Dipyridylamine Ligands − Synthesis, Coordination Chemistry of the Group 10 Metals and Application of Nickel Complexes in Ethylene Oligomerization

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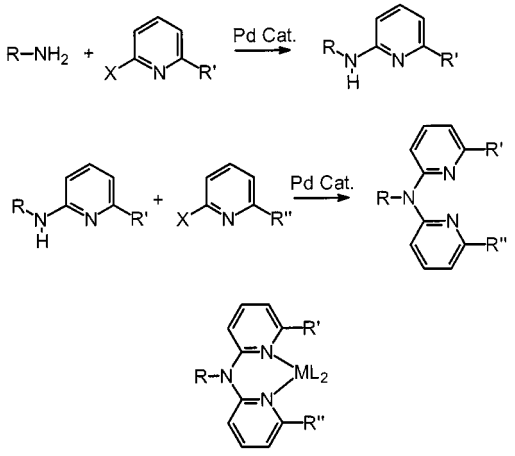
Keywords: N ligands / Nickel / Palladium / Polymerization / Catalysis

A great variety of 2,2′-bipyridylamines can be synthesized starting from primary amines or 2-aminopyridines (for instance, symmetrically and unsymmetrically substituted as well as chiral ligands) by palladium-catalyzed aryl amination. The reaction of such ligands with [$PdCl_2$(COD)] or [$NiBr_2$(DME)] (COD = cycloocta-1,5-diene; DME = 1,2-dimethoxyethane) led to the corresponding dichloro or dibromo complexes. The results of X-ray crystal structure analyses of selected compounds show that the ligands coordinate through the two pyridine N-atoms. Their palladium complexes have a slightly distorted planar coordination (in the case of nickel a distorted tetrahedral coordination), with N–M–N angles of 96.0(2)° (M = Ni) and 85.7° (averaged, M = Pd). The nickel complexes are highly active ethylene oligomerization catalysts if activated with $Et_3Al_2Cl_3$.

Introduction

2,2′-Bipyridylamines are accessible by sequential palladium-catalyzed aryl amination reactions starting from a primary amine[1,2] (Scheme 1, above). Such compounds have three sites where coordination to a transition metal may occur: the two pyridine moieties and the amine function. Since the amine N-atom can only bind in a strained fashion together with one or two pyridyl units, such ligands act as bidentate chelates with binding only to the pyridyls. In contrast to the classical 2,2′-bipyridine type ligand, which was described recently as the most widely used ligand,[3] six-membered rings are formed (Scheme 1, below). Recently N-ligands have received much attention,[4] as bipyridylamines might be an interesting alternative to diphosphane or diimine ligands, the latter of which has recently attracted considerable interest in regard to its combination with the group 10 metals as olefin polymerisation catalysts.[5,6] Due to the great variety of substitution patterns which can be easily established for the bipyridylamines (variation of R, R′ and R′′, Scheme 1) it may be possible to fine-tune transition metal complex reactivity. To the best of our knowledge, work on applications of bipyridylamine ligand complexes in olefin polymerization has not been published yet.[6] The coordination chemistry of the simplest member of the bipyridylamine group, the 2,2′-dipyridylamine (commercially available), has been described in detail for copper.[7] However, compounds of other transition metals such as complexes of the chromium triad,[8] of rhodium,[9] cobalt,[10] nickel,[11] palladium,[12] ruthenium,[13] and cadmium[14] are much rarer. In this article we report on the ligand synthesis and coordination chemical studies of novel bipyridylamines, as well as some applications of the synthesized nickel complexes in ethylene oligomerization.



Scheme 1. Synthesis of bipyridylamines and the coordination mode of these ligands in transition metal complexes (R, R′, R′′ = alkyl, aryl substituents; X = Cl, Br; L = additional ligands)

Results and Discussion

Ligand Syntheses

Palladium-catalyzed aryl−X activation (X = I, Br or Cl) reactions are an efficient tool for the synthesis of bi- and triarylamines by C−N bond formation.[1] If 2-X-pyridines are used X can be Cl as the systems are activated, although the formation of catalyst-deactivating palladium pyridine complexes has to be avoided. In order to prevent this the palladium catalyst has to be stabilized by chelating bisphosphane ligands.[1a] Reactions of 2-aminopyridines with one or two equivalents of the corresponding 2-halopyridines and 1.25 or 2.5 equiv. of sodium-*tert*-butoxide in the presence of 1 mol % 1,3-bis(diphenylphosphanyl)propane and 0.5 mol % Pd_2dba_3 in toluene at 80 °C leads, usually after less than one hour, to a color change to yellow. After stirring for an additional 12 hours, work up with dichlorome-

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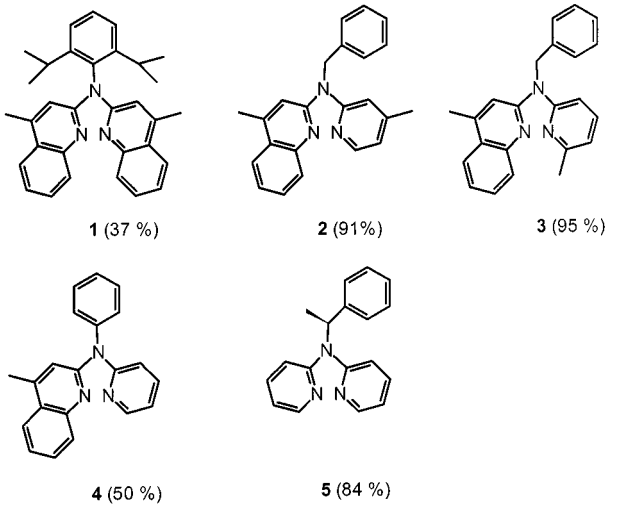
  1434−1948/01/0909−2421 $ 17.50+.50/0

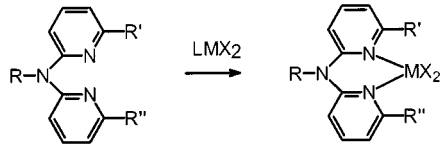
thane, or ether, and water followed. The compounds were purified by chromatography, distillation or crystallization. Compound **1** was prepared from 2,6-diisopropylaniline, compound **2** from 2-(benzylamino)-4-methylpyridine, compound **3** from 2-(benzylamino)-6-methylpyridine, compound **4** from 2-pyridylaniline and compound **5** from (*S*)-1-phenylethylamine (Scheme 2).



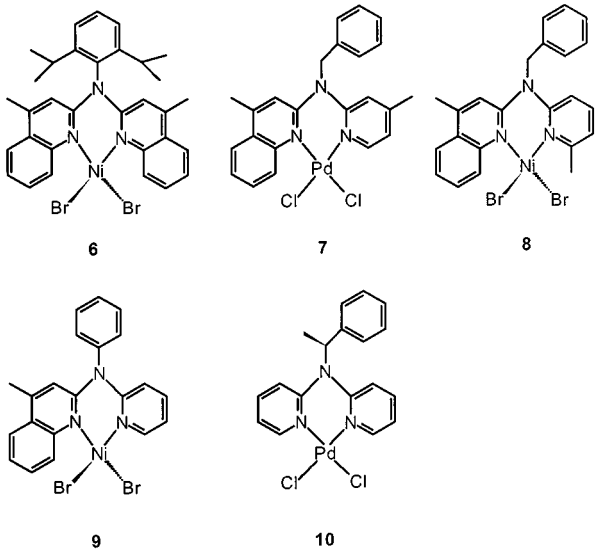
Scheme 2. The bipyridylamine ligands used, including numbering

Group 10 Metal Complex Syntheses and Structures

The reaction of **1**, **3** and **4** with [$NiBr_2$(DME)] (DME = dimethoxyethane) gave rise to blue- or purple-colored crystalline materials (Scheme 3). The structures of all the synthesized group 10 metal complexes are summarized in Scheme 4. NMR investigation of **6**, **8** and **9** gave rather broad signals indicating the existence of d^8 high-spin complexes. EPR spectra in dilute CH_2Cl_2 solutions could not be recorded either at room or at lower temperatures. Single crystals of **8** suitable for an X-ray crystal structure analysis (Figure 1) could be grown from a CH_2Cl_2 solution; crystallographic details are listed in Table 1. The coordination of the nickel center is best described as tetrahedral as observed for dibromodipyridylnickel(II) complexes[15] {dibromodipyridylnickel(II) = [$NiBr_2$(dipy)]}. The $Ni-N_{pyridine}$ bond lengths of **8** (mean = 1.99 Å) are well in accordance with those observed for (dipy)$NiBr_2$ complexes (mean = 2.00 Å). The N−Ni−N angle in **8** [96.0(2)°] is significant larger than that observed in [$NiBr_2$(dipy)] complexes (mean = 82.8°). Thus it can be concluded that the bipyridylamine-type ligands may favor tetrahedral coordination, similar to bipyridyl ligands, since the six-membered chelate is closer to the ideal tetrahedral angle, although still far from the ideal value.



Scheme 3. Synthesis of the group 10 metal complexes (R, R′, R′′ = alkyl, aryl substituents; X = Cl, Br; L = additional ligands)



Scheme 4. Synthesized Ni and Pd complexes, including numbering

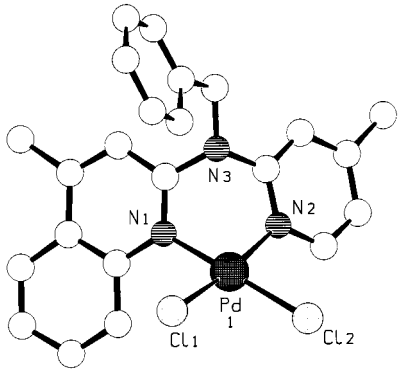


Figure 1. Molecular structure of **7**; selected bond lengths [Å] and angles [°]: N1−Pd1 2.032(3), N2−Pd1 2.012(3), Cl1−Pd1 2.3033(11), Cl2−Pd1 2.2980(10), N2−Pd1−N1 84.82(11), N2−Pd1−Cl2 91.80(8), N1−Pd1−Cl2 173.83(8), N2−Pd1−Cl1 170.54(8), N1−Pd1−Cl1 92.79(8), Cl2−Pd1−Cl1 91.36(4)

The reaction of **2** and **5** with [$PdCl_2$(COD)] (COD = cycloocta-1,5-diene) gave rise to yellow crystalline materials (Scheme 3). NMR investigation of **2** and **5** revealed a sharp single signal set suggesting the existence of monomeric diamagnetic species in solution. The X-ray crystal structure analyses of both compounds confirm these complexes to be mononuclear in the solid state as well; crystallographic details are listed in Table 1. The coordination of the palladium centers is best described as square planar, in contrast to the nickel compounds but well in agreement with what was observed previously for dipyridyldichloropalladium(II) complexes {dichlorodipyridylpalladium(II) = [$PdCl_2$(dipy)]}. A CSD[16] search for [$PdCl_2$(dipy)] complexes revealed ten hits with a mean of the Pd−N bond length of 2.029(18) and a mean of the N−Pd−N bond angle of 80.1(7)°. Similar Pd−N distances (mean = 2.02 Å) have been found in **7** and **10** (Figure 2 and 3) The N−Pd−N

Table 1. Details of the X-ray crystal structure analyses

Compound	**7**	**8**	**10**
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/c$	$P2_12_12_1$
a, Å	8.772(2)	9.194(2)	10.434(2)
b, Å	10.721(2)	19.609(4)	12.164(3)
c, Å	13.849(3)	12.522(3)	14.856(3)
α, deg	77.53(2)	–	–
β, deg	86.38(2)	98.75(3)	–
γ, deg	80.88(2)	–	–
V, Å^3	1255.1(5)	2231.3(9)	1885.5(7)
Z	2	4	4
Crystal size, mm	0.5 × 0.3 × 0.3	0.7 × 0.3 × 0.1	0.4 × 0.4 × 0.35
ρ_{calcd}, g cm^{-3}	1.592	1.661	1.595
μ, cm^{-1} (Mo-K_α)	1.183	4.465	1.271
T, K	200(2)	200(2)	293(2)
θ range, deg	1.97–24.13	1.95–24.22	2.39–24.29
No. of reflections	3644	6518	8678
No. of reflections unique	3644	3342	2940
No. of reflections obs. [$I > 2\sigma(I)$]	3063	2096	2854
No. of parameters	325	262	234
*wR*2 (all data)	0.073	0.119	0.090
R value [$I > 2\sigma(I)$]	0.029	0.047	0.030

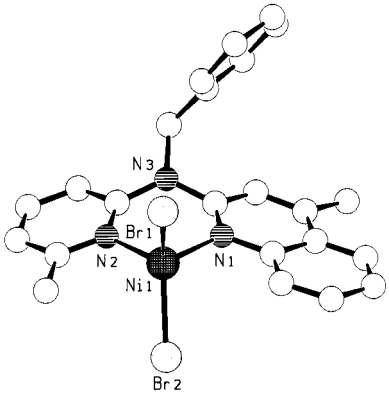


Figure 2. Molecular structure of **8**; selected bond lengths [Å] and angles [°]: N1–Ni1 1.977(5), N2–Ni1 1.997(6), Ni1–Br1 2.3699(13), Ni1–Br2 2.3898(12), N1–Ni1–N2 96.0(2), N1–Ni1–Br1 105.1(2), N2–Ni1–Br1 107.8(2), N1–Ni1–Br2105.07(15), N2–Ni1–Br2 107.5(2), Br1–Ni1–Br2 130.04(5)

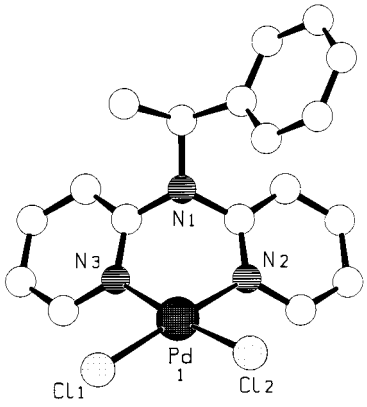


Figure 3. Molecular structure of **10**; selected bond lengths [Å] and angles [°]: N2–Pd1 2.025(4), N3–Pd1 2.020(4), Cl1–Pd1 2.2993(14), Cl2–Pd1 2.267(2), N3–Pd1–N2 86.5(2), N3–Pd1–Cl2 174.47(12), N2–Pd1–Cl2 91.23(12), N3–Pd1–Cl1 91.85(12), N2–Pd1–Cl1 175.37(13), Cl2–Pd1–Cl1 90.77(6)

bond angle (mean = 85.7°) differs by more than 5° and is even 4.5° larger than the highest value observed in known [$PdCl_2$(dipy)] complexes.

Ethylene Oligomerization Studies

Recently, considerable effort has been devoted to the synthesis of hyperbranched oligomers from inexpensive monomers such as ethylene and propene.[17] Such materials are useful in the lubricant industry as base stocks and as precursors to lubricant additives, especially since the demand for synthetic lubricants is rising.[18]

Complexes **6**, **8** and **9** were investigated with regard to catalytic applications in ethylene oligomerization after activation with chloroaluminum alkyls. The results of the oligomerization experiments are summarized in Table 2. Remarkably high activities are observed for all Ni complexes when using $Et_3Al_2Cl_3$ as a co-catalyst and CH_2Cl_2 as the solvent. All nickel complexes show a high tendency towards the formation of C4–C6 fraction products. Highly branched oligomers with a ratio of methyl protons (at δ = 0.87)/total alkyl protons (by ^{1}H NMR integration) of 0.61 were obtained for the higher boiling fraction. An important quantity of these oligomeric products were saturated, as found by GC-IR studies. A low temperature and low ethylene pressure were used due to the high activity of the systems under the described conditions.

Table 2. Oligomerization of ethylene with Ni complexes (5×10^{-6} mol_{Ni}, Al/Ni = 600, activator $Et_3Al_2Cl_3$, 200 mL of dichloromethane)

Comp.	T [°C]	p [bar]	t [min]	yield [g]	TON[a]	Products [%] C4−C6:C8−C16:>C16
6	12	1.3	60[b]	58.8	420 000	57:18:25
8	20	0.6	60[c]	85.1	608 000	68[d]:17:15
9	30	1.0	60[c]	83.6	597 000	71[d]:23:6

[a] TON = turnover number [$mol_{ethene}/mol_{catalyst}$]. − [b] Thereafter no gas uptake. − [c] Thereafter only marginal gas uptake. − [d] >90% butenes.

Conclusion

Several conclusions can be drawn from this study. Firstly, palladium-catalyzed aryl amination is an efficient tool in the preparation of a great variety of 2,2′-bipyridylamine ligands. Secondly, these compounds act as bidentate ligands to stabilize group 10 metal complexes. Thirdly, the nickel complexes are highly active ethylene oligomerization catalysts if activated with $Et_3Al_2Cl_3$.

Experimental Section

Materials and Procedures: All reagents were obtained commercially and used as supplied. Column chromatography was performed on silica gel 60 (0.063−0.200 mm) from Merck. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in dried Schlenk-type glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line, or in an argon-filled glovebox (mBraun labmaster 130) with a high-capacity recirculator (<1.5 ppm O_2). Solvents (Aldrich) and NMR solvents (Cambridge Isotope Laboratories all 99 atom% D) were freshly distilled from sodium tetraethylaluminate.

Physical Measurements: NMR spectra were recorded on a BRUKER ARX 400 instrument with a variable temperature unit. ^1H and ^{13}C chemical shifts were referenced to the solvent resonances and reported relative to TMS. Elemental analysis were performed with a Leco CHNS-932 elemental analyzer. X-ray diffraction data were collected on a STOE-IPDS diffractometer using graphite monochromated Mo-K_α radiation. The crystals were mounted in a cold nitrogen stream. The structure was solved by direct methods (SHELXS-86)[19] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[20] SCHAKAL was used for structure representations.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159116 (**7**), CCDC-159117 (**8**) and CCDC-159118 (**10**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of the Ligands

Synthesis of 1: 2,6-Diisopropylaniline (0.89 g, 5.0 mmol), 2-chlorolepidine (1.78 g, 10.0 mmol), 1,3-bis(diphenylphosphanyl)propane (25 mg, 6×10^{-5} mol), dipalladiumtris(benzylideneacetone) (28 mg, 3×10^{-5} mol) and sodium *tert*-butoxide (1.20 g, 12.5 mmol) were combined in a Schlenk vessel under argon. Toluene (20 mL) was then added and the mixture stirred at 80 °C for 120 h. After cooling, the resulting mixture was taken up with diethyl ether and washed twice with a saturated aqueous sodium chloride solution. The organic solution was dried over sodium sulfate and the solvent removed in a rotary evaporator. The resulting dark red oil was subjected to fast column chromatography over silica gel (eluent: petroleum ether/ethyl acetate, 10:1 v/v) to remove polar by-products. Recrystallization of the resulting semi-solid oil from *n*-hexane yielded 0.82 g (37%) of colorless needles. − ^1H (C_6D_6): δ = 7.95 (d, 2 H), 7.62 (d, 2 H), 7.45 (s, 2 H), 7.36 (m, 3 H), 7.29 (m, 2 H), 7.17 (m, 2 H), 3.57 (hept, J = 6.7 Hz, 2 H), 2.19 (s, 6 H), 1.11 (d, J = 6.7 Hz, 12 H). − ^{13}C NMR(C_6D_6): δ = 156.4, 148.7, 147.9, 144.5, 139.0, 129.3, 129.0, 125.9, 124.8, 124.2, 123.8, 116.9, 29.1, 24.1, 18.7. − $C_{32}H_{33}N_3$ (459.62): calcd. C 83.62, H 7.24, N 9.14; found C 82.98, H 7.54, N 9.26.

Synthesis of 2: 2-(Benzylamino)-4-methylpyridine (2.77 g, 14 mmol), 2-chloro-4-methyl-quinoline (2.5 g, 14.1 mmol), 1,3-bis(diphenylphosphanyl)propane (0.23 g, 0.56 mmol), dipalladiumtris(benzylideneacetone) (0.26 g, 0.28 mmol) and sodium *tert*-butoxide (4.06 g, 42.2 mmol) were combined in a Schlenk vessel under argon. Toluene (40 mL) was then added and the resulting brown mixture stirred at 70 °C for 40 h. After cooling to room temperature the solvent was evaporated in vacuo into a dry-ice-cooled trap. The resulting slurry was taken up with diethyl ether and the solution washed three times with a saturated aqueous sodium chloride solution. The organic solution was dried over magnesium sulfate, and the solvent removed on a rotary evaporator. The resulting brown oil was purified by column chromatography over silica gel (eluent: petroleum ether/ethyl acetate, 4:1 v/v). Yield: 4.38 g (91%) of a yellow oil, which didn′t solidify even after drying in vacuum and prolonged standing. − ^1H NMR (C_6D_6): δ = 8.41 (d, 1 H), 8.24 (d, 1 H), 7.83 (d, 2 H), 7.70 (dd, 1 H), 7.56 (td, 1 H), 7.31 (s, 2 H), 7.29 (s, 1 H), 7.08 (s, 1 H), 6.50 (d, 1 H), 6.06 (s, 2 H, benzyl. CH_2), 2.21 (d, J = 7.0 Hz, 3 H, Lp-CH_3), 1.91 (s, 3 H, py-CH_3). − ^{13}C NMR (C_6D_6): δ = 157.63, 155.72, 148.13, 147.90, 147.69, 143.93, 140.13, 135.64, 128.93, 128.38, 127.44, 126.37, 125.16, 123.38, 123.25, 118.83, 115.75, 115.43, 51.31, 20.29, 18.12. − $C_{23}H_{21}N_3$ (339.43): calcd. C 81.38, H 6.24, N 12.38; found C 81.32, H 6.21, N 12.15.

Synthesis of 3: 2-(Benzylamino)-6-methylpyridine (1.49 g, 7.5 mmol), 2-chloro-4-methyl-quinoline (1.33 g, 7.5 mmol), 1,3-bis(diphenylphosphanyl)propane (0.124 g, 0.30 mmol), dipalladiumtris(benzylideneacetone) (0.140 g, 0.153 mmol) and sodium *tert*-butoxide (0.96 g, 10 mmol) were combined in a Schlenk vessel under argon. Dry toluene (25 mL) was then added and the resulting brown mixture stirred at 70 °C for 40 h. After cooling, the solvent was removed on a rotary evaporator, the resulting slurry taken up with diethyl ether and the solution washed three times with a saturated aqueous sodium chloride solution. The organic solution was dried over magnesium sulfate and the solvents evaporated. The resulting brown oil was purified by fast column chromatography over silica gel (eluent: petroleum ether/ethyl acetate, 5:1 v/v). Yield: 2.42 g (7.13 mmol, 95%) of a yellow highly viscous oil, which didn′t solidify even after drying in vacuum and prolonged standing. − ^1H NMR (C_6D_6): δ = 2.00 (s, 3 H), 2.30 (s, 3 H), 5.53 (s, 2 H, benzyl. CH_2), 6.34 (d, 1 H), 6.79 (d, 1 H), 6.9 (t, 1 H), 6.95 (t, 1 H), 7.05 (m, 1 H), 7.07 (m, 1 H), 7.10 (m, 4 H), 7.33 (dt, 1 H), 7.48 (dd, 1 H), 7.59 (m, 2 H), 8.01 (m, 1 H). − ^{13}C NMR (C_6D_6): δ = 157.9, 157.4, 156.4, 148.6, 144.5, 140.9, 137.7, 129.6, 129.1, 128.2, 127.1, 125.8, 124.1, 124.0, 117.3, 116.1, 112.9, 51.8, 24.7, 18.8. −

$C_{23}H_{21}N_3$ (339.43): calcd. C 81.38, H 6.24, N 12.38; found C 81.05, H 6.00, N 12.31.

Synthesis of 4: 2-Pyridylaniline (1.702 g, 10 mmol), 2-chloro-4-methylquinoline (1.78 g, 10 mmol), 1,3-bis(diphenylphosphanyl)-propane (0.165 g, 0.40 mmol), dipalladiumtris(benzylideneacetone) (0.18 g, 0.20 mmol) and sodium *tert*-butoxide (1.35 g, 14 mmol) were combined in a Schlenk vessel under argon. Toluene (30 mL) was then added and the dark green mixture stirred at 70 °C for 54 h. Workup as for **3**, but with dichloromethane solvent. The raw product was isolated as a dark brown solid, which was recrystallized from absolute ethanol. Yield: 1.57 g (5.04 mmol, 50%) of yellow crystalline needles. – ^{1}H (C_6D_6): δ = 1.98 (d, 3 H, CH_3), 6.64 (m, 1 H), 6.93 (m, 2 H), 7.0–7.1 (m, 6 H), 7.18 (m, 2 H), 7.24 (ddd, 1 H), 7.48 (dd, 1 H), 7.89 (dd, 1 H), 8.15 (m, 1 H). – ^{13}C (C_6D_6): δ = 157.7, 156.1, 147.6, 147.2, 144.7, 143.8, 135.9, 128.7, 128.4, 128.2, 127.7, 125.1, 124.8, 123.4, 122.7, 117.2, 116.9, 116.8, 17.5. – $C_{21}H_{17}N_3$ (311.38): calcd. C 81.00, H 5.50, N 13.49, found C 81.00, H 5.74, N 13.27.

Synthesis of 5: 2-Bromopyridine (2.53 g, 16.0 mmol), (*S*)-1-phenylethylamine (0.97 g, 8.00 mmol), $Pd_2(DBA)_3$ (0.18 g, 0.20 mmol, 4 mol % Pd), 1,3-bis(diphenylphosphanyl)propane (0.16 g, 0.39 mmol), sodium *tert*-butoxide (1.34 g, 13.9 mmol) and 50 mL of toluene were combined in a Schlenk vessel. The mixture was stirred at 70 °C for 36 h. After cooling to room temperature the solvent was evaporated in vacuo into a dry-ice-cooled trap. Ether (50 mL) and water (50 mL) were added to the reaction mixture and, after separation, the organic phase was extracted twice with a saturated aqueous sodium chloride solution. The solution was dried over magnesium sulfate and the solvent removed on the rotary evaporator. Vacuum distillation at 150 °C/0.1 mbar yielded 1.85 g (84%) of a colorless oil. – ^{1}H NMR (C_6D_6): δ = 1.47 (d, *J* = 6.7 Hz, 3 H, CH_3), 4.64 (quint, *J* = 6.7 Hz, 1 H, CH), 6.08–6.12 (m, 2 H), 6.43–6.47 (m, 2 H), 7.13–7.17 (m, 2 H), 7.20–7.31 (m, 5 H), 7.80–8.00 (m, 2 H). – ^{13}C NMR (C_6D_6): δ = 24.3 (CH_3), 54.6 (CH), 107.2, 117.3, 117.9, 127.8, 128.7, 137.9, 145.2, 148.8, 156.2. – $C_{18}H_{17}N_3$ (275.35): calcd. C 78.52, H 6.22, N 15.26; found C 78.37, H 6.45, N 15.31.

Synthesis of the Metal Complexes

Synthesis of 6: [$NiBr_2$(DME)] (0.23 g, 0.74 mmol) was suspended in 5 mL dichloromethane. A solution of **1** (0.34 g, 0.76 mmol) in 5 mL dichloromethane was then added, the color of the solution changing to a deep purple. After standing overnight the solution was filtered and the grey residue washed with 10 mL of dichloromethane. 10 mL of toluene was then added to the solution and the solvents were evaporated until about 8 mL of toluene remained. After some days of standing crops of purple crystals precipitated, and these were separated and washed with 5 mL of toluene. Yield: 0.31 g (54%). – ^{1}H NMR ($CDCl_3$): δ = 12.70 (br. s), 7.25–7.40 (m), 7.13–7.22 (m), 2.98 (s), 2.37 (s), 1.46 (s), 1.16 (d). – ^{13}C NMR ($CDCl_3$): δ = 142.9, 133.6, 129.5, 128.7, 125.8, 123.4, 121.9, 116.8, 24.7. The NMR spectra obtained were rather broad due to the paramagnetism of the Ni. – $C_{39}H_{41}Br_2N_3Ni$ (**5**·toluene: 770.26): calcd. C 60.81, H 5.37, N 5.46; found C 61.17, H 5.21, N 5.42.

Synthesis of 7: Compound **2** (0.125 g, 0.37 mmol) was dissolved in 3 mL of dichloromethane and added to [$PdCl_2$(COD)] (0.105 g, 0.37 mmol, 1 equiv.) in a Schlenk vessel. After a week orange crystals separated from the solution, and these were used directly for an X-ray analysis. In a separate run, the solvent was removed with a syringe under argon, the crystals were washed twice with 1 mL portions of diethyl ether and dried in vacuum to yield 0.11 g (49%) of product. The crystals appeared to lose dichloromethane on vacuum treatment: the X-ray analysis showed dichloromethane, whereas the elemental analysis of the material from the second run showed none. – ^{1}H (CD_2Cl_2): δ = 9.37 (d, *J* = 8.4 Hz, 1 H), 8.60 (d, *J* = 7.4 Hz, 1 H), 7.90 (d, 2 H), 7.81 (m, 2 H), 7.57 (dt, *J* = 1.5, *J* = 8.4 Hz, 1 H), 7.43 (t, *J* = 7.4 Hz, 2 H), 7.31 (br. t, *J* = 7.5 Hz, 1 H), 7.16 (s, 1 H), 7.03 (m, 2 H), 5.45 (m, 2 H, N–CH_2), 2.66 (s, 3 H), 2.36 (s, 3 H). – $C_{23}H_{21}Cl_2N_3Pd$ (516.76): calcd. C 49.51, H 3.79, N 7.53; found C 49.50, H 3.81, N 7.59. – ^{13}C NMR (CD_2Cl_2): δ = 151.8, 150.3, 149.8, 144.5, 133.1, 130.1, 129.7, 128.5, 127.5, 126.8, 126.0, 125.6, 122.2, 121.8, 114.9, 113.0, 53.9, 28.7, 18.5.

Synthesis of 8: A solution of **3** (0.34 g, 1 mmol) in 10 mL of dichloromethane was added to [$NiBr_2$(DME)] (0.31 g, 1 mmol) in a Schlenk vessel, resulting in a purple solution. After 4 days at room temperature the solution was filtered and the remaining solid washed with three 5 mL portions of dichloromethane. The washings were added to the filtrate. The combined solution was layered with 15 mL of diethyl ether and kept for one week at room temperature. The solvent was then removed from the resulting purple prismatic crystals, which were washed with two 10 mL portions of diethyl ether. Yield: 0.32 g (0.57 mmol, 57%). – ^{1}H ($CDCl_3$): δ = (all broad singlets due to the paramagnetism of the Ni) 11.16 (0.3 H), 10.50 (0.8 H), 7.17 (3 H), 7.02 (1 H), 6.88 (2 H), 6.17/6.02 (4 H), 2.59 (1 H), 1.40 (1 H), 0.00 (12 H). – $C_{23}H_{21}Br_2N_3Ni$ (557.93): calcd. C 49.51, H 3.79, Br 28.64, N 7.53; found C 49.50, H 3.81, Br 28.45, N 7.59.

Synthesis of 9: [$NiBr_2$(DME)] (0.30 g, 0.9 mmol) was suspended in 5 mL of THF and a warm solution of **4** (0.28 g, 0.9 mmol) in 5 mL of THF was added in four portions with a syringe. A purple solid precipitated after 5 min. The next day, filtration yielded a purple, microcrystalline solid, which was dried in vacuo. The yield was not determined. For recrystallisation, a small amount was dissolved in 5 mL hot dichloromethane, cooled to room temperature and layered with 3 mL of diethyl ether. Again, only a microcrystalline powder was obtained.^{1}H ($CDCl_3$): δ = (all broad due to the paramagnetism of the Ni) 12.4 (br. s, 2 H), 8.8 (s, 1 H), 8.35 (d, 1 H), 7.97 (m, 2 H), 7.7 (m, 7 H), 7.54 (m, 1 H), 6.83 (br. s, 2 H), 6.65 (br. s, 5 H), 6.53 (s, 1 H), 2.67 (s, 3 H). – $C_{21}H_{17}Br_2N_3Ni$ (M_w = 529.88 g/mol): calcd. C 47.60, H 3.23, Br 30.16, N 7.93; found C 47.45, H 3.21, Br 29.39, N 7.74.

Synthesis of 10: [$PdCl_2$(COD)] (0.13 g, 0.47 mmol) was added to a solution of **5** (0.14 g, 0.50 mmol) in 30 mL of dichloromethane. The mixture was stored at –78 °C for crystallization. Filtration yielded 0.13 g (61%) of orange crystals. – ^{1}H NMR (C_6D_6): δ = 1.73 (d, *J* = 6.4 Hz, 3 H, CH_3), 5.44 (q, *J* = 6.4 Hz, 1 H, CH), 6.88–6.94 (m, 2 H), 7.15–7.19 (m, 2 H), 7.25–7.29 (m, 3 H), 7.43–7.49 (m, 1 H), 7.53–7.58 (m, 2 H), 7.78–7.85 (m, 1 H), 8.64–8.85 (m, 2 H). – ^{13}C NMR (C_6D_6): δ = 22.6 (CH_3), 59.7 (CH), 118.3, 119.0, 120.2, 120.8, 126.5, 127.3, 128.5, 138.7, 139.7, 140.2, 150.3, 151.2, 151.6, 152.5. – $C_{18}H_{17}Cl_2N_3Pd$ (452.68): calcd. C 62.14, H 5.05, N 7.51; found C 62.08, H 5.21, N 7.33.

Polymerization Studies: The oligomerization of ethylene (99.95%) was carried out in a batch process using a 1-L glass autoclave fitted with a gas inlet, dosing device, pressure gauge, and a magnetically driven and continuously regulated paddle stirrer with a hollow shaft (0 to 800 rpm). The solvent, dichloromethane, was dried by standard methods and distilled under argon. $Et_3Al_2Cl_3$ was used as supplied (Aldrich). 5×10^{-3} mmol of the Ni complexes were dissolved in 200 mL of dichloromethane and introduced under inert conditions into the autoclave. After the temperature of the mixture had been adjusted and $Et_3Al_2Cl_3$ had been added as a cocata-

lyst the oligomerization reaction started at an internal pressure as described in Table 2. After a reaction time of 1 hour the contents of the autoclave were decomposed by addition of methanolic HCl. The oligomers were analyzed by GC, GC-IR and NMR spectroscopy.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (Heisenberg-Stipendium for RK), the Bundesministerium für Bildung und Forschung, the Fonds der Chemischen Industrie, the Max-Planck-Gesellschaft, the Karl-Winnacker-Stiftung, Aventis R & D GmbH, Degussa-Hüls AG, SKW Trostberg AG, Grünenthal GmbH, SynTec Wolfen GmbH and Organica Wolfen GmbH is gratefully acknowledged.

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Received March 14, 2001
[I01097]