signals from (NB)C–C_6F_5 indicated that the polymerization process starts with the insertion of NB into the Pd–C_6F_5 bond [77,78]. From the cationic complex *trans*-$[Pd(C_6F_5)(AsRfPh_2)_2(NCMe)]BF_4$ and norbornene (NB:Pd = 10:1), the polymerization starts with the substitution of an $AsRfPh_2$ ligand *cis* to

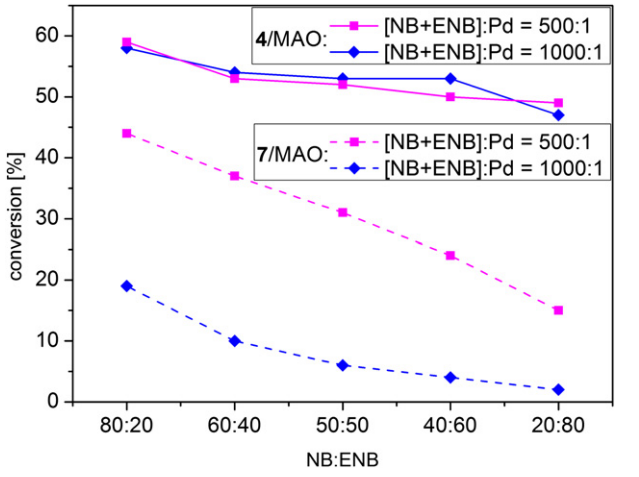


Fig. 9. Total conversion in the copolymerization of norbornene (NB) and 5-ethylidene-2-norbornene (ENB) with **4**/MAO and **7**/MAO as a function of the molar NB:ENB ratio. Conditions: NB + ENB 10.6 mmol, molar ratio Al:Pd = 100:1, temperature 22 °C, reaction time 1 h, total volume 10.0 ml; see Table S3, entries 1–10 and 11–20, respectively.

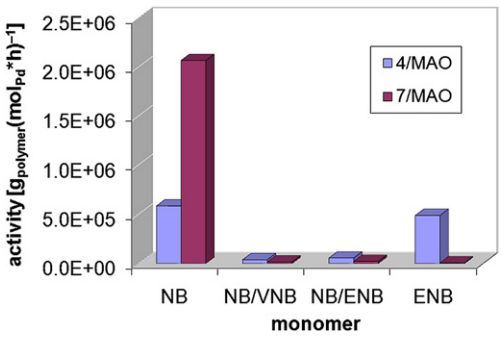


Fig. 10. Activity comparison for the different polymerization types and the catalytic systems **4**/MAO and **7**/MAO (NB:Pd ratios are 500:1); given are the maximal observed activities from Tables S1–S4. Note that some of the activity differences are due to the different polymerization times ranging from 0.5 min to 1 h.

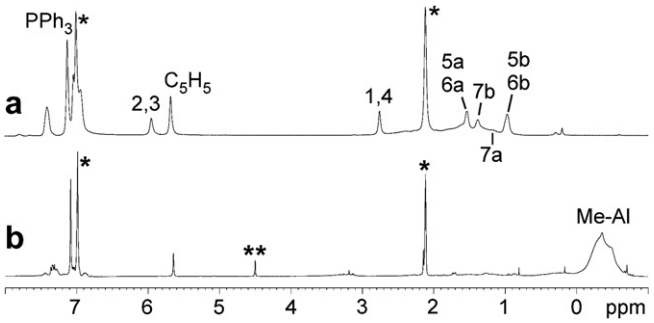


Fig. 11. ^{1}H-NMR spectrum of NB-MAO-**4** reaction mixtures with (a) the molar NB:Al:Pd ratio of 10:10:1 (*toluene-d_8), (b) the molar NB:Al:Pd ratio of 10:100:1 (toluene-d_8/CD_2Cl_2, */**). NB signals are numbered according to Scheme 6.

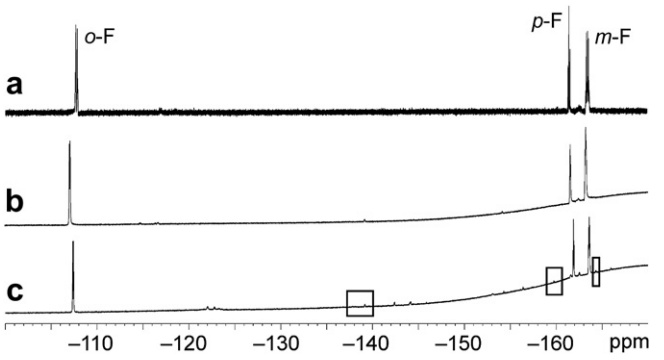


Fig. 12. ^{19}F-NMR spectrum of (a) complex **4** ($CDCl_3$), and NB-MAO-**4** reaction mixtures with (b) the molar NB:Al:Pd ratio of 10:10:1 (toluene-d_8), (c) the molar NB:Al:Pd ratio of 10:100:1 (CD_2Cl_2/toluene-d_8). Boxes mark signals assigned to C_6F_5 attached to an NB polymer chain.

the C_6F_5 group followed by insertion of norbornene into the Pd−C_6F_5 bond and the chain growth (by ^{1}H-NMR and ^{19}F-NMR) [77].

The complex (η^5-C_5H_5)Ni(CH_3)(PPh_3) reacts with B(C_6F_5)$_3$ to a structurally characterized, albeit NB-polymerization inactive, contact ion pair [(η^5-C_5H_5)Ni(PPh_3)$_2$][CH_3-B(C_6F_5)$_3$] and a ^{19}F NMR study shows the polynorbornene obtained with (η^5-C_5H_5)Ni(CH_3)(PPh_3)/B(C_6F_5)$_3$ to have the C_6F_5 end group [18]. From cationic [(tmeda)Pd(OEt_2)(CH_3)][B(ArF)$_4$] (tmeda = N,N,N′,N′-tetramethylethylenediamine, ArF = C_6H_3-3,5-(CF_3)$_2$) the propagating species and resting state [(tmeda)Pd(CH_3-(NB)$_2$)][B(ArF)$_4$] was identified by extensive NMR studies and single X-ray diffraction analysis [79].

Complex **4** was chosen for an investigation of the polymerization mechanism. Polymerization reactions were set up in 5 ml Schlenk flasks with the two different molar NB:Al:Pd ratios of 10:10:1 and 10:100:1. To a solution of **4** and NB in toluene-d_8 (for a ratio of 10:10:1) or a 1:1 mixture of CD_2Cl_2 and toluene-d_8 (for a ratio of 10:100:1) the appropriate amount of MAO (dried in high vacuum and re-dissolved in toluene-d_8) was added. After stirring for 5 min at 22 °C the reaction mixtures were transferred into NMR tubes under argon and the NMR-spectra were measured. An Al:Pd ratio of 10:1 was sufficient to create an active palladium center for norbornene polymerization. However, no quantitative monomer conversion was reached as the still present NB-olefin resonance shows (Fig. 11a, 2,3-label). The broad NB resonances in Fig. 11a are suggested due to formation of a complex [(C_5H_5)Pd(C_6F_5)(π-NB)] where NB replaces the phosphane at the palladium center in an NB-PPh_3 equilibrium according to Eq. (3). Pd−NB complexes are known [80]. Even when NB coordinates to Pd the subsequent insertion reaction into the Pd−C_6F_5 bond is known to be slow on neutral complexes [77]. For an Al:Pd ratio of 100:1 complete norbornene conversion within 5 min was achieved (Fig. 11b). Because of polymer precipitation at this ratio no broad PNB signals are observed anymore in the aliphatic region (compare Fig. 11a and b).

A comparison of the ^{19}F-NMR spectra of complex **4** (Fig. 12a) with those of an NB-MAO-**4** reaction mixture at the molar NB:Al:Pd ratios of 10:10:1 (Fig. 12b) and 10:100:1 (Fig. 12c) shows that the pentafluorophenyl ligand remains bound to the palladium atom. There are no significant shifts of the resonances for the *ortho*-, *meta*- and *para*-fluorine atoms of **4** upon MAO activation. In addition, hardly any new sets of resonances appear. A set of very small signals at the NB:Al:Pd ratio of 10:100:1 (Fig. 12c) at −139, −160 and −164 ppm can be assigned to signals for C_6F_5 attached to an NB polymer chain (cf. Fig. 14b) [77,78]. The almost unchanged ^{19}F NMR of **4** upon activation indicates that either only a very small fraction of complex molecules is activated and takes part in the polymerization with a monomer insertion into the Pd−C_6F_5 bond or that the starting monomer does not insert into the Pd−C_6F_5 bond in **4**.

Activation experiments of complex **4** and MAO at the molar Al:Pd ratios of 10:1 and 100:1, with no NB monomer present, showed a dark precipitate within a short time after MAO was added to a solution of **4**. This fine precipitate did not settle so that no NMR spectrum of this suspension could be obtained. This dark precipitate was insoluble even in DMSO-d_6 and after filtration the violet solution still gave the ^{1}H NMR of **4**.

Complex **12** was found unstable in solution after several weeks. Hence, the possibility of a norbornene polymerization without MAO as cocatalyst was investigated. At an NB:Pd ratio of 11:1, NB (32.7 mg, 3.48×10^{-1} mmol) and **12** (30 mg, 3.16×10^{-2} mmol) were irradiated with ultrasound at 50 °C in 0.8 ml of a 1:1 mixture of toluene-d_8 and CD_2Cl_2 in an NMR tube. After 6 h of ultrasonic radiation ^{1}H-NMR spectra showed still the signals of unreacted **12** and NB (Fig. 13a). The signal intensities of C_5Ph_4H and the two

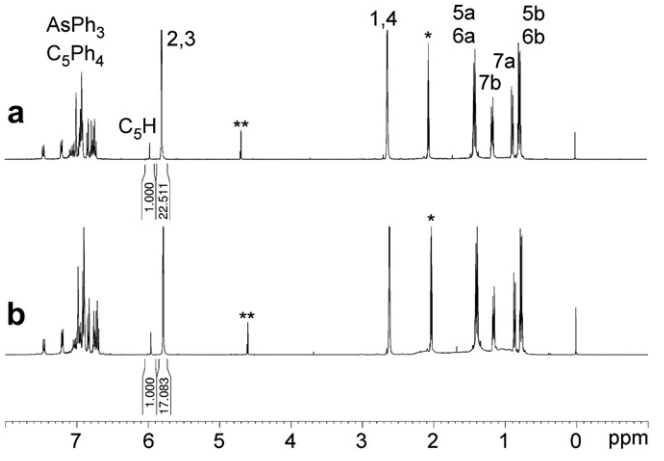
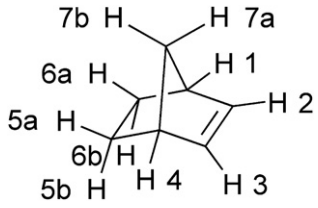


Fig. 13. ^{1}H-NMR spectrum of the reaction mixture of **12** and NB (NB:Pd 11:1) after (a) 6 h, (b) 24 h treatment with ultrasonic radiation in toluene-d_8/CD_2Cl_2 (*/**) at 50 °C. NB signals are numbered according to Scheme 6.



Scheme 6. NMR numbering for norbornene.

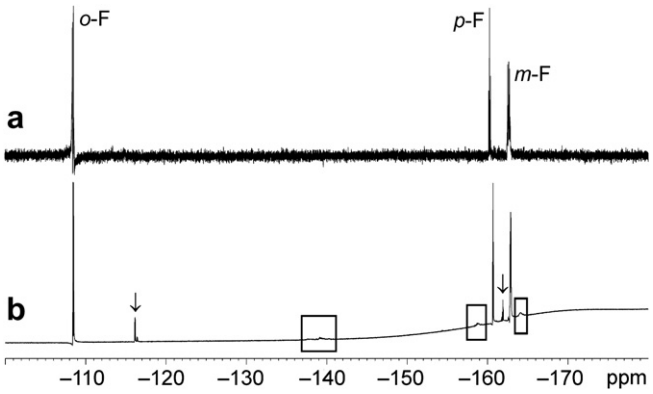


Fig. 14. ^{19}F-NMR spectrum of (a) complex **12**, (b) **12**/NB after 24 h treatment with ultrasonic radiation in toluene-d_8/CD_2Cl_2 at 50 °C. Boxes mark the resonances assigned to C_6F_5 attached to a growing polymer chain; arrows mark the resonances assigned to $[PdCl(C_6F_5)(AsPh_3)_2]$. The rising base line in (b) does not allow for a reasonable integration upfield from −150 ppm. Hence, the position of the third signal to the arrow set (below *p*-F or *m*-F of Pd-C_6F_5) could not be determined.

olefinic protons of NB are 1:22.5 (Fig. 13a) and match the starting NB:Pd ratio of 11:1. After 24 h of ultrasonic treatment a monomer conversion of around 24% is indicated by the broadened signals in the aliphatic region and a decrease in the olefinic ratio from 1:22.5 to 1:17.1 (Fig. 13b). Furthermore the tetraphenylcyclopentadienyl ligand remains bound to the palladium atom during the reaction, judged by the fact, that there is no signal shift for the proton of this substituent.

After 24 h ultrasonic irradiation the ^{19}F-NMR spectrum of **12**/NB shows the signals of **12** with the three resonances at −108.5 ($2F_o$), −160.3 ($1F_p$) and −162.6 ppm ($2F_m$) (Fig. 14a and b). In addition, a new set of broad resonances at −138 to −140 ppm, ~−158.8 and ~−164.1 ppm (marked with boxes) occurred which corresponds to C_6F_5 attached to a growing polymer chain [77,78]. This indicates the insertion of the first norbornene monomer into the Pd−C_6F_5 bond in the absence of MAO as cocatalyst. Furthermore, a second set of resonances at −116.2 to −116.4 ($2F_o$) and −161.9 ppm (marked with arrows) evolved. The intensities of the *ortho*-F signals at −108 and −116 ppm is about 5:1. This second set of resonances could be assigned to a complex $[PdCl(C_6F_5)(AsPh_3)_2]$ (akin to the decomposition product **14** from **13**) with the chlorine picked up from CD_2Cl_2 [75] under the ultrasonic conditions. The arrow-marked ^{19}F NMR resonances in Fig. 14b match those for $[PdCl(C_6F_5)(AsMePh_2)_2]$ (−116.40 F_o, −161.17 F_p, −162.91 F_m) [77].

5. Conclusions

The half-sandwich η^5-cyclopentadienylpalladium complexes $[(\eta^5\text{-}C_5H_5)Pd(C_6X_5)_2]^-$, $[(\eta^5\text{-}C_5H_5)Pd(C_6X_5)(L)]$ (X = F, Cl, L = 2-electron donor ligand), $(\eta^5\text{-}C_5Ph_4H)Pd(C_6F_5)(AsPh_3)$ and $(\eta^5\text{-}C_5Bn_5)Pd(C_6F_5)(AsPh_3)$ are air stable pseudo-trigonal compounds. $[(\eta^5\text{-}C_5H_5)Pd(C_6F_5)(L)]$ (L = PPh_3, **4** and $AsPh_3$, **7**) in the presence of MAO polymerize norbornene (NB), 5-vinyl-2-norbornene (VNB) and 5-ethylidene-2-norbornene (ENB) in a vinyl addition polymerization. The ligand L controls the activity so that **7**/MAO with the more weakly bound $AsPh_3$ is more active than **4**/MAO in the NB homopolymerization. The olefin functionality in the substituted norbornenes VNB and ENB slows down the insertion reaction in the copolymerizations with NB through the obvious formation of diolefin complexes and α-olefin insertion (VNB). Yet, the presence of PPh_3 is activity enhancing, apparently through competition for a Pd coordination site, so that **4**/MAO becomes more active than **7**/MAO in NB-VNB and −ENB copolymerization. Further, this NB-insertion directing role of PPh_3 leads to almost the same activity of **4**/MAO in NB and ENB homopolymerization.

Acknowledgment

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Appendix. Supplementary material

Supplementary material associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.08.050.

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