Dinuclear Nickel(II) and Palladium(II) Complexes in Combination with Different Co-Catalysts as Highly Active Catalysts for the Vinyl/Addition Polymerization of Norbornene

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Z. Naturforsch. **58b,** 1152 – 1164 (2003); received September 30, 2003

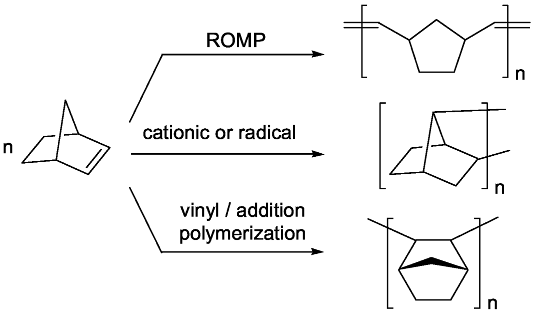
Dinuclear nickel(II) and palladium(II) complexes with Schiff-base ligands (derived form salicylaldehyde condensed with 2-amino-1-alcohols or from 2-hydroxy-5-methylisophthaldialdehyde and pyridine-2-carboxaldehyde condensed with semicarbazide, thiosemicarbazide, carbonodihydrazide, or thiocarbonodihydrazide) can be activated with the co-catalysts methylalumoxane (MAO) or tris(pentafluorophenyl)borane/triethylaluminium, $B(C_6F_5)_3/AlEt_3$ for the vinyl/addition polymerization of norbornene to reach activities of up to $2.4 \cdot 10^7$ $g_{polymer}$/mol(metal)·h (molar ratios metal:$Al_{MAO} = 1{:}100$, metal:borane:$AlEt_3 = 1{:}9{:}10$). Polymer characterization by GPC gave molar mass distributions of $M_w/M_n \approx 2$, thereby indicating a coordination polymerization with a single-site character of the active species.

Key words: Polymerization, Norbornene, Nickel, Palladium, Co-Catalyst

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. Particularly the homopolymer of norbornene (bicyclo[2.2.1]hept-2-ene) is of interest as a specialty polymer with good mechanical strength, heat resistance, and optical transparency, *e.g.* for deep ultraviolet photoresists, interlevel dielectrics in microelectronics applications or as cover layer for liquid-crystal displays [1, 2]. Norbornene can be polymerized *via* ring-opening metathesis polymerization (ROMP) [3 – 5], cationic or radical polymerization [6] and by vinyl or addition polymerization [7] (Scheme 1). In the latter case the bicyclic structure remains intact and only the π-bond of the cycloolefin is opened.

Catalysts containing the metals titanium [8, 9], zirconium [10 – 14], chromium [15], and currently the late transition-metals cobalt [16 – 18], nickel [19 – 33], and palladium [31, 34 – 51] are described in the literature for the vinyl/addition polymerization of norbornene [1, 29, 52 – 57]. The late transition-metal complexes are commonly activated with methylalumoxane (MAO) [20 – 23, 36], except for the cationic palladium-complexes $[Pd(NCR)_4]^{2+}2A^-$ (NCR weakly bound nitrile-ligand; A = “non”-coordinating counter ion) [37 – 47]. Another co-catalytic system for the activation of metal complexes is the organo-Lewis acid tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ with or without triethylaluminum ($AlEt_3$). This co-catalytic system is applied for the activation of transition-



Scheme 1. Modes of norbornene polymerization and different types of poly(norbornene).

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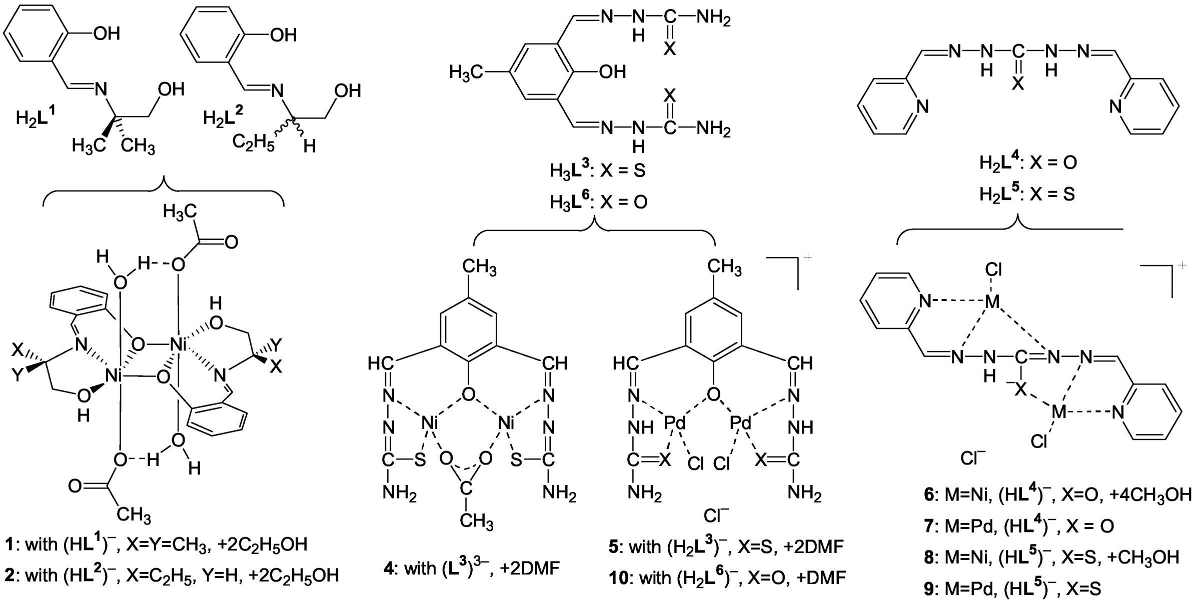


Scheme 2. Nickel(II) and palladium(II) complexes employed in the vinyl polymerization of norbornene (DMF = dimethyl formamide).

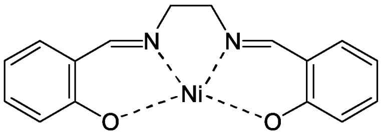
metal group 4 metallocene catalysts in olefin polymerization [58–66] and was recently also applied to the activation of late transition-metal complexes for the (co)polymerization of cyclopentene [67], ethene [68], norbornene and norbornene derivatives [19, 29, 33, 34, 50–57].

During our work, we became aware that only singular examples of homodinuclear Ni^{II}-, Pd^{II}-, Co^{II}- and Cr^{III}-complexes [15, 18, 22, 24, 69] were investigated. Thus, we present here the first polymerization results of a series of homodinuclear nickel(II) and palladium(II) complexes **1** to **10** with Schiff-base ligands derived from different (di)-aldehydes condensed with 2-amino-1-alcohols or with (thio)-semicarbazide and (thio)-carbonodihydrazide (Scheme 2) which can be activated with MAO, $B(C_6F_5)_3$, or a combination of both $B(C_6F_5)_3/AlEt_3$. The Ni(salen)-complex **3** is included as a mononuclear reference system.

Experimental Section

General procedures

All work involving air- and/or moisture-sensitive compounds was carried out by using standard vacuum, Schlenk or drybox techniques. IR spectra (KBr pellet) were measured on a Bruker Optik IFS 25. NMR spectra were recorded with a Bruker AXS 200 at 300 K and 200 MHz (^1H NMR).



3

The NMR spectra for compound 1,2-bis-(2-hydroxo-benzylamino)-ethane-nickel(II) (**3**) were recorded with a Varian O-300 at 300 K and 300 MHz (^1H NMR). ^1H NMR spectra were calibrated against the solvent signal (CD_2Cl_2 5.32 ppm, DMSO-d_6 2.53 ppm). Elemental analyses were obtained on a VarioEL from Elementaranalysensysteme GmbH. ESI-MS measurements for **1**, **2** and **6** were carried out using a Thermo Finnigan LCQ Advantage spectrometer with methanol as the solvent. A pre-injector column contained impurities of trifluoroacetic acid (CF_3COOH, M = 114). Mass spectra were measured in positive mode in the range $m/z = 200-1200$. Nickel containing ions had a clearly visible metal isotope pattern, arising from the distribution: ^{58}Ni 100%, ^{60}Ni 38.2%, ^{61}Ni 1.6%, ^{62}Ni 5.3%, ^{64}Ni 1.3% [70]. Peaks were given for the most abundant combinations of the nickel isotopes. For Ni_2-containing ions the most intense peak stems from $^{58}Ni_2$ (100%) with $^{58}Ni^{60}Ni$ of ∼ 80% relative intensity. For Ni_3 the most abundant combinations have $^{58}Ni_2{}^{60}Ni$, followed by $^{58}Ni_3$ (∼ 80%), $^{58}Ni^{60}Ni_2$ (∼ 50%) etc. For Ni_4 the species with $^{58}Ni_3{}^{60}Ni$ is most intense followed by $^{58}Ni_2{}^{60}Ni_2$ (∼ 80%), $^{58}Ni_4$ (∼ 60%) etc. Gel permeation chromatography (GPC) analyses were performed on

Table 1. Crystal data for the nickel complexes **1** and **6**.

Compound	**1**	**6**
Formula	$C_{30}H_{50}N_2Ni_2O_{12}$	$C_{17}H_{27}Cl_3N_6Ni_2O_5$
M	748.14	619.22
Crystal size/mm	$0.40 \times 0.40 \times 0.38$	$0.40 \times 0.17 \times 0.15$
T/K	173(2)	216(2)
θ range/°	2.15 – 30.88	2.63 – 29.08
h; k; l range	-12, 12; -20, 12; -18, 18	-10, 10; -15, 15; -20, 20
Crystal system	monoclinic	triclinic
Space group	$P2(1)/c$	$P-1$
a/Å	9.4712(11)	7.8109(15)
b/Å	14.0363(16)	11.544(2)
c/Å	13.3882(15)	15.260(3)
α/°	90.00	68.993(3)
β/°	105.772(2)	89.350(3)
γ/°	90.00	82.466(3)
V/Å^3	1712.8(3)	1272.4(4)
Z	2	2
D/g cm^{-3}	1.451	1.616
μ/mm^{-1}	1.161	1.834
$F(000)$	792	636
Measured refl.	13820	11693
Unique refl. (R_{int})	4951 (0.0242)	6062 (0.0903)
Obs. refl. $[I > 2\sigma(I)]$	4211	5001
Parameters refined	308	302
Max/min $\Delta\rho$/e Å^{-3}[a]	0.361; -0.516	0.730; 0.7718
$R1/wR2[I > 2\sigma(I)]$[b]	0.0265; 0.0661	0.0376; 0.0920
$R1/wR2$ (all data)[b]	0.0340; 0.0691	0.0466; 0.0996
GOF on F^2[c]	1.045	1.070
Weight. scheme w; a/b[d]	0.0354 / 0.3797	0.0348 / 0.3626

[a] Largest difference peak and hole; [b] $R1 = [\Sigma(\|F_o| - |F_c\|)/\Sigma|F_o|]$; $wR2 = [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]]^{1/2}$; [c] Goodness-of-fit $= [\Sigma[w(F_o{}^2 - F_c{}^2)^2]/(\mathrm{n} - \mathrm{p})]^{1/2}$; [d] $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$ where $P = (\max(F_o{}^2 \text{ or } 0) + 2F_c{}^2)/3$.

a PL-GPC 220 (columns PL gel 10 μm MIXED-B) with polymer solutions in 1,2,4-trichlorobenzene (concentration of 2 – 3 mg/ml). The GPC was measured at 140 °C with an injection volume of 200 μl and with a rate of 1 ml/min.

X-ray crystallography

Diffraction data were collected by the ω-scan method with Mo-K_α radiation ($\lambda = 0.71073$ Å) and the use of a graphite monochromator on a Bruker Smart CCD. Data collection and cell refinement with SMART [71], data reduction with SAINT [71]. An experimental absorption correction was performed with SADABS [72]. Structure Analysis and Refinement: The structures were solved by direct methods (SIR97 for **1**, SHELXS-97 for **6**) [73, 74]; refinement was done by full-matrix least squares on F^2 using the SHELXL-97 program suite [74]. All non-hydrogen positions were found and refined with anisotropic temperature factors. The hydrogen atoms in **1** were found from the difference Fourier map and refined isotropically with free temperature factors. The hydrogen atoms in **6** were placed at calculated positions, using appropriate riding models (HFIX 43 for aromatic and methine CH and NH, HFIX 33 for CH_3, HFIX 83 for OH) and isotropic temperature factors of $U(H) = 1.2\ U_{eq}$(CH and NH) or U(H) = 1.5 $U_{eq}(CH_3)$. The temperature factor for (O)H was free to refine. Details of the X-ray structure determinations and refinements are provided in Table 1. Graphics were obtained with ORTEP 3 for Windows [75]. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. The structural data has been deposited with the Cambridge Crystallographic Data Center (No. CCDC-223113 for **1** and CCDC-223114 for **6**).

Materials

Salicylaldehyde (Aldrich), 2-amino-2-methyl-1-propanol (Aldrich), 2-amino-1-butanol (Aldrich), 1,2-diaminoethane (Aldrich), 2-hydroxy-5-methylisophthaldialdehyde (Aldrich), thiosemicarbazide (Aldrich), pyridine-2-carboxaldehyde (Aldrich), carbonodihydrazide (Aldrich), thiocarbonodihydrazide (Aldrich), semicarbazide hydrochloride (Aldrich), sodium carbonate (Riedel-de Haën), nickel(II) acetylacetonate (Merck), nickel(II) acetate tetrahydrate (Aldrich), nickel(II) chloride hexahydrate (Acros), palladium(II) chloride (Merck-Schuchardt), methylalumoxane (10 wt.-% solution in toluene, Witco), tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, Aldrich), and triethylaluminum ($AlEt_3$, 1 mol/l solution in hexane, Merck-Schuchardt) were used as received. Toluene was dried over sodium metal, distilled and stored under nitrogen. Methylene chloride was dried over CaH_2. Norbornene (Aldrich) was purified by distillation and used as a solution in toluene. 1,2-bis(2-hydroxo-benzylamino)-ethane [76], 2,3-bis-thiosemicarbazide-4-methylphenol ($H_3\mathbf{L^3}$) [77], diacetonitrile-palladium(II)-chloride [78], 1,5-bis(2-pyridylmethylene)-thiocarbonohydrazide ($H_2\mathbf{L^5}$) [79] were synthesized by the published literature procedures.

Preparation of the pre-catalysts

[Bis{mer-2-(N-(2-oxobenzylide)amino)-2-methyl-1-propanol-N, O,O'}-di(acetato)-di(aqua)-nickel(II)]-di(ethanol) (**1** = $[\{Ni(H\mathbf{L^1})(CH_3CO_2)H_2O\}_2]\cdot 2Et\ OH$): 2-Amino-2-methyl-1-propanol (10.0 mmol) was added to a methanolic solution (30 ml) of salicylaldehyde (10.0 mmol). The resulting yellow solution was refluxed for 30 min. Nickel(II) acetate tetrahydrate (10.0 mmol) was added to this solution which turned green with stirring for 30 min at 60 °C. Well-shaped, green crystals suitable for X-ray study were obtained by slow evaporation of the solvent from the mother liquor. Yield 3.51 g (4.71 mmol, 94.1%). $C_{30}H_{50}N_2Ni_2O_{12}$ (748.11): calcd. C 48.17, H 6.74, N 3.74; found C 47.96, H 6.60, N 3.64. IR: 3271s, 2972w, 2928w, 2873w, 2639w,

1642s, 1600m, 1545s, 1478w, 1445m, 1406w, 1335w, 1304m, 1274w, 1239w, 1169s, 1127w, 1091m, 1053s, 990w, 945w, 914m, 896w, 879w, 859w, 810w, 780w, 758s, 670m, 623w, 590w, 565m. ESI-MS: 250 $[\mathrm{Ni(H\mathbf{L}^1)}]^+$ (9%), 268 $[\mathrm{Ni(H\mathbf{L}^1)+H_2O}]^+$ (21), 282 $[\mathrm{Ni(H\mathbf{L}^1)+CH_3OH}]^+$ (82), 499 $[\mathrm{Ni_2(H\mathbf{L}^1)\ (\mathbf{L}^1)}]^+$ (100), 750 $[\mathrm{Ni_3(H\mathbf{L}^1)\ (\mathbf{L}^1)_2}]^+$ (98), 999 $[\mathrm{Ni_4(H\mathbf{L}^1)(\mathbf{L}^1)_4}]^+$ (20). m. p.: > 200 °C.

[Bis{mer-2-(N-(2-oxobenzylidene)amino)-1-butanol-N,O,O'}-di(acetato)-di(aqua)-nickel(II)]-di(ethanol) (**2** = $[\{\mathrm{Ni(H\mathbf{L}^2)(CH_3CO_2)H_2O}\}_2]\cdot$2Et OH): 2-Amino-1-butanol (10.0 mmol) was added to a methanolic solution (30 ml) of salicylaldehyde (10.0 mmol). The resulting yellow solution was refluxed for 30 min. Nickel(II) acetate tetrahydrate (10.0 mmol) was added to this solution which turned green with stirring for 30 min at 60 °C. Well-shaped, green crystals were obtained by slow evaporation of the solvent from the mother liquor. Yield 3.38 g (4.52 mmol, 90.4%). $\mathrm{C_{30}H_{50}N_2Ni_2O_{12}}$ (748.11): calcd. C 48.17, H 6.74, N 3.74; found C 47.92, H 7.04, N 3.63. IR: 3269w, 2958m, 2878w, 1645s, 1600m, 1546m, 1475s, 1447m, 1339w, 1308m, 1227w, 1195m, 1159m, 1130w, 1115m, 1089w, 1046s, 978w, 943m, 906m, 880w, 860w, 842w, 756s, 668m, 585m, 507m. ESI-MS is identical to that of **1**, since $M(\mathbf{L}^2) = M(\mathbf{L}^1)$. m. p.: > 200 °C.

[1,2-Bis(2-hydroxo-benzylamino)ethane-nickel(II)] (**3**): A hot methanolic solution (100 ml) of 1,2-bis(2-hydroxobenzylamino)ethane (10.0 mmol) was added to a hot methanolic solution (60 ml) solution of nickel(II) acetylacetonate (10.0 mmol). The resulting red-brown suspension was stirred for 60 min at r.t., filtered, and dried *in vacuo*. Yield 3.13 g (9.63 mmol, 96.3%). The compound was recrystallized from toluene. $\mathrm{C_{16}H_{14}N_2NiO_2}$ (324.99): calcd. C 59.13, H 4.34, N 8.62; found C 59.94, H 4.98, N 8.51. IR: 3023w, 2358w, 1623s, 1600m, 1536s, 1451s, 1385w, 1348m, 1317w, 1201m, 1146w, 1128m, 1090w, 1026w, 950w, 905m, 848w, 802w, 734m, 667w, 632w, 600w. ^{1}H NMR ($\mathrm{CD_2Cl_2}$): δ 3.32 (s, 4H, =N-$\mathrm{CH_2}$-$\mathrm{CH_2}$-N=), 6.4-7.2 (m, 8H, aromatic H-atoms), 7.35 (s, 2H, C-CH=N-). m.p.: > 200 °C.

[(2,6-Bis-thiosemicarbazide-4-methylphenolato-N,O,S)-acetato-di{nickel(II)}]-bis(dimethylformamide) (**4** = $[\mathrm{Ni_2(\mathbf{L}^3)(CH_3CO_2)}]\cdot$2DMF): A hot solution of the ligand $\mathrm{H_3\mathbf{L}^3}$ (0.5 mmol) in DMF (20 ml) and methanol (20 ml) was added to a hot solution of nickel(II) acetate tetrahydrate (1.0 mmol) in DMF (15 ml) and methanol (10 ml). The deep brown solution was quickly filtered and allowed to cool to r.t. when the black product precipitated. The product was filtered, washed with cold DMF, and dried *in vacuo*. Yield 0.268 g (0.424 mmol, 84.8%). $\mathrm{C_{19}H_{28}N_8Ni_2O_5S_2}$ (629.99): calcd. C 36.22, H 4.48, N 17.79, S 10.18; found C 36.24, H 5.25, N 19.09, S 10.02. IR: 3311w, 3123w, 2911w, 2806w, 1650s, 1557w, 1504s, 1459w, 1407w, 1382w, 1330m, 1254w, 1233w, 1147m, 1074w, 993w, 931w, 854w, 756w, 688w, 662w, 625m, 537w. m.p.: > 200 °C.

[(2,6-Bis-thiosemicarbazide-4-methylphenolato-N,O,S)-dichloro-di{palladium(II)}]-bis(dimethylformamide) (**5** = $[\mathrm{Pd_2(H_2\mathbf{L}^3)Cl_2}]\mathrm{Cl}\cdot$DMF): A hot solution of the ligand $\mathrm{H_3\mathbf{L}^3}$ (0.5 mmol) in DMF (20 ml) and methanol (20 ml) was added to a hot solution of di(acetonitrile)palladium(II) chloride (1.0 mmol) in DMF (15 ml) and methanol (10 ml). The deep brown solution was quickly filtered and allowed to cool to r.t. when the deep brown product precipitated. The product was filtered, washed with cold DMF, and dried *in vacuo*. Yield 0.295 g (0.399 mmol, 79.8%). $\mathrm{C_{17}H_{27}Cl_2N_8O_3Pd_2S_2}$ (739.33): calcd. C 27.62, H 3.68, N 15.16, S 8.67; found C 25.76, H 3.15, N 14.96, S 8.47. IR: 3279w, 3105s, 2859w, 1646s, 1627w, 1549w, 1504m, 1446w, 1380w, 1331w, 1236w, 1161w, 1095w, 1043w, 1002w, 837w, 799w, 746w, 723w, 676m, 613w, 546w, 520w. m.p.: > 200 °C.

1,5-Bis(2-pyridylmethylene)carbonohydrazide ($\mathrm{H_2\mathbf{L}^4}$): Pyridine-2-carboxaldehyde (20.0 mmol) was added dropwise to a hot solution of carbonodihydrazide (10.0 mmol) in methanol (30 ml) and refluxed for 1 h. The solvent was removed, the residue stirred for 30 min in diethyl ether (30 ml), filtered, and dried *in vacuo*. The compound was recrystallized from DMF:$\mathrm{H_2O}$ (1:7). Yield 1.76 g (6.56 mmol, 65.6%). $\mathrm{C_{13}H_{12}N_6O}$ (268.28): calcd. C 58.20, H 4.51, N 31.33; found C 53.55, H 4.88, N 29.32. IR: 3199m, 1685s, 1610m, 1586w, 1536s, 1471m, 1433m, 1361m, 1312w, 1284m, 1234w, 1136s, 1090w, 1016w, 998w, 937m, 893w, 774m, 743w, 584w, 522w. ^{1}H NMR (DMSO-$\mathrm{d_6}$): δ7.3 – 8.6 (m, 8H, aromatic H-atoms), 8.26 (s, 2H, C-CH=N-), 10.93 (s, 2H, =N-NH-C(O)). m. p.: 191 – 193 °C.

[(1,5-Bis(2-pyridylmethylene)carbonohydrazide-N,N',N"',N"",N""',O)-dichloro-tetra(methanol)-di{nickel(II)}]-chloride (**6** = $[\mathrm{Ni_2(H\mathbf{L}^4)Cl_2(CH_3OH)_4}]$ Cl): A methanolic solution (20 ml) of nickel(II) acetate tetrahydrate (2.0 mmol) was added dropwise to a solution of $\mathrm{H_2\mathbf{L}^4}$ (1.0 mmol) in methanol (20 ml) and refluxed for 30 min. The solution was allowed to cool to room temperature and diethyl ether was condensed slowly onto the reaction mixture over a period of several days resulting in a green, microcrystalline precipitate which contained crystals suitable for X-ray studies. The green precipitate was filtered, washed with diethyl ether and dried *in vacuo* whereby the color changed from green to brown. Yield 0.373 g (0.713 mmol, 71.3%). $\mathrm{C_{14}H_{15}Cl_3N_6Ni_2O_2}$ (523.05): calcd. C 32.15, H 2.89, N 16.07; found C 30.87, H 3.27, N 16.20. IR: 3198s, 3019w, 1592s, 1485m, 1458m, 1440w, 1371s, 1342w, 1298w, 1272m, 1224m, 1150s, 1100w, 1013w, 937w, 881w, 776m, 751w, 605w, 527w. ESI-MS: 325 $[\mathrm{Ni(H\mathbf{L}^4)}]^+$ (3%), 495 $[\mathrm{Ni_2(\mathbf{L}^4)TFA}]^+$ (100), 609 $[\mathrm{Ni_2(\mathbf{L}^4)TFA(TFAH)}]^+$ (19), 743 $[[\mathrm{Ni_3(\mathbf{L}^4)_2Cl}]^+$ (19), 821 $[\mathrm{Ni_3(\mathbf{L}^4)_2TFA}]^+$ (62), 935 $[\mathrm{Ni_3(\mathbf{L}^4)_2TFA(TFAH)}]^+$ (20) (TFA/H = $\mathrm{CF_3COO^{--}}$/H). m.p.: > 200 °C.

[(1,5-Bis(2-pyridylmethylene)carbonohydrazide-N,N',N"',N"",N""',O)-dichloro-di{palladium(II)}]-chloride (**7** = $[Pd_2(H\mathbf{L^4})Cl_2]Cl$): Methanol (40 ml) was added to a mixture of $H_2\mathbf{L^4}$ (0.5 mmol) and di(acetonitrile)palladium(II) chloride (1.0 mmol) and the mixture was refluxed for 30 min. The orange precipitate was filtered, washed with diethyl ether, and dried *in vacuo*. Yield 0.292 g (0.498 mmol, 99.6%). $C_{13}H_{11}Cl_3N_6Pd_2O$ (586.47): calcd. C 26.62, H 1.89, N 14.33; found C 26.46, H 2.04, N 14.27. IR: 3028w, 1602m, 1572w, 1549w, 1476s, 1453w, 1433m, 1372m, 1356w, 1306w, 1271m, 1228m, 1151s, 1107w, 1018w, 865w, 770m, 714w, 629w, 574w, 518w. m.p.: > 200 °C.

[(1,5-Bis(2-pyridylmethylene)thiocarbonohydrazide-N,N',S)-dichloro-di{nickel(II)}]-chloride-(methanol) (**8** = $[Ni_2(H\mathbf{L^5})Cl_2]Cl\cdot CH_3OH$): Methanol (20 ml) was added to a mixture of $H_2\mathbf{L^5}$ (1.0 mmol) and nickel(II) chloride hexahydrate (2.0 mmol) and the mixture was stirred for 1 h at r. t. The brown precipitate was filtered, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 0.398 g (0.738 mmol, 73.8%). $C_{14}H_{15}Cl_3N_6Ni_2OS$ (539.12): calcd. C 31.19, H 2.80, N 15.59, S 5.95; found C 32.06, H 2.90, N 18.21, S 6.19. IR: 3383m, 1612m, 1561w, 1511w, 1468m, 1445w, 1406s, 1336s, 1300w, 1272m, 1231s, 1201m, 1148m, 1101w, 1014w, 916m, 879w, 771m, 746w, 545w, 516w. m.p.: > 200 °C.

[(1,5-Bis(2-pyridylmethylene)thiocarbonohydrazide-N,N',S)-dichloro-di{palladium(II)}]-chloride (**9** = $[Pd_2(H\mathbf{L^5})Cl_2]Cl$): Methanol (50 ml) was added to a mixture of $H_2\mathbf{L^5}$ (0.5 mmol) and di(acetonitrile)palladium(II) chloride (1.0 mmol) and the mixture was heated for 20 min. The red suspension was allowed to cool to r.t. and the red precipitate was filtered, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 0.243 g (0.403 mmol, 80.6%). $C_{13}H_{11}Cl_3N_6Pd_2S$ (602.54): calcd. C 25.91, H 1.84, N 13.95, S 5.32; found C 26.09, H 2.21, N 14.22, S 5.02. IR: 3016w, 1601w, 1560w, 1525m, 1473w, 1391s, 1330s, 1287w, 1225w, 1156w, 1116w, 1085m, 928w, 877w, 769m, 651w, 607w, 515w. m.p.: > 200 °C.

2,6-Bis-semicarbazide-4-methylphenol ($H_3\mathbf{L^6}$): To a solution of semicarbazide hydrochloride (2.0 mmol) in ethanol (20 ml) was added a solution of sodium carbonate (1.0 mmol) in H_2O (5 ml) by heating. After complete dissolution a ethanolic solution (20 ml) of 2-hydroxy-5-methylisophthaldialdehyde (1.0 mmol) was added and the reaction mixture was refluxed for 2 h. The solution was allowed to cool to r.t. The precipitate was filtered, washed with cold ethanol and diethyl ether, and dried *in vacuo*. Yield 0.213 g (0.764 mmol, 76.4%). $C_{11}H_{14}N_6O3$ (278.27): calcd. C 47.48, H 5.07, N 30.20; found C 47.29, H 5.49, N 30.27. IR: 3474s, 3267w, 1699s, 1658w, 1581m, 1534s, 1439m, 1348s, 1306w, 1272w, 1255w, 1233w, 1153s, 1024w, 948m, 867w, 802w, 754m, 651w, 564w, 547w, 525w. ^1H NMR (DMSO-d_6): δ 2.31 (s, 3H, C-CH_3), 6.40 (s, 4H, -C(O)-NH_2), 7.52 (s, 2H, aromatic H-atoms), 8.18 (s, 2H, C-CH=N-), 10.27 (s, 2H, =N-NH-C(O)), 10.75 (s, 1H, C-OH). m. p.: > 200 °C.

[(2,6-Bis-semicarbazide-4-methylphenolato-N,O,O')-dichloro-di{palladium(II)}]-(dimethylformamide) (**10** = $[Pd_2(H_2\mathbf{L^6})Cl_2]Cl\cdot DMF$): A solution of di(acetonitrile)palladium(II) chloride (1.0 mmol) in DMF (5 ml) and methanol (5 ml) was added dropwise to a solution of $H_3\mathbf{L^6}$ (0.5 mmol) in DMF (5 ml) and methanol (5 ml). The reaction mixture was refluxed for 10 min and allowed to cool to r.t. The orange precipitate was filtered, washed with methanol and diethyl ether, and dried *in vacuo*. Yield 0.277 g (0.414 mmol, 82.8%). $C_{14}H_{20}Cl_3N_7O_4Pd_2$ (669.56): calcd. C 25.11, H 3.01, N 14.64; found C 24.82, H 3.27, N 14.24. IR: 3324s, 3184w, 2925w, 1651s, 1522m, 1435w, 1385w, 1305w, 1236w, 1195w, 1103m, 1061w, 1014w, 915w, 834w, 756w, 706w, 664w, 578w, 543m. m.p.: > 200 °C.

Polymerization procedures

General: The pre-catalytic complexes were applied as solutions (for complexes **1**, **2**, and **3**) or as fine suspensions (ultrasonication) in methylene chloride (for complexes **4** to **10**). Polymerizations were conducted at r.t. in a water bath to ensure a constant temperature during the reaction. Polymerization runs were carried out at least three times to ensure reproducibility. The IR spectra of the poly(norbornene)s obtained with the catalysts based on **1** to **10** showed the absence of double bond bands at 1620 to 1680 cm^{-1} and at about 960 cm^{-1} characteristic for the trans form of double bonds [80]. The absorption peak at about 941 cm^{-1} could be assigned to the ring system of norbornene [6a, 81]. This ensured the vinyl/addition polymerization instead of a ring-opening metathesis polymerization (ROMP). The conversion was calculated by gravimetric analysis of the polymer.

General procedure for the homopolymerization of norbornene with MAO as co-catalyst: A Schlenk-flask was charged with the norbornene solution and the MAO-solution was added. After 1 min the solution or suspension of the complex was added *via* syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped through the addition of 30 ml of a 10:1 methanol/conc. HCl mixture. The precipitated polymer was filtered, washed with methanol and dried *in vacuo* for 5 h.

General procedure for the homopolymerization of norbornene with $B(C_6F_5)_3/AlEt_3$ as co-catalysts: A Schlenk-flask was charged with the norbornene solution. The solution or suspension of the complex followed by the separate co-catalyst components [$B(C_6F_5)_3$ and $AlEt_3$] were quickly added *via* syringe and the mixture was stirred with a magnetic stirrer. The polymerization was stopped through the addition of 40 ml of a 10:1 methanol/conc. HCl mixture. The precipitated polymer was filtered, washed with methanol and dried *in vacuo* for 5 h.

From studies of a number of metal complexes which did not show any polymerization activity with $B(C_6F_5)_3/AlEt_3$, we conclude that the combination of $B(C_6F_5)_3/AlEt_3$ alone is not polymerization active.

Results and Discussion

Synthesis and molecular structures of the complex pre-catalysts

The Schiff-base ligands $H_2\mathbf{L^1}$ and $H_2\mathbf{L^2}$ (Scheme 2) were synthesized *in situ* from salicylaldehyde with 2-amino-2-methyl-1-propanol and 2-amino-1-butanol, respectively, and reacted with nickel(II) acetate tetrahydrate to form the methanol adducts **1** and **2**. The complexes are green solids and could be crystallized from the reaction mixture in high yields.

The molecular structure of **1** is shown in Fig. 1. A dinuclear and centrosymmetric complex is formed by the bridging action of the phenoxo oxygen atom between the two nickel atoms. The nickel atom has a distorted octahedral coordination with the three donor atoms from the Schiff-base mono-anion $(H\mathbf{L^1})^-$ and one phenoxo-group of the second bridging ligand lying in one (equatorial) plane. An aqua ligand and an acetate anion occupy the two remaining (axial) coordination sites. Hydrogen bonding from the aqua to the acetate ligand on the neighboring nickel atom and to an ethanol molecule of crystallization together with hydrogen bonding from the alcohol group to the acetate ligand completes the molecular structure as demonstrated in Fig. 1. There is no π-stacking [82] between the phenyl rings in the crystal structure of **1**. Part of the packing is controlled by C-H$\cdots\pi$ interactions [83, 84] from C11 and C13 to the phenyl rings of neighboring molecules. ESI-MS indicates that the dinuclear Ni_2L_2-species are dominant in methanol solutions of **1** and **2**, yet, with higher nuclear Ni_3L_3- and Ni_4L_4-species also a distinct possibility.

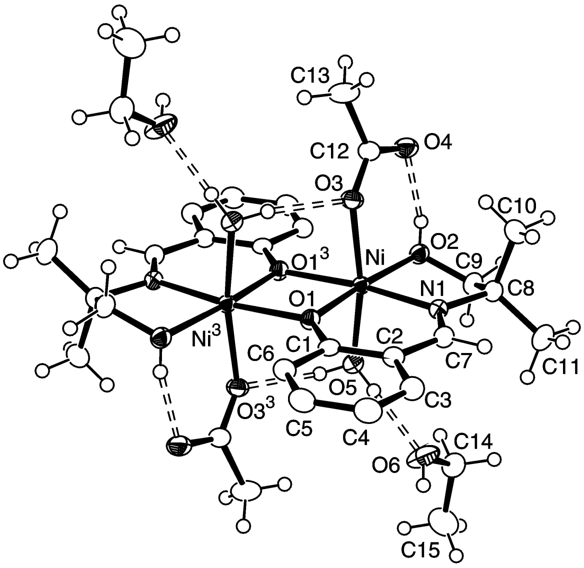


Fig. 1. Molecular structure of [bis(*mer*-2-(N-(2-oxobenzylidene)amino)-2-methyl-1-propanol-*N,O,O'*)-di(acetato)-di(aqua)-nickel(II)]-di(ethanol) (**1**) (phenyl hydrogen atoms omitted for clarity). Selected distances (Å) and angles (°): Ni-O1 2.0119(9), Ni-O1^3 2.0777(9), Ni-O2 2.1003(10), Ni-N1 2.0200(11), Ni-O3 2.0994(9), Ni-O5 2.0995(10), O1-Ni-N1 92.24(4), O1-Ni-O1^3 81.22(4), O1^3-Ni-O2 105.30, O1-Ni-O3 89.42(4), O1^3-Ni-O3 85.44, O1-Ni-O5 90.36(4), O1^3-Ni-O5 82.53, N1-Ni-O2 81.27(4), N1-Ni-O3 97.91(4), N1-Ni-O5 94.22(4), O2-Ni-O3 90.90(4), O2-Ni-O5 90.70(4), O3-Ni-O5 167.87(4), (O5-)H$\cdots$O3^3 2.02(2) (166(2)°), (O5-)H$\cdots$O6 1.90(2) (167(2)°), (O2-)H$\cdots$O4 1.82(2) (165(2)°); symmetry transfomation $^3\ -x+1, -y, -z+2$.

The complexes **4** to **10** were designed from two different ligand systems whose donor atoms can be easily varied by the choice of the starting materials. This opens the possibility to synthesize a great number of similar nickel(II) and palladium(II) complexes differing only in the donor atoms of the ligand and possibly not in the molecular structure (Scheme 2).

The ligands $H_3\mathbf{L^3}$, $H_2\mathbf{L^4}$, $H_2\mathbf{L^5}$, and $H_3\mathbf{L^6}$ were synthesized through condensation of the aldehydes [here 2-hydroxy-5-methylisophthaldialdehyde ($\rightarrow H_3\mathbf{L^3}$ and $H_3\mathbf{L^6}$) and pyridine-2-carboxaldehyde ($\rightarrow H_2\mathbf{L^4}$ and $H_2\mathbf{L^5}$)] with thiosemicarbazide ($\rightarrow H_3\mathbf{L^3}$), semicarbazide hydrochloride ($\rightarrow H_3\mathbf{L^6}$), carbonodihydrazide ($\rightarrow H_2\mathbf{L^4}$), and thiocarbonodihydrazide ($\rightarrow H_2\mathbf{L^5}$). Subsequent reaction of the ligands with different nickel(II) and palladium(II) salts resulted in the formation of the dinuclear complexes presented in Scheme 2. Except for complex **6** the complexes are insoluble in common organic solvents (methanol and ethanol, pentane, hexane and cyclohexane, chloroform and methylene chloride, and toluene) or only slightly soluble in coordinating solvents like DMSO and DMF (for complexes **5**, **9**, and **10**), which may be due to the formation of polymeric instead of molecular structures. Therefore, it was not possible to

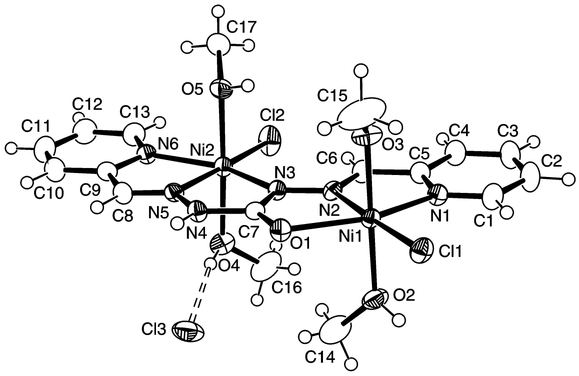


Fig. 2. Molecular structure of [*mer*-(1,5-bis(2-pyridylmethylene)carbonohydrazide-*N,N’,N”’,N””,N”””,O*)-dichloro-tetra(methanol)-di{nickel(II)}]-chloride (**6**). Selected distances (Å) and angles (°): Ni1-N1 2.08(2), Ni1-N2 2.0133(18), Ni1-O1 2.1700(17), Ni1-Cl1 2.3416(7), Ni1-O2 2.0813(17), Ni1-O3 2.0699(17), Ni2-N3 2.1104 (19), Ni2-N5 2.0389(19), Ni2-N6 2.152(2), Ni2-Cl2 2.3304(8), Ni2-O4 2.1371(18), Ni2-O5 2.1103 (17), C6-N2 1.280(3), N2-N3 1.368(3), N4-N5 1.353(2), N5-C8 1.279(3), N1-Ni1-Cl1 99.56(6), Cl1-Ni1-O1 106.03(5), N2-Ni1-O1 75.58(7), N2-Ni1-N1 78.83(8), N1-Ni1-O2 90.66(9), O3-Ni1-N1 89.28(8), N1-Ni1-O2 92.43(7), N2-Ni1-O3 88.39(7), O3-Ni1-O2 179.15(7), N3-Ni2-N5 75.39(7), N5-Ni2-N6 76.49(7), N6-Ni2-Cl2 98.97(6), Cl2-Ni2-N3 109.19(6), O4-Ni2-N6 90.19(7), N6-Ni2-O5 88.55(7), O4-Ni2-N5 88.38(8), N5-Ni2-O5 89.30(7), O5-Ni2-O4 177.57(7), (O4-)H$\cdots$Cl3 2.18 (168°), not shown are (O3-)H$\cdots$Cl3^1 2.18 (173°) and (O5-)H$\cdots$Cl3^1 2.24 (159°), symmetry operation ^{1} $x+1, y, z$.

obtain NMR data or crystals for X-ray diffraction. The formulation of the insoluble complexes **4**, **5**, and **7** to **10** as given in Scheme 2 is mainly based on elemental analysis and on the analogy to the structurally elucidated compound **6**.

The hexadentate mono-deprotonated ligand (H**L**^{4})$^-$ and nickel(II) form the dinuclear complex **6** whose structure is illustrated in Fig. 2. Both nickel atoms have an octahedral coordination sphere with the donor atoms from (H**L**^{4})$^-$ and a chloro ligand lying in one (equatorial) plane. The mono-deprotonated ligand (H**L**^{4})$^-$ gives rise to different coordination environments of the two nickel atoms: Ni1 shows an N_2,O,Cl-coordination whereas Ni2 features an N_3,Cl-coordination. The remaining (axial) sites are occupied by two methanol solvent molecules. A third (hydrogen-bonded) chloride atom in the crystal lattice compensates the positive charge of the dinuclear complex. The pyridyl rings in the crystal structure of **6** give rise to intermolecular π-stacking interactions [82, 85–87]. The two different pyridyl ring planes (symmetry relation x, $y \pm 1$, z) are almost parallel with a small dihedral angle of 1.7°. The ring slippage is typical [82] with a slip angle of 18.8° or 20.3° (depending on which phenyl is taken as the reference plane). This corresponds to a vertical displacement between the ring centroids of 1.27 Å (centroid separation 3.78 Å, interplanar distance 3.55 or 3.58 Å, respectively). In comparison, these intermolecular π-stackings exhibit rather short centroid-centroid contacts (< 3.8 Å), small slip angles (< 25°) and vertical displacements (< 1.5 Å) which translate into a sizable overlap of the pyridyl-plane areas [85].

Catalytic studies

The dimeric nickel(II) complexes **1** and **2** were found active in the homopolymerization of norbornene. The results of the polymerization activities using methylalumoxane (MAO), $B(C_6F_5)_3$ in combination with $AlEt_3$ or $B(C_6F_5)_3$ alone as co-catalysts are summarized in Table 2 and Fig. 3. As a reference point for the activity of the new pre-catalysts the Ni(salen)-complex **3** with a similar N_2,O_2-coordination was tested under the same polymerization conditions.

In comparison to the mononuclear reference system **3** and in general [19, 34–36, 50, 51] the catalysts based on the dinuclear nickel(II) complexes **1** and **2** show rather high polymerization activities in combination with different co-catalytic systems. The activities covered a range between $1.1 \cdot 10^6$ (**1**/$B(C_6F_5)_3$ and **2**/$B(C_6F_5)_3$) to $2.3 \cdot 10^7$ $g_{polymer}$/mol(Ni)·h (**1**/MAO). Complexes **1** and **2** also revealed similar or even higher

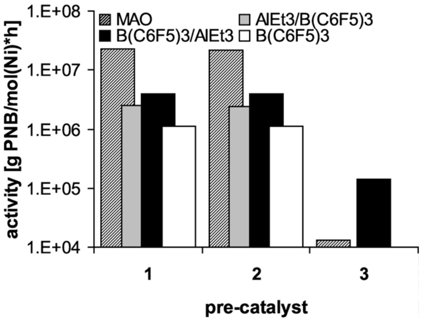


Fig. 3. Activities of **1** to **3** with different co-catalysts in the polymerization of norbornene. Detailed conditions are given in Table 2.

Table 2. Polymerization of norbornene (NB) with complexes **1** to **3** and different co-catalysts.

Catalyst[a]	Time [min]	Conversion [%]	Activity [g PNB/mol(Ni)·h]	M_w [g·mol^{-1}]	M_n [g·mol^{-1}]	M_w/M_n
1/MAO[b]	1/6	67.9	$2.3\cdot10^7$	$5.5\cdot10^5$	$6.2\cdot10^4$	8.8
2/MAO[b]	1/6	64.7	$2.2\cdot10^7$	$1.2\cdot10^6$	$3.9\cdot10^5$	3.2
3/MAO[b]	60	13.6	$1.3\cdot10^4$	$2.4\cdot10^6$	$1.3\cdot10^6$	1.8
1 – 3[c]	60	0	no activity observed	–	–	–
1/$AlEt_3/B(C_6F_5)_3$[d]	1	44.0	$2.5\cdot10^6$	$5.1\cdot10^5$	$2.2\cdot10^5$	2.3
1/$B(C_6F_5)_3/AlEt_3$[d]	1	71.2	$4.0\cdot10^6$	$2.7\cdot10^5$	$9.3\cdot10^4$	2.9
2/$AlEt_3/B(C_6F_5)_3$[d]	1	41.8	$2.4\cdot10^6$	$4.9\cdot10^5$	$2.2\cdot10^5$	2.3
2/$B(C_6F_5)_3/AlEt_3$[d]	1	69.1	$3.9\cdot10^6$	$3.3\cdot10^5$	$1.2\cdot10^5$	2.8
3/$B(C_6F_5)_3/AlEt_3$[d]	5	12.0	$1.4\cdot10^5$	$8.0\cdot10^5$	$1.8\cdot10^5$	4.4
1 – 3/$AlEt_3$[e]	60	0	no activity observed	–	–	–
1/$B(C_6F_5)_3$[f]	1	20.2	$1.1\cdot10^6$	$1.2\cdot10^6$	$6.4\cdot10^5$	1.9
2/$B(C_6F_5)_3$[f]	1	20.2	$1.1\cdot10^6$	$1.2\cdot10^6$	$6.6\cdot10^5$	1.8
3/$B(C_6F_5)_3$[f]	60	0	no activity observed	–	–	–

General conditions: room temperature, toluene/methylene chloride solution, [Ni]:[NB] = 1:1000; [a] the ordering of the components refers to the order of addition to the monomer solution; [b] 10.6 mmol norbornene (NB), [Ni]:[Al] = 1:100, total volume: 10.0 ml; [c] 10.6 mmol NB, total volume: 10.0 ml; [d] 30.1 mmol NB, [Ni]:[B]:[Al] = 1:9:10, total volume: 40.0 ml; [e] 30.1 mmol NB, [Ni]:[Al] = 1:10, total volume: 40.0 ml; [f] 30.1 mmol NB, [Ni]:[B] = 1:9, total volume: 40.0 ml.

polymerization activities than the known pre-catalyst nickel(II) acetylacetonate [19]. We also note that complexes **1** and **2** could be activated with $B(C_6F_5)_3$ alone. Addition of $AlEt_3$ further increased the conversion and the polymerization activity. Higher activities with the combination of $B(C_6F_5)_3$ and $AlEt_3$ can be explained by a scavenger effect of $AlEt_3$, the presence of alkyl transfer agents [88] or by the formation of highly activating $Al(C_6F_5)_3$. A combination of $B(C_6F_5)_3$ with $AlEt_3$ (molar ratio 1:1) undergoes a facile aryl/alkyl ligand exchange reaction to give $Al(C_6F_5)_3$ and BEt_3 as the main products [31, 34, 51, 89]. The ^{19}F NMR spectrum showed the expected signals of $Al(C_6F_5)_3$ at -122.3 ppm (*o*-F), -152.2 ppm (*p*-F) and -161.7 ppm (*m*-F). Also, the ^{19}F NMR spectrum revealed the formation of heteroleptic and possibly dimeric aluminum species of the type $[AlEt_{3-x}(C_6F_5)_x]_2$ ($x = 1-2$) as side products. A similar ligand exchange has been described for $B(C_6F_5)_3$ and $AlMe_3$ to give $Al(C_6F_5)_3$ and BMe_3 [90, 91].

GPC of the soluble polymers (see Table 2) gave a number-averaged molar mass (M_n) between $9.3\cdot10^4$ (**1**/$B(C_6F_5)_3/AlEt_3$) and $1.3\cdot10^6$ g·mol^{-1} (**3**/MAO) corresponding to an average chain length between 1000 and 14000 monomer units ($M_{NB} = 94.16$ g·mol^{-1}). The poly(norbornene)s displayed a monomodal molar mass distribution except for the polymers from **1**/MAO. The polydispersities Q are mostly narrow and close to a value of 2 which is the theoretical dispersity for a Schulz-Flory type distribution arising from an ideally behaved polymerization reaction with a chain-termination reaction [92]. A dispersity of $Q \approx 2$ then indicates a single-site character, *i.e.* a highly homogeneous structure of the active catalyst species.

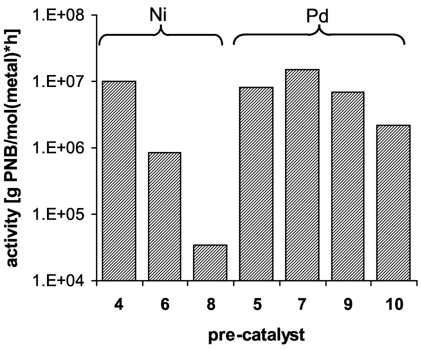


Fig. 4. Activities of **4 – 10** with MAO as co-catalyst in the polymerization of norbornene. Detailed conditions are given in Table 3.

Results of the polymerization activities of the dinuclear nickel(II) and palladium(II) complexes **4** to **10** with methylalumoxane (MAO) as co-catalyst are summarized in Table 3 and Fig. 4.

The dinuclear nickel(II) and palladium(II) complexes **4** to **10** can be transformed into polymerization-active species by addition of the co-catalyst MAO. The catalytic systems **4 – 10**/MAO showed remarkable differences in the polymerization activities de-

Table 3. Polymerization of norbornene (NB) with complexes **4 – 10** and methylalumoxane (MAO) as co-catalyst.

Catalyst[a)]	Time [min]	Conversion [%]	Activity [g PNB/mol(metal)·h]	M_w [g·mol^{-1}]	M_n [g·mol^{-1}]	M_w/M_n
4/MAO	1/6	28.5	$9.8 \cdot 10^6$	$1.5 \cdot 10^6$	$7.1 \cdot 10^5$	2.1
5/MAO	1/6	24.6	$8.3 \cdot 10^6$		not soluble	
6/MAO	1	15.2	$8.6 \cdot 10^5$	$1.8 \cdot 10^6$	$9.8 \cdot 10^5$	1.9
7/MAO	1/6	43.6	$1.5 \cdot 10^7$		not soluble	
8/MAO	5	3.0	$3.4 \cdot 10^4$	$2.6 \cdot 10^6$	$1.6 \cdot 10^6$	1.6
9/MAO	1/6	20.7	$7.0 \cdot 10^6$		not soluble	
10/MAO	1/6	6.5	$2.2 \cdot 10^6$		not soluble	
4 – 10[b)]	60	0	no activity observed	–	–	–

General conditions: room temperature, toluene/methylene chloride solution, 10.6 mmol norbornene (NB), [Ni]:[NB] = 1:1000, total volume: 10.0 ml; [a)] The complexes were applied as a fine suspension *via* ultrasonication; [Ni]:[Al] = 1:100;[b)] polymerization attempts without MAO.

Table 4. Polymerization of norbornene (NB) with complexes **4 – 10** and $B(C_6F_5)_3/AlEt_3$ as co-catalysts.

Catalyst[a)]	Time [min]	Conversion [%]	Activity [g PNB/mol(metal)·h]	M_w [g·mol^{-1}]	M_n [g·mol^{-1}]	M_w/M_n
4/$B(C_6F_5)_3/AlEt_3$[b)]	1	49.7	$2.8 \cdot 10^6$	$5.9 \cdot 10^5$	$2.2 \cdot 10^5$	2.6
5/$B(C_6F_5)_3/AlEt_3$[b)]	1/6	30.8	$1.0 \cdot 10^7$		not soluble	
6/$B(C_6F_5)_3/AlEt_3$[b)]	5	6.7	$7.6 \cdot 10^4$	$7.0 \cdot 10^5$	$3.3 \cdot 10^5$	2.2
7/$B(C_6F_5)_3/AlEt_3$[b)]	1/6	69.7	$2.4 \cdot 10^7$		not soluble	
8/$B(C_6F_5)_3/AlEt_3$[b)]	5	4.5	$5.1 \cdot 10^4$	$7.3 \cdot 10^5$	$3.0 \cdot 10^5$	2.4
9/$B(C_6F_5)_3/AlEt_3$[b)]	1/6	45.6	$1.6 \cdot 10^7$		not soluble	
10/$B(C_6F_5)_3/AlEt_3$[b)]	1	22.6	$1.3 \cdot 10^6$		not soluble	
4/$AlEt_3$[c)]	60	0.3	$3.2 \cdot 10^2$	$1.7 \cdot 10^5$	$2.5 \cdot 10^4$	6.7
5 – 10/$AlEt_3$[c)]	60	0	no activity observed	–	–	–
4/$B(C_6F_5)_3$[d)]	60	0.8	$7.7 \cdot 10^2$	$1.6 \cdot 10^6$	$6.7 \cdot 10^5$	2.3
5/$B(C_6F_5)_3$[d)]	60	0.7	$6.3 \cdot 10^2$		not soluble	
7/$B(C_6F_5)_3$[d)]	60	28.5	$2.7 \cdot 10^4$		not soluble	
10/$B(C_6F_5)_3$[d)]	60	0.6	$5.3 \cdot 10^2$		not soluble	
6, **8**, **9**/$B(C_6F_5)_3$[d)]	60	0	no activity observed	–	–	–

General conditions: room temperature, toluene/methylene chloride solution, 30.1 mmol NB, [Ni]:[NB] = 1:1000, total volume: 40.0 ml; [a)] The complexes were applied as a fine suspension *via* ultrasonication;[b)] [Ni]:[B]:[Al] = 1:9:10; [c)] [Ni]:[Al] = 1:10; [d)] [Ni]:[B] = 1:9.

pending on the metal. In the case of the palladium(II) complexes the polymerization activities covered a narrow range between $2.2 \cdot 10^6$ (**10**/MAO) and $1.5 \cdot 10^7$ $g_{polymer}$/mol(Pd)·h (**7**/MAO) with high monomer conversions in short polymerization times of 10 sec. In contrast the polymerization activities of the nickel(II) complexes varied between $3.4 \cdot 10^4$ (**8**/MAO) and $9.8 \cdot 10^6$ $g_{polymer}$/mol(Ni)·h (**4**/MAO). The observed activity trends and differences are difficult to explain in the absence of a more profound knowledge of the active species. Mechanistic investigations with MAO as a co-catalyst are hampered by the unknown exact composition and structure of MAO [62,66,93]. Catalysts **4 – 10**/MAO show no clear activity trends with respect to variation in counter ion ($CH_3CO_2^-$ or Cl^-) or donor atoms of the ligands (O or S).

In order to gain additional information about the activation process the activator was changed from MAO to the better defined co-catalyst $B(C_6F_5)_3$ with or without triethylaluminum ($AlEt_3$). The results are summarized in Table 4 and Fig. 5.

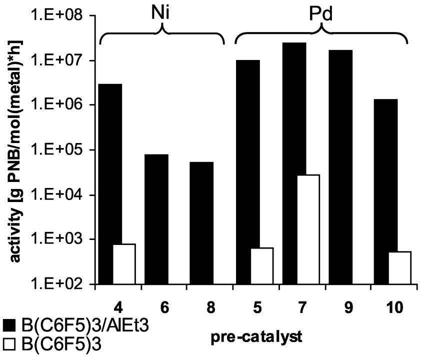


Fig. 5. Activities of **4 – 10** and $B(C_6F_5)_3$ with or without $AlEt_3$ as co-catalyst in the polymerization of norbornene. Detailed conditions are given in Table 4.

The new dinuclear pre-catalysts **4** to **10** could be also activated with the co-catalytic system $B(C_6F_5)_3$/

$AlEt_3$ and the activities are similar to those observed with MAO. Again the palladium(II) systems exhibit comparative polymerization activities in a small range between $1.3 \cdot 10^6$ (**10**/$B(C_6F_5)_3/AlEt_3$) and $2.4 \cdot 10^7$ $g_{polymer}$/mol(Pd)·h (**7**/$B(C_6F_5)_3/AlEt_3$). The nickel(II) systems have again activities in a wider range between $5.1 \cdot 10^4$ (**8**/$B(C_6F_5)_3/AlEt_3$) and $2.8 \cdot 10^6$ $g_{polymer}$/mol(Ni)·h (**4**/$B(C_6F_5)_3/AlEt_3$). The similar polymerization behavior of the dinuclear complexes **4** to **10** in combination with MAO and $B(C_6F_5)_3/AlEt_3$ should be the result of a similar activation process and polymerization mechanism. Activation of the new dinuclear complexes with $B(C_6F_5)_3$ alone was only successful in the case of the complexes **4**, **5**, **7**, and **10**. There, the polymerization activities were rather low between $5.3 \cdot 10^2$ (**10**/$B(C_6F_5)_3$) and $2.7 \cdot 10^4$ $g_{polymer}$/mol(metal)·h (**7**/$B(C_6F_5)_3$).

Elaborate investigations on the activation mechanism of coordination compounds towards norbornene polymerization have been performed in the case of $[Ph_3PCH_2C(O)CH_3]_2[Pd_2Cl_6]/B(C_6F_5)_3$ [34] and $Pd(L)Cl_2/B(C_6F_5)_3/AlEt_3$ [L = $Ph_2P(CH_2)_{2,3}PPh_2$] [51]. Multinuclear NMR studies together with other analyses suggested the *in-situ* formation of $PdCl_2$ and $[Pd(L)]^{2+}$ or naked "Pd^{2+}", respectively, as active species. It is evident that activation of the metal complexes has to include an opening of the coordination sphere through (partial) ligand abstraction by the co-catalyst. Thus, more weakly bound ligands may promise higher activities. Of course, a compromise has to be made in terms of the stability of the pre-catalytic complex for preparation, handling and storage.

Solubilities of the polymers from **4 – 10**/co-catalyst were as expected from the literature [1, 19, 35 – 39, 52] with only the nickel-based catalysts yielding soluble polymers whereas the palladium-derived polymers were insoluble in 1,2,4-trichlorobenzene even at elevated temperature. GPC data of the nickel-catalyzed polymers gave M_n-values between $7.1 \cdot 10^5$ (**4**/MAO) and $1.6 \cdot 10^6$ g·mol^{-1} (**8**/MAO) for activation with MAO and between $2.2 \cdot 10^5$ (**4**/$B(C_6F_5)_3/AlEt_3$) and $3.3 \cdot 10^5$ g·mol^{-1} (**4**/$B(C_6F_5)_3$) with the co-catalyst system $B(C_6F_5)_3/AlEt_3$. This corresponds to average chain lengths between 7500 and 17000 monomer units with MAO and between 2300 and 3500 monomer units with $B(C_6F_5)_3/AlEt_3$ (M_{NB} = 94.16 g·mol^{-1}). The polymer samples displayed a monomodal molar mass distribution with a narrow dispersity around 2 indicating a single-site character of the active species [92].

Conclusion

Dinuclear nickel(II) and palladium(II) complexes represent a new class of pre-catalysts for the vinyl/addition polymerization of norbornene. Both the complexes and the semicarbazide- and carbonohydrazide-based ligands can easily be prepared. The new dinuclear pre-catalysts can be activated with both MAO and $B(C_6F_5)_3/(AlEt_3)$ as co-catalyst. It was also possible to activate several complexes with $B(C_6F_5)_3$ alone. Rather high polymerization activities above 10^7 $g_{polymer}$/mol(metal)·h could be achieved in some cases. Polymer characterization by GPC revealed polydispersities around $M_w/M_n = 2$ indicating a single-site character of the active species.

Acknowledgments

The research was supported by the Fonds der Chemischen Industrie LG Chem (Korea) and the Wissenschaftliche Gesellschaft in Freiburg. Structural investigations of the coordination compounds were supported by the DFG (grant JA466/10-1,-2) We appreciate a gift of $PdCl_2$ by Degussa-Hüls AG and a gift of MAO by Witco GmbH.

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