

# Metal Complexes for the Vinyl Addition Polymerization of Norbornene: New Compound Classes and Activation Mechanism with $B(C_6F_5)_3/AlEt_3$

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**Summary:** Classes of mainly nickel(II) and palladium(II) complexes are comparatively presented in their norbornene polymerization activity to vinyl polynorbornene when activated with methylalumoxane, MAO, tris(pentafluorophenyl)borane/triethylaluminum,  $B(C_6F_5)_3/AlEt_3$  or even  $B(C_6F_5)_3$  alone. Classes include Ni and Pd complexes with  $\alpha$ -dioxime ligands, salts with  $[PdCl_4]^{2-}$  and  $[Pd_2Cl_6]^{2-}$  units, dinuclear Ni and Pd complexes with multidentate Schiff-base ligands, polynuclear Ni- and Cr/Ni-carboxylate cage complexes, and dihalo(bisphosphane) Ni and Pd complexes. The study of activation mechanism by  $^{31}P$ - and  $^{19}F$ -NMR together with X-ray structural data points to the formation of  $PdCl_2$  units and “naked”  $Pd^{2+}$  cations as highly active species.

**Keywords:** cobalt; insertion polymerization; nickel; palladium; polynorbornene

## Introduction

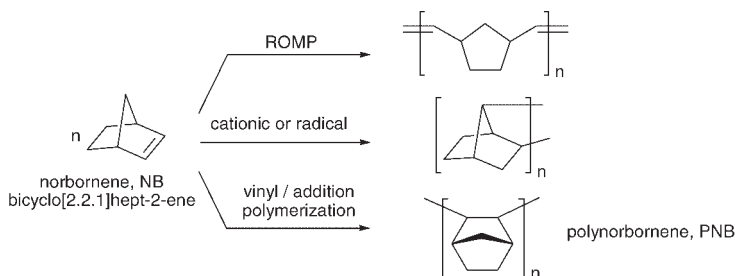
The attractive properties of cyclic olefin (co)-polymers such as low birefringence, high glass transition temperature, high optical transparency, and low moisture absorption have increased the interest in these materials over the past decade. Norbornene can be polymerized *via* ring-opening metathesis polymerization (ROMP),<sup>[1]</sup> cationic or radical polymerization<sup>[2]</sup> and by vinyl (or) addition polymerization (Scheme 1).<sup>[3]</sup> In the latter case the bicyclic structure remains intact and only the  $\pi$ -bond of the cycloolefin is opened.

Vinyl addition norbornene polymers are of interest as specialty polymer with good mechanical strength, edge and heat resistance, and optical transparency. Vinyl polynorbornenes are among auditioned

new polymeric materials as binder resins in photoresist formulations on their transparency at 193 nm to which the photolithography processes migrate in the quest for smaller features.<sup>[4,5]</sup>

Catalysts containing the metals titanium,<sup>[6]</sup> zirconium (zirconocenes),<sup>[7]</sup> chromium,<sup>[8]</sup> and the late transition-metals cobalt,<sup>[9–11]</sup> nickel,<sup>[10–18]</sup> and palladium<sup>[11,12,14,15,18–23]</sup> are described in the literature for the vinyl/addition polymerization of norbornene.<sup>[4,24]</sup> Late transition-metal complexes are commonly activated with methylalumoxane, MAO, except for the cationic palladium-complexes  $[Pd(NCR)_4]^{2+}2A^-$  (NCR weakly bound nitrile-ligand; A = “non”-coordinating anion).<sup>[12–23]</sup> The Lewis acid tris(pentafluorophenyl)borane,  $B(C_6F_5)_3$  with or without triethylaluminum,  $AlEt_3$  was recently also applied as a co-catalytic system to the activation of late transition-metal complexes for the (co)polymerization of cyclopentene,<sup>[25]</sup> ethene,<sup>[26]</sup> norbornene and norbornene derivatives.<sup>[13–16,19–22]</sup> A large number of publications within the last 5 years underscores the

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**Scheme 1.**

Modes of norbornene polymerization and different types of polynorbornene.

interest in late transition-metal catalysts for the vinyl addition polymerization of norbornene.<sup>[9–23]</sup>

Our aim is to provide air- and moisture- or shelf-stable metal complexes which can be highly activated with MAO or  $B(C_6F_5)_3/AlEt_3$  cocatalysts. Figure 1 gives an overview on the compound classes which were investigated for their norbornene (NB) polymerization activity under mostly identical conditions: room temperature; with MAO: molar ratio metal:Al:NB = 1:100:1000; metal concentration 0.0106 mmol/10 ml total volume (6 ml toluene + 4 ml  $CH_2Cl_2$ ); with  $B(C_6F_5)_3/AlEt_3$ : molar ratio metal:B:Al:NB = 1:9:10:1000; metal concentration 0.030 mmol/40 ml total volume (30 ml toluene + 10 ml  $CH_2Cl_2$ ). Each polymerization was carried out at least three times to ensure reproducibility. In the discussion we will emphasize systems with activities above  $10^7 \text{ g}_{PNB} \cdot \text{mol}_{\text{metal}}^{-1} \cdot \text{h}^{-1}$ .

#### Ni and Pd $\alpha$ -dioxime Complexes (A1–A6)

Figure 2 depicts nickel(II) and palladium(II) complexes with the  $\alpha$ -dioxime ligands dimethylglyoxime, diphenylglyoxime, and 1,2-cyclohexanedioxime which were activated with MAO or  $B(C_6F_5)_3/AlEt_3$  for the vinyl polymerization of norbornene. The Pd complexes could also be activated with  $B(C_6F_5)_3$  alone. The activity of compound **A2** is markedly higher than that of the other congeners and reaches  $3.2 \cdot 10^7 \text{ g}_{PNB}/(\text{mol}_{\text{metal}} \cdot \text{h})$  [**A2**/ $B(C_6F_5)_3/AlEt_3$ ] (Figure 1).<sup>[14]</sup> We trace this to the presence of  $PdCl_2$  which is coordinated by neutral  $\alpha$ -

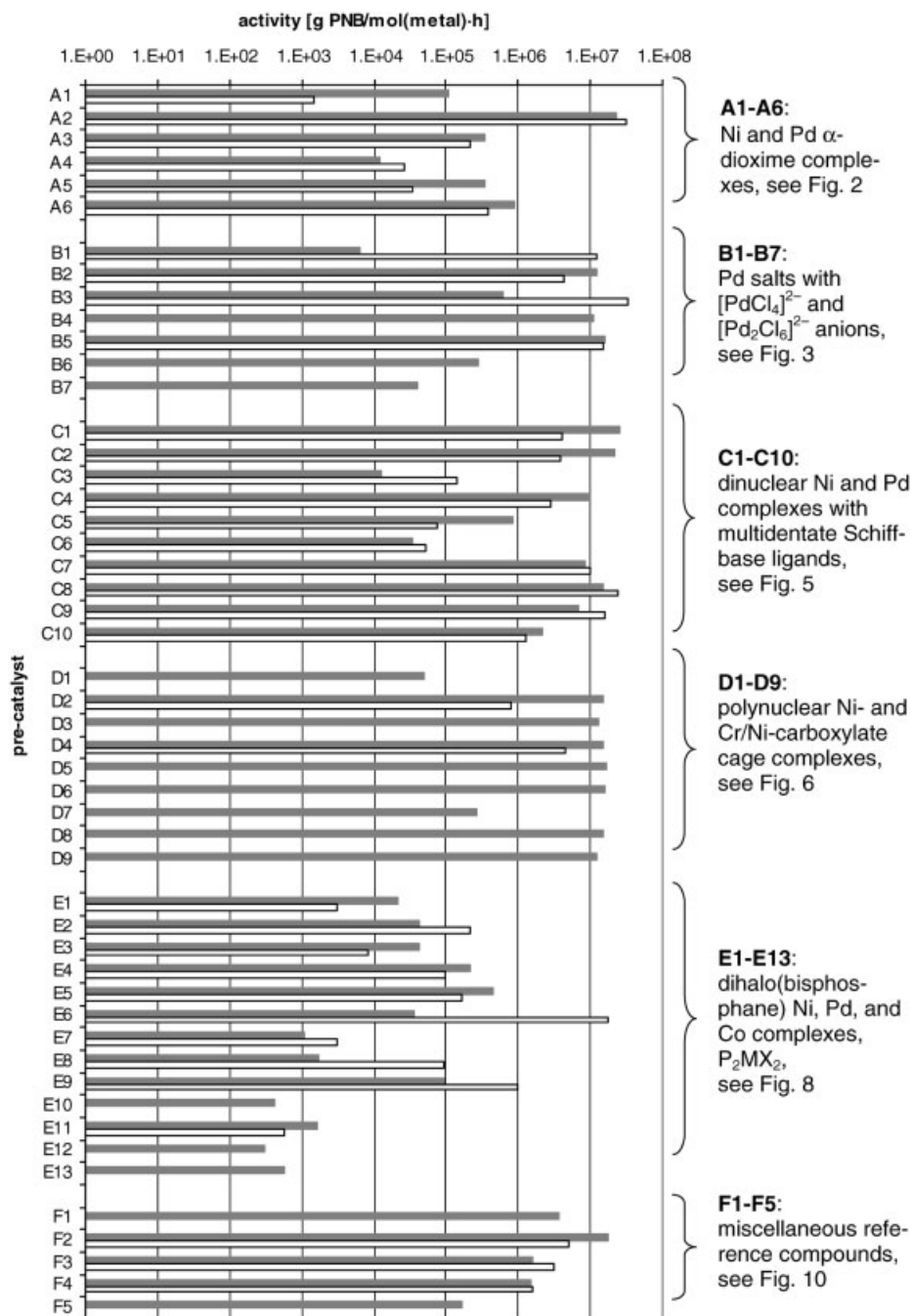
dioxime ligands, based on the formation of  $PdCl_2$  upon activation in  $[Ph_3PCH_2C(O)CH_3][Pd_2Cl_6]/B(C_6F_5)_3$  (see Figure 2).<sup>[19]</sup>

#### Pd Salts with $[PdCl_4]^{2-}$ and $[Pd_2Cl_6]^{2-}$ Anions (B1–B7)

Figure 3 illustrates palladium(II) salts containing  $[PdCl_4]^{2-}$  or  $[Pd_2Cl_6]^{2-}$  anions and the organic cations  $[K(18\text{-crown-6})]^+$ ,  $[H_3O(18\text{-crown-6})]^+$ ,  $[Ph_3PCH_2C(O)CH_3]^+$  or  $[imidazolium]^+$  which were activated with MAO or  $B(C_6F_5)_3/AlEt_3$  for norbornene polymerization. These compounds show all very high activities of over  $10^7 \text{ g}_{PNB}/(\text{mol}_{\text{metal}} \cdot \text{h})$  with MAO or  $B(C_6F_5)_3/AlEt_3$  activation (Figure 1) and proved also active with  $B(C_6F_5)_3$  alone, yielding  $10^4$ – $10^5 \text{ g}_{PNB}/(\text{mol}_{\text{metal}} \cdot \text{h})$ . The inorganic Pd(II) compounds  $PdCl_2$  and  $K_2PdCl_4$ , tested for comparison under the same conditions, were considerably less active.<sup>[19]</sup>

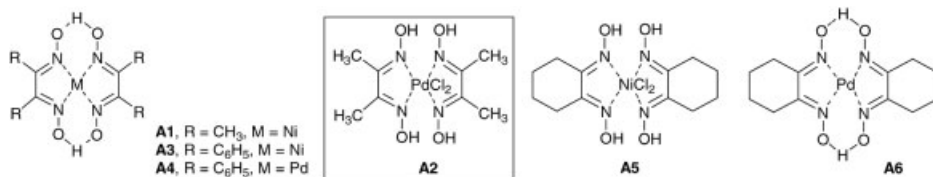
The activation process of the pre-catalyst  $[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]$  (**B5**) in combination with  $B(C_6F_5)_3$  was followed by multinuclear ( $^1H$ -,  $^{13}C$ -,  $^{19}F$ -, and  $^{31}P$ -)NMR investigations and points to the *in situ* formation of molecular  $PdCl_2$  which may represent the active species in the polymerization process (Scheme 2).<sup>[19]</sup>

The higher activity of *in situ* prepared  $PdCl_2$  from **B5** (and the other Pd salts **B1–B4**) over commercial, solid-state  $PdCl_2$  (**B6**, Figure 4) is traced to a higher solubility, larger surface area or the polymer initiation



**Figure 1.**

Compound classes used in the vinyl polymerization of norbornene to polynorbornene (PNB) and their activity. Gray bars: cocatalyst MAO, white bars:  $\text{B}(\text{C}_6\text{F}_5)_3/\text{AlEt}_3$ . Note the logarithmic activity scale.

**Figure 2.**

Ni(II) and Pd(II) complexes with  $\alpha$ -dioxime ligands; highly active **A2** is marked.

by molecular PdCl<sub>2</sub> and its stabilization by the growing polymer chain.

### Dinuclear Ni and Pd Complexes with Schiff-base Ligands (C1–C10)

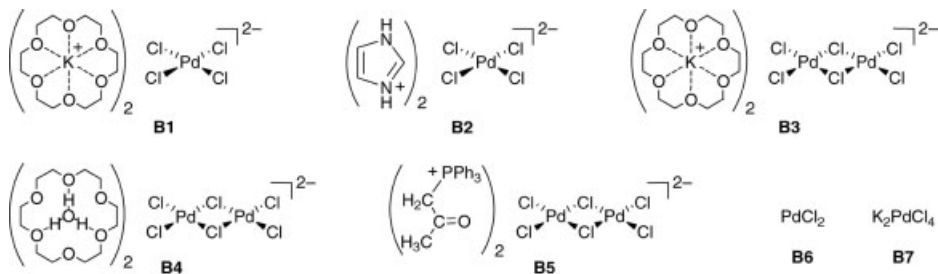
Figure 5 shows nickel(II) and palladium(II) complexes with multidentate Schiff-base ligands which were derived from salicylaldehyde condensed with 2-amino-1-alcohols or derived from 2-hydroxy-5-methylisophthaldialdehyde and pyridine-2-carboxaldehyde condensed with semicarbazide, thiosemicarbazide, carbonodihydrazide, or thiocarbonodihydrazide. The mononuclear Ni-salen complex **C3** was included for comparison.<sup>[15]</sup>

The nickel catalysts **C1**/MAO and **C2**/MAO and the palladium catalysts **C8** and **C9**, with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>, yield activities of over 10<sup>7</sup> g<sub>PNB</sub>/(mol<sub>metal</sub> · h). The systems **C4**/MAO and **C7**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> are close to the 10<sup>7</sup> g<sub>PNB</sub>/(mol<sub>metal</sub> · h) benchmark (Figure 1). So, most of the dinuclear complexes with Schiff-base ligands can become highly active in the vinyl polymerization of norbornene. The dinuclear nickel complexes **C1**, **C2** and **C4**, **C5** can reach higher activities than the mononuclear Ni complex **C3**.<sup>[15]</sup>

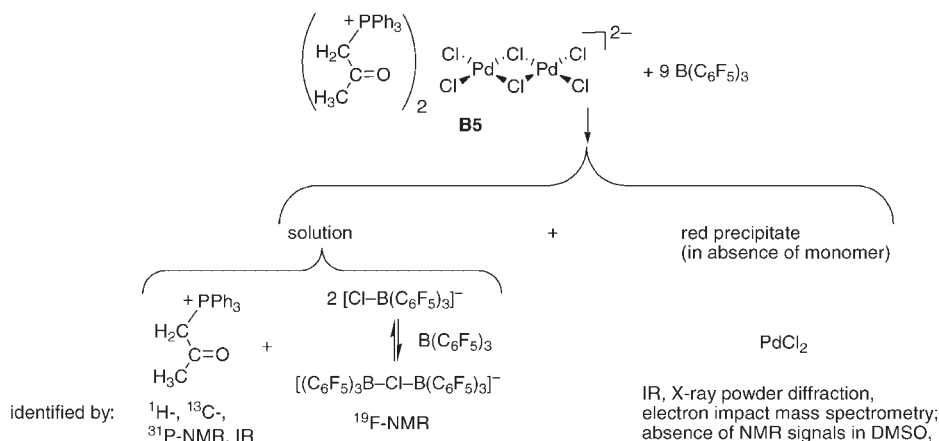
The typically high polymerization activities seen for dinuclear complexes with Schiff-base ligands (**C1–C10**) or as [Pd<sub>2</sub>Cl<sub>6</sub>]<sup>2–</sup> anions (**B3–B5**) prompted us to look specifically at polynuclear complexes to see if even higher activities may be achievable with tri-, tetra- nuclear etc. metal compounds (see Figure 6).

### Polynuclear Ni- and Cr/Ni-Carboxylate Cage Complexes (D1–D9)

Figure 6 depicts two {Cr<sub>3</sub>O} and {Cr<sub>2</sub>NiO} oxo-centred triangles (**D1**, **D2**), a series of homometallic {Ni<sub>2</sub>} and {Ni<sub>4</sub>} cages (**D3–D6**) and three {Cr<sub>7</sub>M(μ-F)<sub>8</sub>} wheels (**D7–D9**) (M = Cr<sup>III</sup>, Ni<sup>II</sup>). The homo- and heterometallic cage complexes can be activated with MAO or with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> and proved also active with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> alone. From Figure 1 and 7 nickel(II) is clearly vital for a high polymerization activity. The {Cr<sub>3</sub>O}, Ni-free triangle **D1** is much less active and also, with no nickel present, the activity of the {Cr<sub>8</sub>(μ-F)<sub>8</sub>} wheel **D7** is mediocre. Incorporation of Ni(II) in the triangle or the wheel increases

**Figure 3.**

Pd(II) complexes with [PdCl<sub>4</sub>]<sup>2–</sup> or [Pd<sub>2</sub>Cl<sub>6</sub>]<sup>2–</sup> anions and PdCl<sub>2</sub> and K<sub>2</sub>PdCl<sub>4</sub> for comparison.



### Scheme 2.

Activation process of pre-catalyst **B5** with  $\text{B}(\text{C}_6\text{F}_5)_3$ .

the activity by about two orders or magnitude (Figure 1 and 7).<sup>[16]</sup>

A comparison of the activities of **D2-D6** and **D8, D9** shows an approximately equivalent activity *per metal* of  $10^7 \text{ g}_{\text{PNB}}/(\text{mol}_{\text{metal}} \cdot \text{h})$  when at least one Ni(II) is present, regardless of whether the cage contains four Ni centers, or seven Cr and only one Ni (Figure 1 and 7). Yet the activity *per nickel* is highest in the heterometallic  $\{\text{Cr}_2\text{NiO}\}$  triangle **D2** and  $\{\text{Cr}_7\text{Ni}(\mu\text{-F})_8\}$  wheels **D8** and **D9** with

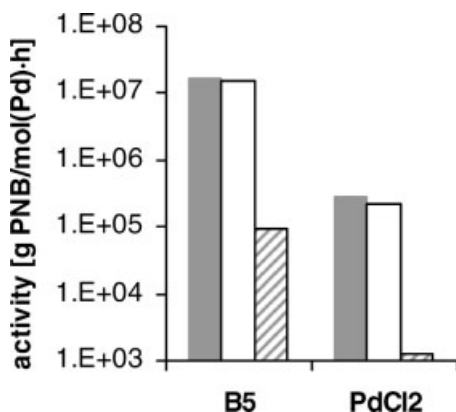


Figure 4.

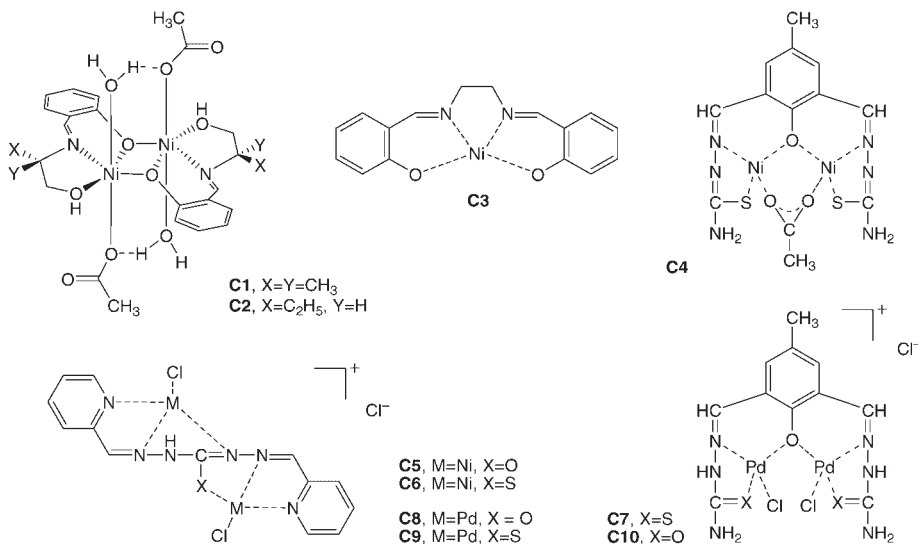
Activity comparison between **B5** and commercial  $\text{PdCl}_2$  (**B6**) in the vinyl polymerization of norbornene. Gray bars: cocatalyst MAO, white bars:  $\text{B}(\text{C}_6\text{F}_5)_3/\text{AlEt}_3$ , hatched bars:  $\text{B}(\text{C}_6\text{F}_5)_3$  alone. Note the logarithmic activity scale.

the latter two approaching  $10^8 \text{ g}_{\text{PNB}}/(\text{mol}_{\text{metal}} \cdot \text{h})$  (Figure 7). This higher activity in the heterometallic over the homometallic cages suggests that the cages retain some portion of their structure in solution. Complete decomposition would lead to similar activities *per nickel* rather than *per metal*. The activity-enhancing effect of the “inert metals” requires their close proximity to the active centers within a single compound, since a mixture of  $\text{Ni}(\text{acac})_2$  and  $\text{Cr}(\text{acac})_3$  with the molar ratio of  $\text{Ni}/\text{Cr} = 1/7$  as in the  $\{\text{Cr}_7\text{Ni}(\mu\text{-F})_8\}$  wheels was found less active than both  $\text{Ni}(\text{acac})_2$  alone and the same amount of **D8** or **D9**.<sup>[16]</sup>

Admittedly, the activity work on the Ni(II) and Pd(II) complexes with multidentate Schiff-base ligands and the polynuclear Ni- and Cr/Ni-carboxylate cage complexes was quite empirical. A more detailed characterization and understanding of the active species clearly seems desirable. In the following we present a study where such an elucidation of the active species became possible.

### Dihalo(bisphosphane) Ni, Pd, and Co Complexes, $\text{P}_2\text{MX}_2$ (E1-E13)

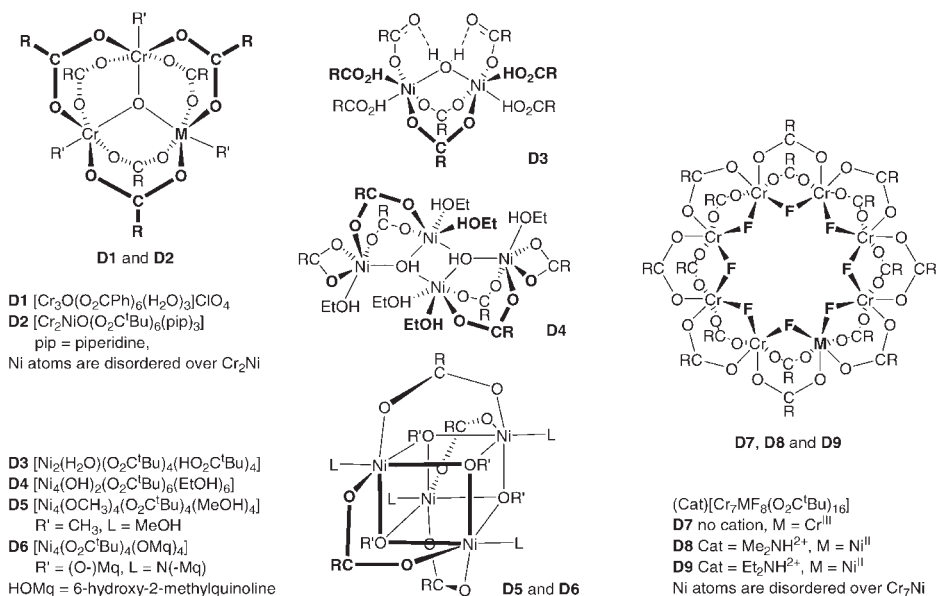
Figure 8 compiles the series of nickel(II), palladium(II) and cobalt(II) complexes of the general formula  $[\text{M}\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}\text{Cl}_2]$  with  $n=2$  to 5 and  $\text{M}=\text{Ni}, \text{Pd}, \text{Co}$ . Most of these complexes did not exhibit

**Figure 5.**

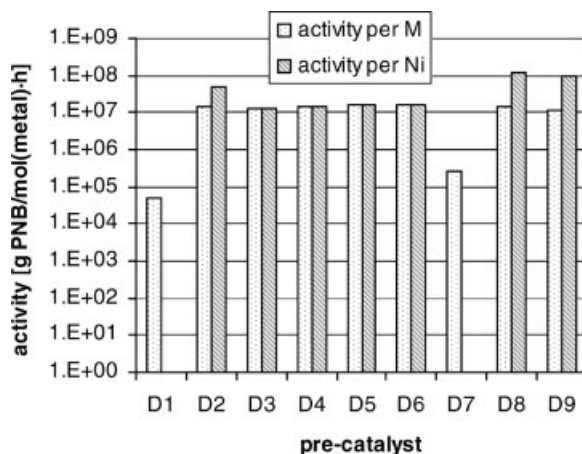
Ni(II) and Pd(II) complexes with multidentate Schiff-base ligands.

very high activities, except for compound [Pd(dppe)Cl<sub>2</sub>] (**E6**). The catalyst **E6**/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub> gave over 10<sup>7</sup> g<sub>PNB</sub>/(mol<sub>metal</sub>·h) which set it apart from the other systems by more than one order of

magnitude. So, the focus of the study quickly fell onto **E6** in comparison to the closely related compound [Pd(dppp)Cl<sub>2</sub>] (**E7**); both differ in their activity by a factor 6 × 10<sup>3</sup> when activated with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>

**Figure 6.**

Polynuclear Ni- and Cr/Ni-carboxylate cage complexes.



**Figure 7.**

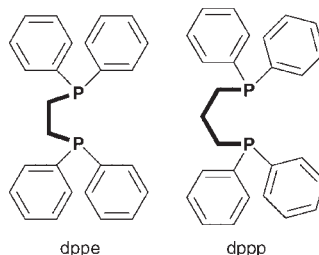
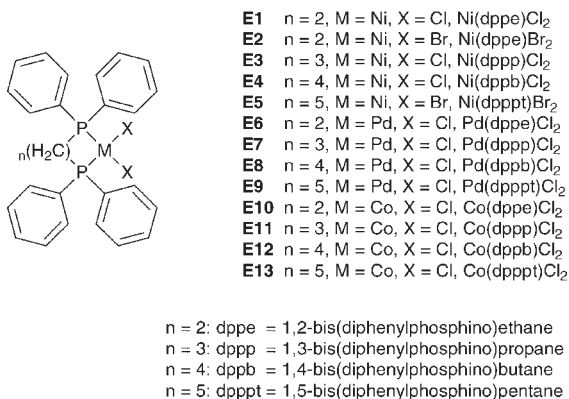
Polymerization activities for the polynuclear Ni- and Cr/Ni-carboxylate cage complexes calculated *per metal* (dotted bars) and *per nickel* (hatched bars).

(Figure 9).<sup>[20,21]</sup> For both complexes two equivalents of borane are needed to reach polymerization activity which then continues to increase somewhat with the borane ratio in combination with  $\text{AlEt}_3$ . This suggests that these two equivalents react with  $\text{AlEt}_3$  under ligand transfer and the resulting  $\text{Al-C}_6\text{F}_5$  species then abstract two ligand atoms.<sup>[21]</sup>

A combined  $^{19}\text{F}$ - and  $^{31}\text{P}$ -NMR study on the reaction of **E6** and **E7** with  $\text{B}(\text{C}_6\text{F}_5)_3$  indicated chlorine abstraction with formation of a fast equilibrium between free excess borane and chloro-borane and a second slow equilibrium to chloro-dibor-

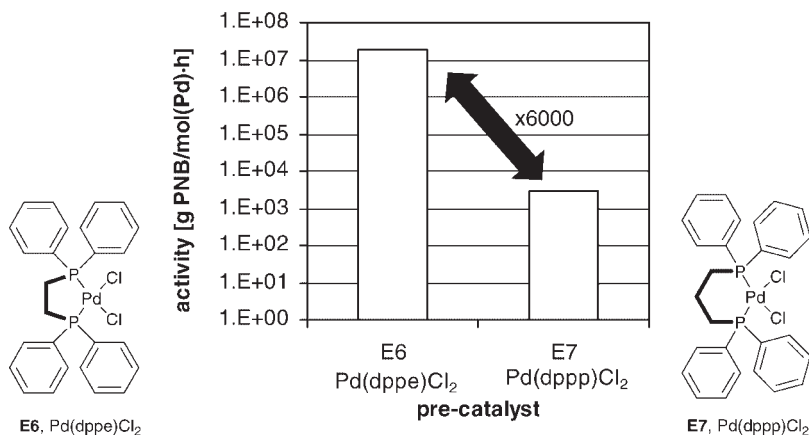
anate (Scheme 3),<sup>[21]</sup> as also seen in the activation process of pre-catalyst  $\text{Pd}_2\text{Cl}_6^{2-}$  with  $\text{B}(\text{C}_6\text{F}_5)_3$  (cf. Scheme 2).<sup>[19]</sup> Furthermore, there was no indication of a phosphane ligand abstraction from **E6** or **E7**. These salient features did not change when the NMR-study was repeated with  $\text{B}(\text{C}_6\text{F}_5)_3/\text{AlEt}_3$ . On the other hand, the NMR results did not explain the activity difference since apparently the same  $[\text{Pd}(\text{bisphosphane})]^{2+}$ -species was seen.<sup>[21]</sup>

Results from X-ray structural investigations based on single-crystal products from the reactions of **E6** and **E7** with  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{Ag}[\text{closo-1-CB}_{11}\text{H}_{12}]$ ,



**Figure 8.**

Dihalo(bisphosphane) Ni, Pd, and Co complexes.



**Figure 9.**

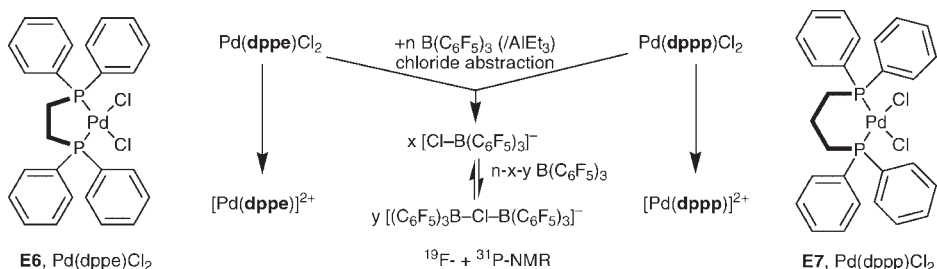
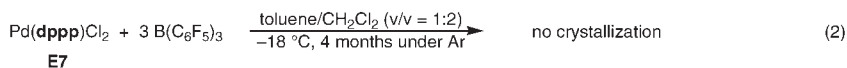
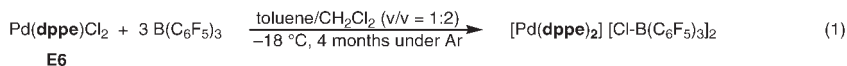
Activity comparison between **E6** and **E7** in the vinyl polymerization of norbornene, cocatalyst B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>/AlEt<sub>3</sub>.

however, revealed a different stability and solution behavior of these [Pd(phosphane)]<sup>2+</sup>-species: Reaction with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> yielded crystals only for **E6** and the product showed a Pd<sup>2+</sup>-cation with *two* dppe-bisphosphane ligands, [Pd(dppe)<sub>2</sub>]<sup>2+</sup> (eq. 1 and 2).

In order to obtain crystalline products based on **E7**, the chloride abstraction was carried out with the silver salt of the monocarba-*closo*-dodecaborane(12) anion,

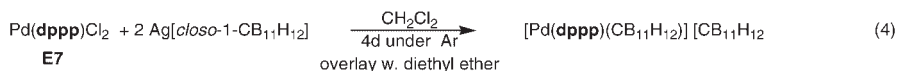
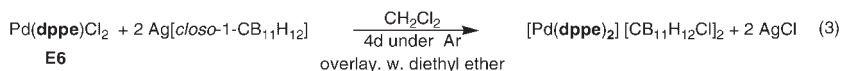
Ag[*closo*-1-CB<sub>11</sub>H<sub>12</sub>]. Crystals from **E6** again showed the Pd<sup>2+</sup>-cation with two dppe ligands, [Pd(dppe)<sub>2</sub>]<sup>2+</sup> (eq. 3), while crystals from **E7** contained the expected Pd<sup>2+</sup>-cation with a *single* dppp ligand, [Pd(dppp)]<sup>2+</sup> (eq. 4). The [Pd(dppp)]<sup>2+</sup>-cation is stabilized by B–H-coordination from a dodecaborane anion to fill the coordination sphere of the metal ion.

The X-ray crystallographic results support the notion of chloride abstraction and

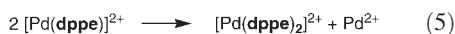


**Scheme 3.**

Part of the activation process of pre-catalyst **E6** and **E7** with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.



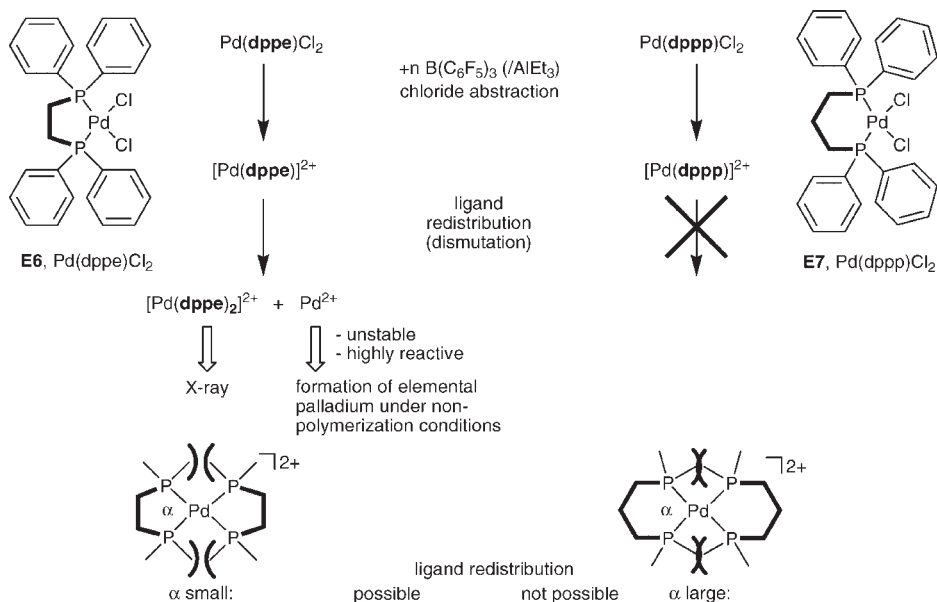
formation of  $[\text{Pd}(\text{bisphosphane})]^{2+}$ -species from the above NMR data. Yet, with diphenylbis(phosphino)ethane, dppe as a ligand, the  $[\text{Pd}(\text{bisphosphane})]^{2+}$ -cation obviously is unstable with respect to a ligand redistribution (dismutation) reaction which yields a bis-dppe cation,  $[\text{Pd}(\text{dppe})_2]^{2+}$  together with an un-ligated  $\text{Pd}^{2+}$ -ion (eq. 5).



The formation of an un-ligated  $\text{Pd}^{2+}$ -cation, which can be expected to be highly unstable, is supported by the formation of elemental palladium under non-polymerization conditions. There is no evidence that the cation from **E7**,  $[\text{Pd}(\text{dppp})]^{2+}$  can enter in a similar ligand redistribution reaction.<sup>[21]</sup> Hence, we trace the activity

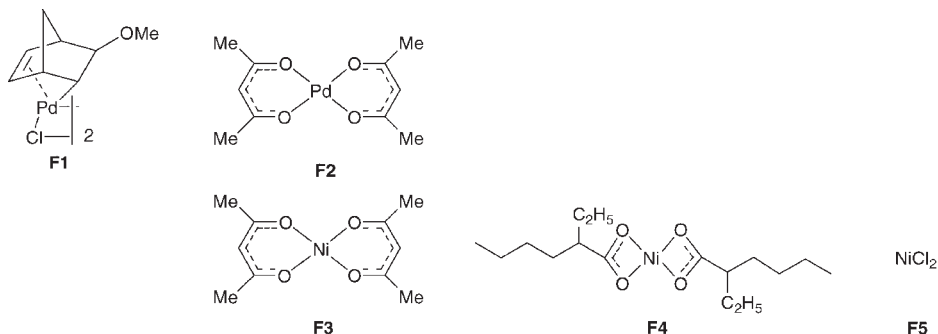
difference to the formation of a highly reactive “naked”  $\text{Pd}^{2+}$ -cation in the case of **E6** and the absence of the same for **E7** (Scheme 4). The  $[\text{Pd}(\text{bisphosphane})]^{2+}$ -cations themselves are apparently only of mediocre activity in the addition-polymerization of norbornene.

The ligand redistribution with dppe in the case of **E6** and the absence of this dismutation reaction with dppp for **E7** can be explained with steric arguments due to the different bite angle and chelate ring size which results in a different steric demand of the chelate ligands around the metal. The features of the dppe ligand allow for the formation of two five membered  $\text{Pd}(\text{dppe})$ -rings around a square-planar  $\text{Pd}^{2+}$ -ion center. With the dppp ligand two six-membered  $\text{Pd}(\text{dppp})$ -rings in a square-planar geometry are not possible (and have



**Scheme 4.**

Activation process of pre-catalyst **E6** and **E7** with  $\text{B}(\text{C}_6\text{F}_5)_3$  or  $\text{B}(\text{C}_6\text{F}_5)_3/\text{AlEt}_3$  and the possibility of ligand redistribution for dppe and dppp ligands.



**Figure 10.**

Reference compounds. **F1** = di- $\mu$ -chloro-bis(6-methoxybicyclo[2.2.1]hept-2-ene-5 $\sigma$ ,2 $\pi$ )-dipalladium(II), **F2** and **F3** = palladium and nickel bis(acetylacetonate), M(acac)<sub>2</sub>, **F4** = nickel-bis(2-ethylhexanoate), **F5** = nickel(II) chloride (anhydrous).

not been structurally authenticated in the literature) because of inter-ligand repulsion between the sterically demanding phenyl groups.<sup>[21]</sup>

### Reference Compounds (F1–F5)

The compounds depicted in Figure 10 have been used at various points to reference and scale our activity data to the literature, to check for reproducibility when new charges of solvent or cocatalysts were used, to study concentration effects of MAO, Pd and Ni pre-catalyst and monomer in the vinyl polymerization of norbornene<sup>[12]</sup> or to introduce borane activators for norbornene polymerization.<sup>[12]</sup>

### Conclusions

Our studies on the activation mechanism of late transition metal complexes in the vinyl addition polymerization of norbornene suggest that high activation requires fast and substantial, if not complete ligand abstraction. Yet, weakly bound ligands, which are easily lost, are contradictory to the aimed for shelf-stable complexes. Hence, a careful ligand design should try to combine air- and moisture stability with a high ligand lability towards abstraction by appropriate Lewis-acid cocatalysts such as methylalumoxane, MAO, aluminum alkyls or boranes and mixtures thereof. Our future research in this area will also address questions that still need to be satisfactorily answered, such as, the aspect of metal-

ligand start species for the first olefin insertion, possible chain transfer mechanism and the polymer microstructure of insoluble polynorbornene products.

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