

Alternative Coordination Modes in Palladium(II)-Diimino-Bispyridine Complexes with an Axially Chiral Biphenyl Backbone

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The chiral biphenyl-bridged diimino-bispyridine ligands *N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)-diimine (**1**) and *N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)bis[(6-methyl-2-pyridyl)methyl]diimine (**2**) react with Pd(COD)Cl₂ to give, depending on the reaction conditions, either mono- or binuclear PdCl₂ complexes. In the binuclear complex **1**-(PdCl₂)₂, the Pd nuclei are held at a distance of 3.37 Å by the ligand backbone. *N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)bis[(5-methyl-2-furyl)methyl]diimine (**3**), with furyl instead of pyridyl rings, gives mononuclear, C₂-symmetric complexes only. Reactions of [Pd(NCCH₃)₄]²⁺(BF₄⁻)₂ with ligand **1** or **3** give the C₂-symmetric cations [1-Pd]²⁺ or [3-Pd(NCCH₃)₂]²⁺,

respectively, as their BF₄⁻ salts. Solid-state structures of the chloride complexes **1**-PdCl₂, **1**-(PdCl₂)₂ and **3**-PdCl₂, and of the complex cations [1-Pd]²⁺ and [3-Pd(NCCH₃)₂]²⁺ with tetradentate and bidentate ligand coordination, respectively, all show square-planar coordination, with some distortion toward tetrahedral geometry due to the twisted biaryl-backbone. Preliminary observations on norbornene polymerization with the catalysts **1**-PdCl₂/MAO, **2**-PdCl₂/MAO and [(3-Pd(NCCH₃)₂)₂]²⁺ suggest that a certain degree of stereoregularity of the polymers is induced by these chiral catalysts.

Introduction

Considerable attention has lately been focused on binuclear organometallic compounds, based on expectations that their reactivity in synthesis and catalysis may differ significantly from that of analogous mononuclear species.^[1] Interactions between closely adjacent metal centers might cause increased reaction rates or transformations not occurring with monometallic species, as was recently shown for copolymerization of styrene and ethene by binuclear titanocene complexes.^[2] The distance between two metal centers and their orientation to each other can be important for catalytic performance, as had been noted for binuclear rhodium hydroformylation catalysts^[3] and for palladium complexes that catalyze hydration reactions.^[4] Additional oxidation states might also be accessible in binuclear complexes as a result of stabilizing metal-metal interactions.^[5]

Late transition metal complexes with nitrogen-based ligands have found a wide range of applications in homogeneous catalysis including polymerization of olefins or acrylates as well as hydrogenation reactions.^[6] Pyridylimine-Pd^{II} chelates as dendrimeric complexes and binuclear Pd^{II} complexes with long aliphatic spacers have recently been de-

scribed as effective catalyst precursors for Heck coupling^[7] and for ethene polymerization,^[8] respectively, as well as with shorter chiral spacers to produce optically active polyketones.^[9] Palladium complexes with chiral bidentate bis-(oxazoline) ligands have been shown to be efficient in asymmetric allylic alkylation,^[10] while biaryl Schiff base Cu complexes catalyze the aziridination of alkenes.^[11]

With a structurally rigid 6,6'-disubstituted biaryl ligand backbone, the configuration of the ligand is fixed and its axial chirality can efficiently be transmitted to the stereotopicity of the active site.^[12] Biphenyl-bridged ligands form, in general, mononuclear complexes,^[13] but binuclear complexes, e. g. with Cu^{II}, have also been reported.^[14] Tetradentate N₄, N₂O₂ and N₂P₂ ligands are known to form both mono- and binuclear Pd^{II} complexes,^[15,16,17] but only few of these have chiral biaryl backbones.^[16a,17c]

Since cationic Pd^{II} complexes bearing diimine ligands with bulky substituents have been discovered to catalyze copolymerizations of α-olefins with functional vinyl monomers,^[18] significant amounts of research have been aimed at tuning the electronic and steric properties of these ligands. Bulky aryls disfavor associative displacement and chain transfer reactions by steric protection of the electrophilic metal center; ligands with labile donor atoms like oxygen or sulfur in their side arms might likewise hinder β-H elimination by temporarily occupying a vacant site on the metal center.^[19] Interesting features might thus be expected for C₂-symmetric Pd^{II} diimine complexes with side-arm donors bridged by a chiral ligand backbone.

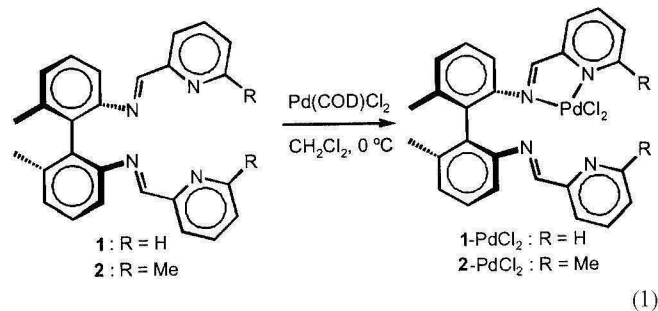
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In previous contributions, we have studied complexes of tetradentate 6,6'-dimethylbiphenyl-based ligands with metals such as Zr, Fe, Co or Cr in regard to their structures and catalytic activities.^[20] In this work, we extend these studies to mono- and bimetallic Pd^{II} complexes bearing chiral diimino ligands with a biphenyl backbone.

Results and Discussion

Ligands **1**, **2** and **3** were prepared, as described earlier,^[20] by imine condensation of *N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)diamine with the required aldehydes. Reaction of *N,N'*-(6,6'-dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)di-imine (**1**) with one equivalent of Pd(COD)Cl₂ at 0 °C gave 1-PdCl₂, which precipitated from the reaction mixture in almost quantitative yield [Equation (1)]. When the reaction was repeated in an NMR tube, starting at 0 °C and continuing at room temperature, the rate of the reaction was found to be quite fast; 95% of the Pd(COD)Cl₂ was consumed after 30 minutes. Ligand **2** likewise reacted readily with Pd(COD)Cl₂ under similar reaction conditions, but 2-PdCl₂ was isolated with lower yield due to its higher solubility.



A single-crystal X-ray structure analysis of 1-PdCl₂ confirms an approximately square-planar coordination of the Pd^{II}*cis*-dichloro unit to one of the pyridylimine moieties of ligand **1** (Figure 1), which thus forms a five-membered pyridylimine chelate, with Pd–N and Pd–Cl distances (Table 1) close to values reported for similar complexes.^[15–17] In the solid state, the non-coordinated pyridylimine moiety lies on the backside of the biphenyl bridge, pointing away from the PdCl₂ unit.

The ¹H NMR spectrum of 1-PdCl₂ in [D₆]DMSO solution reveals, instead of two singlets expected for the non-equivalent methyl groups in 6- and 6'-positions of the biaryl backbone, three sharp CH₃ signals at δ = 1.82, 2.02 and 2.23 ppm with an integral ratio of 1:2:1.^[21] The occurrence of these three CH₃ signals, as well as non-integer ratios for the aromatic proton signal integrals (see Experimental section), indicate the presence of two isomers in [D₆]DMSO solution of 1-PdCl₂, each with one Pd-coordinated and one non-coordinated ligand moiety. Related phenomena in connection with possible isomers of 1-(PdCl₂)₂ will be discussed below.

For 2-PdCl₂ in [D₆]DMSO solution, however, only two singlets are observed, in agreement with the presence of a

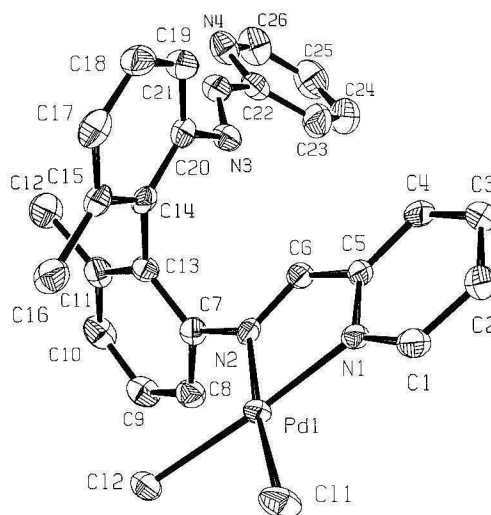
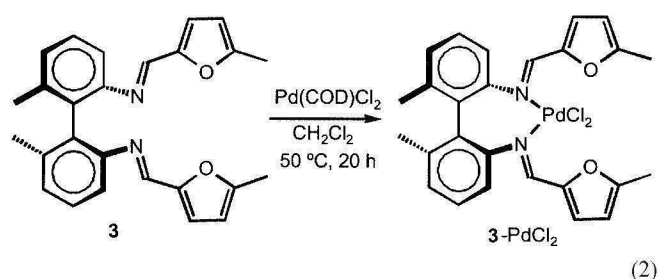


Figure 1. Crystal structure of 1-PdCl₂ (ORTEP plot, thermal ellipsoids drawn at 50% probability, H atoms and CH₂Cl₂ solvent molecules omitted for clarity).

Table 1. Selected bond lengths (Å) and angles [°] for 1-PdCl₂ (c.f. Figure 1).

Pd(1)–N(1)	2.022(3)	N(1)–Pd(1)–N(2)	80.38(12)
Pd(1)–N(2)	2.037(3)	N(1)–Pd(1)–Cl(2)	175.56(9)
Pd(1)–Cl(2)	2.2893(11)	N(2)–Pd(1)–Cl(2)	95.26(9)
Pd(1)–Cl(1)	2.2916(11)	N(1)–Pd(1)–Cl(1)	93.28(9)
		N(2)–Pd(1)–Cl(1)	173.61(9)
		Cl(2)–Pd(1)–Cl(1)	91.06(4)

Pd-coordinated and an uncoordinated ligand moiety, for the methyl groups at the biphenyl bridge (1.96 and 2.05 ppm), for the methyl groups in 6-position of each pyridyl ring (2.47 and 2.80 ppm) and for the imine protons (8.21 and 8.69 ppm).



With ligand **3**, where the side-arm pyridyl groups are replaced by furyl rings, a significantly longer reaction time (20 h) was required for complex formation with Pd(COD)-Cl₂ [Equation (2)]. As shown by the crystal structure of 3-PdCl₂ (Figure 2, Table 2), ligand **3** is bound in a bidentate manner again. Here, however, the two imino nitrogens form a seven-membered chelate with the *cis*-dichloro Pd unit to give an approximately square-planar and C₂-symmetric geometry. Due to the dihedral angle of 67° between the phenyl rings of the biphenyl bridge, the ligand plane at the Pd center is somewhat distorted, with an angle of 5.9(2)° spanned by the planes Cl1–Pd–N1 and Cl2–Pd–N2. The furyl oxy-

gen atoms are located at non-bonding distances of 5.0 and 5.1 Å from the Pd center, from which the side arms are pointing away.^[22] The preference of the Pd center for N over O ligand atoms obviously overrides its preference for five-membered over seven-membered chelate rings to such an extent that a C_2 -symmetric geometry becomes favored for 3-PdCl_2 over the C_1 -symmetric structures of 1-PdCl_2 and 2-PdCl_2 .

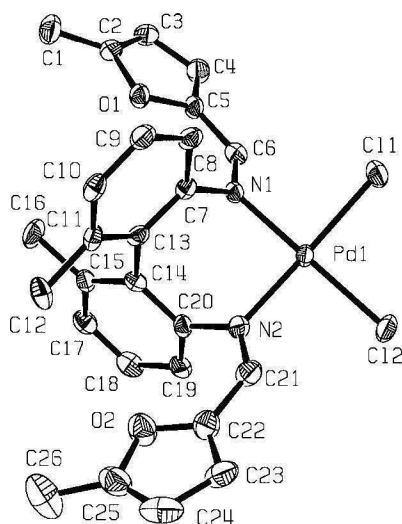
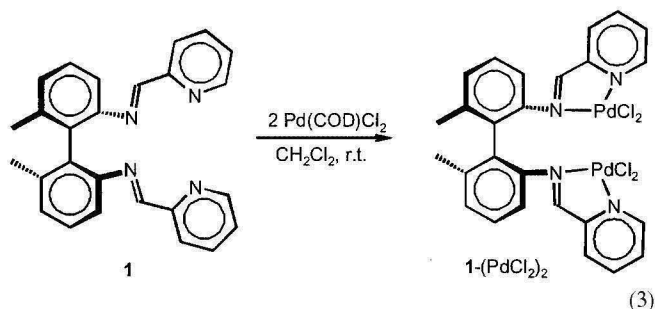


Figure 2. Crystal structure of 3-PdCl_2 (ORTEP plot, thermal ellipsoids drawn at 50% probability, H atoms and CH_2Cl_2 solvent molecule omitted for clarity).

Table 2. Selected bond lengths (Å) and angles [°] for $3\text{-PdCl}_2 \cdot \text{CH}_2\text{Cl}_2$ (c.f. Figure 2).

Pd(1)–N(1)	2.029(3)	N(1)–Pd(1)–N(2)	90.26(11)
Pd(1)–N(2)	2.057(3)	N(1)–Pd(1)–Cl(1)	89.26(8)
Pd(1)–Cl(1)	2.2944(9)	N(2)–Pd(1)–Cl(1)	174.45(9)
Pd(1)–Cl(2)	2.2973(9)	N(1)–Pd(1)–Cl(2)	177.96(9)
		N(2)–Pd(1)–Cl(2)	90.17(8)
		Cl(1)–Pd(1)–Cl(2)	90.51(4)

CDCl_3 solutions of 3-PdCl_2 give ^1H NMR spectra in agreement with an apparent C_2 symmetry, with a singlet at $\delta = 1.88$ ppm due to the two methyl groups in the biphenyl backbone, another singlet at $\delta = 2.18$ ppm due to the methyl groups at the furyl rings, and a singlet at $\delta = 8.32$ ppm assigned to the imine protons. These signals are accompanied, however, by a set of smaller signals located slightly up-field, at $\delta = 1.82$, 2.12 and 8.29 ppm, which integrate to ratios of ca. 1:10 relative to the respective main peaks. The observation of this additional signal set in solutions of 3-PdCl_2 would indicate that some minor isomer is present, in addition to the structure represented in Figure 2. From our data it is not clear, which alternative geometry prevails in this isomer, whether (and how) e. g. furyl oxygen atoms might be coordinated to the Pd^{II} center.^[19]



In 1-PdCl_2 one half of ligand **1** remains available for further coordination and provides a possibility for the preparation of bimetallic complexes. The dipalladium complex $1\text{-(PdCl}_2)_2$ was indeed isolated in 97% yield when ligand **1** was treated with two equivalents of $\text{Pd}(\text{COD})\text{Cl}_2$ at room temperature [Equation (3)].^[23] In the solid-state structure of binuclear $1\text{-(PdCl}_2)_2$, one PdCl_2 unit is coordinated, as expected, to each of the biphenyl-bridged pyridylimine moieties (Figure 3, Table 3). The two square-planar N_2PdCl_2 units are almost parallel to each other, stacking under an angle of $7.40(2)^\circ$. Viewed along the Pd–Pd axis, the two PdCl_2 units are rotated by an angle of 104.9° relative to each other. The Pd(1)–Pd(2) distance of 3.37 Å is in the range of quite a number of binuclear Pd^{II} complexes with relatively short (2–4 atom) bridging ligands.^[24] Apparently a similarly favorable situation for a close $\text{Pd}^{\text{II}} \cdots \text{Pd}^{\text{II}}$ contact is created by the preference of the biaryl bridge for a twist angle of ca. 70° . In addition, some attractive interaction between Pd–Cl dipoles might contribute to keep the Pd centers at a distance close to the sum of their van-der-Waals radii.

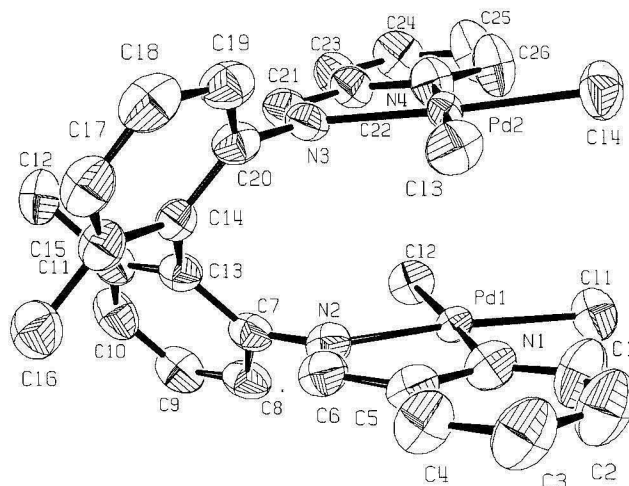


Figure 3. Crystal structure of $1\text{-(PdCl}_2)_2$ (ORTEP plot, thermal ellipsoids drawn at 50% probability, H atoms and CH_2Cl_2 solvent molecules omitted for clarity).

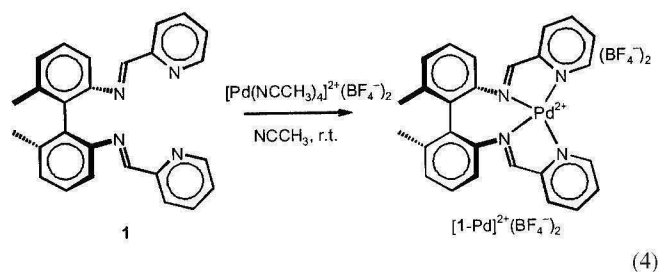
In the ^1H NMR spectra of $1\text{-(PdCl}_2)_2$ in $[\text{D}_6]\text{DMSO}$ solution, the methyl groups at the biphenyl bridge give rise to a sharp signal at $\delta = 2.02$ ppm and a broader one at $\delta = 2.12$ ppm, each corresponding to 3 protons; the 6-posi-

Table 3. Selected bond lengths (Å) and angles [°] for $1\text{-PdCl}_2 \cdot 2\text{CH}_2\text{Cl}_2$ (c.f. Figure 3).

Pd(1)–N(1)	2.034(6)	N(1)–Pd(1)–N(2)	79.8(3)
Pd(1)–N(2)	2.048(6)	N(1)–Pd(1)–Cl(1)	94.4(2)
Pd(1)–Cl(1)	2.292(2)	Cl(1)–Pd(1)–Cl(2)	88.56(7)
Pd(1)–Cl(2)	2.2930(19)	N(2)–Pd(1)–Cl(1)	173.42(19)
		N(1)–Pd(1)–Cl(2)	176.94(19)
		N(2)–Pd(1)–Cl(2)	97.31(18)
		C(1)–N(1)–Pd(1)	127.1(6)
		C(5)–N(1)–Pd(1)	113.7(5)
Pd(2)–N(3)	2.044(6)	N(3)–Pd(2)–N(4)	80.3(2)
Pd(2)–N(4)	2.056(6)	N(3)–Pd(2)–Cl(4)	173.60(18)
Pd(2)–Cl(3)	2.300(2)	N(3)–Pd(2)–Cl(3)	97.19(18)
Pd(2)–Cl(4)	2.281(2)	N(4)–Pd(2)–Cl(4)	93.44(19)
		Cl(4)–Pd(2)–Cl(3)	89.04(8)

tioned protons of the pyridyl rings likewise appear as two doublets at 8.83 and at $\delta = 9.04$ ppm representing one proton each and the other aromatic and imine signals are also grouped in a manner incompatible with a C_2 -symmetric complex. These observations can be explained either by the occurrence of two diastereomers, e.g. *meso*- and *rac*-like conformers of the two complex moieties, in a ratio of ca. 1:1 or by some nonequivalence of the two complex moieties in solution, caused e.g. by co-ordination of a solvent molecule to one of the Pd centers. Our data do not allow us to estimate the lifetimes of isomers of this kind.

The *cis*- PdCl_2 unit considered so far obviously favors formation of a five-membered pyridyl-imine chelate over that of a seven-membered diimine chelate; complexes such as 1-PdCl_2 or 2-PdCl_2 are thus of C_1 symmetry. In order to synthesize complexes which fully exploit the axialsymmetry inherent in the biaryl backbone to generate C_2 -symmetric complexes suitable for asymmetric catalysis,^[25] we have sought to induce tetradentate coordination of ligands **1** and **2** with formation of cationic complexes by use of the more electron-deficient Pd precursor $[\text{Pd}(\text{NCCH}_3)_4]^{2+}(\text{BF}_4^-)_2$ [Equation (4)].



Reaction of ligand **1** with one equivalent of $[\text{Pd}(\text{NCCH}_3)_4]^{2+}(\text{BF}_4^-)_2$ in acetonitrile at room temperature gave the ion pair $[1\text{-Pd}]^{2+}(\text{BF}_4^-)_2$ in high yield. The expected tetradentate coordination of ligand **1** in $[1\text{-Pd}]^{2+}(\text{BF}_4^-)_2$ was verified by single-crystal structure determination (Figure 4). The Pd center forms an approximately C_2 -symmetric seven-membered chelate ring with the biphenyl-bridged imine nitrogens and one five-membered che-

late ring with each of the pyridylimine moieties, with Pd–N distances (Table 4) in the range reported for other Pd-imino complexes.^[15–17] Due to the dihedral angle of 71° in the 2,2'-dimethyl-substituted biphenyl backbone, the square-planar coordination at the Pd atom shows some tetrahedral distortion, so that the planes N1–Pd–N2 and N3–Pd–N4 span an angle of $12.9(5)^\circ$.^[26]

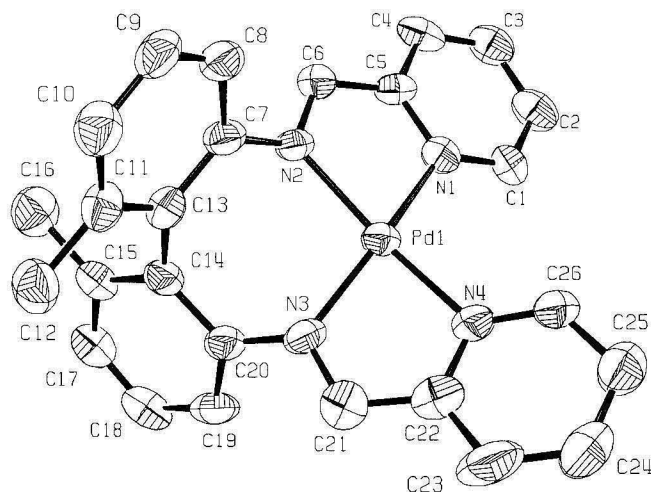


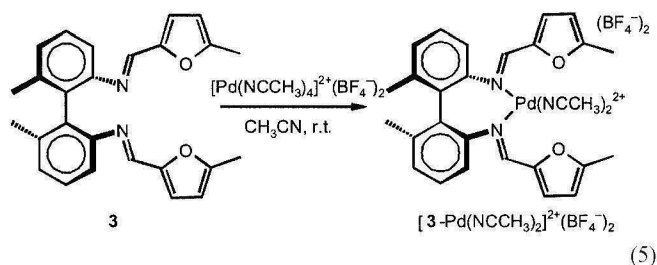
Figure 4. Crystal structure of $[1\text{-Pd}]^{2+}(\text{BF}_4^-)_2$ (ORTEP plot, thermal ellipsoids drawn at 50% probability, H atoms, 0.5 H_2O and BF_4^- omitted for clarity).

Table 4. Selected bond lengths (Å) and angles [°] for $[1\text{-Pd}]^{2+}(\text{BF}_4^-)_2$ (c.f. Figure 4).

Pd(1)–N(3)	2.012(7)	N(3)–Pd(1)–N(2)	99.0(3)
Pd(1)–N(2)	2.017(6)	N(3)–Pd(1)–N(4)	80.4(3)
Pd(1)–N(4)	2.021(7)	N(2)–Pd(1)–N(4)	161.7(3)
Pd(1)–N(1)	2.044(7)	N(3)–Pd(1)–N(1)	164.5(3)
		N(2)–Pd(1)–N(1)	79.7(3)
		N(4)–Pd(1)–N(1)	105.6(3)

^1H NMR spectra in CD_3CN solution indicate, again, some deviations of the cation $[1\text{-Pd}]^{2+}$ from the approximate C_2 symmetry found in the solid state. The 6,6'-positioned methyl groups of the ligand backbone give rise to a multiplet with two maxima at $\delta = 1.72$ and 1.76 ppm, and the aromatic protons are likewise grouped in multiplets which do not appear to be compatible with an overall C_2 symmetry. Even though we do not have any direct evidence in this regard, we would assume that the equivalence of both halves of the complex molecule might be destroyed, as in the cases discussed above, by coordination of a solvent molecule.

In order to test whether a tetradentate coordination similar to that achieved for ligand **1** might also be accessible for the furyl-substituted ligand **3**,^[27] the latter was likewise reacted with $[\text{Pd}(\text{NCCH}_3)_4]^{2+}(\text{BF}_4^-)_2$ in acetonitrile solution. The reaction proceeded fast and with high yield, but gave, instead of a product with tetracoordinate ligand **3**, $[3\text{-Pd}]^{2+}(\text{BF}_4^-)_2$, the bis(acetonitrile) adduct $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}(\text{BF}_4^-)_2$ [Equation (5)].



In the crystal structure of $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}(\text{BF}_4^-)_2$ (Figure 5, Table 5), square-planar coordination at the cationic Pd center is found to involve two *cis*-positioned acetonitrile ligands and the two imino nitrogen atoms of ligand **3**; as in 3-PdCl_2 , the ligand **3** forms again a seven-membered chelate ring with the Pd center. In distinction to 3-PdCl_2 , however, where the furyl oxygen atoms point away from the Pd center, they are now turned towards the latter and lie rather close to it, in pseudo-axial positions at Pd–O distances of 3.0(1) Å. Some (presumably weak) coordination or dipolar attraction of the furyl oxygen atoms to the Pd^{II} center thus appears to be stabilized by the cationic nature of the metal.^[27,28]

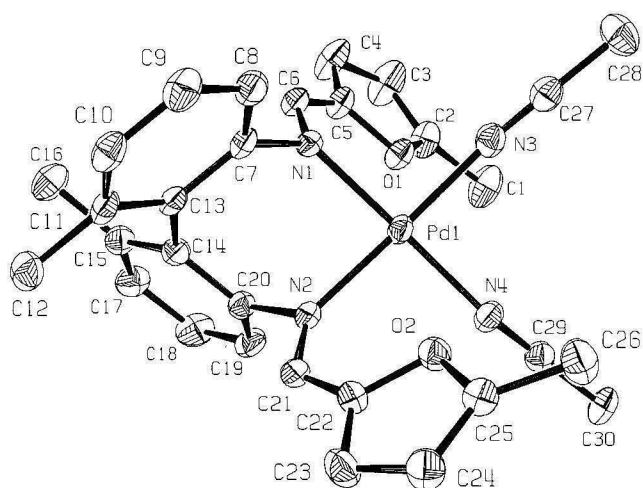


Figure 5. Crystal structure of $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}(\text{BF}_4^-)_2$ (ORTEP plot, thermal ellipsoids drawn at 50% probability, H atoms, CH_3CN solvent molecule and BF_4^- omitted for clarity).

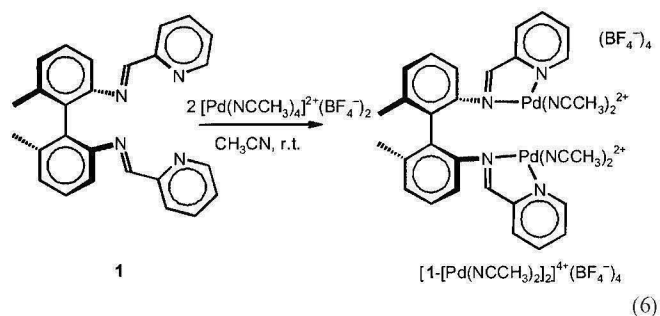
Table 5. Selected bond lengths (Å) and angles [°] for $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}(\text{BF}_4^-)_2$ (c.f. Figure 5).

Pd(1)–N(1)	2.006(2)	N(1)–Pd(1)–N(4)	171.03(8)
Pd(1)–N(4)	2.009(2)	N(1)–Pd(1)–N(2)	86.35(9)
Pd(1)–N(2)	2.016(2)	N(4)–Pd(1)–N(2)	93.37(9)
Pd(1)–N(3)	2.022(2)	N(1)–Pd(1)–N(3)	91.97(9)
		N(4)–Pd(1)–N(3)	89.15(9)
		N(2)–Pd(1)–N(3)	174.21(8)

The ^1H NMR spectrum of $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}$ is entirely in agreement with the overall C_2 symmetry expected from its solid-state structure. Its NCCH_3 ligands and its biphenyl

and furyl methyl substituents give rise to only one singlet signal each, at $\delta = 2.08$, 2.20 and 2.63 ppm, respectively. Apparently, the binding of the furyl groups to the cationic Pd^{II} center, however weak, protects the latter from interaction with a solvent donor, which might otherwise destroy the overall C_2 symmetry of the complex molecule in solution.

Since two nitrogen ligand atoms are sufficient for the formation of a cationic di-acetonitrile complex, ligand **1** was also treated with two equivalents of $[\text{Pd}(\text{NCCH}_3)_4]^{2+}(\text{BF}_4^-)_2$ to prepare the binuclear cationic complex $1\text{-}[\text{Pd}(\text{NCCH}_3)_2]^{2+}_2(\text{BF}_4^-)_4$ [Equation (6)]. The reaction yielded an oily product, the elemental analysis and ^1H NMR spectra of which indicated formation of the expected complex. As no crystals suitable for X-ray diffraction were obtained, it was not possible to study the effect of the increased charges on the mutual arrangement of the metal centers in this binuclear complex.



Preliminary data concerning catalytic activities of the new Pd^{II} complexes described above were obtained with regard to polymerization of norbornene at room temperature.^[29] When activated by addition of methylaluminoxane (MAO), the dichloro complexes 1-PdCl_2 , 2-PdCl_2 and 3-PdCl_2 gave polymers which were insoluble in organic solvents such as trichlorobenzene even at elevated temperatures. The cationic complex $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}(\text{BF}_4^-)_2$ gave, without activation by MAO,^[29] polymers with good solubility, e.g. in toluene or chloroform, in moderate yield. For these polynorbornenes, a molar mass of 33800 g/mol and a polydispersity index of 1.26 were determined. Complex $[1\text{-Pd}]^{2+}(\text{BF}_4^-)_2$, in which the Pd center is bound to all four N atoms of the tetradentate ligand, was found to be inactive for polymerization of norbornene at room temperature.

Decomposition temperatures, determined by thermogravimetric analysis, of the polymers obtained with MAO-activated 1-PdCl_2 , 2-PdCl_2 and 3-PdCl_2 as well as of those obtained with $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}(\text{BF}_4^-)_2$, were found to be exceptionally high (ca. 450 °C), i.e. more than 100 °C higher than that (335 °C) determined for the polymer obtained with $[\text{Pd}(\text{NCCH}_3)_4](\text{BF}_4)_2$.^[29] This might suggest that a certain degree of stereoregularity is induced in the polymer by the chiral ligands of the catalysts $1\text{-PdCl}_2/\text{MAO}$, $2\text{-PdCl}_2/\text{MAO}$, $3\text{-PdCl}_2/\text{MAO}$ and $[3\text{-Pd}(\text{NCCH}_3)_2]^{2+}$.^[30]

Conclusions

Axially symmetric, biphenyl-bridged diimino ligands with additional pyridyl or furyl side arms are highly versatile with respect to Pd^{II} complex formation. Depending on the Pd precursors and the reaction conditions used, mononuclear-bidentate complexes of C₁ or C₂ symmetry, as well as binuclear and mononuclear-tetradentate Pd^{II} complexes can be obtained in a controlled manner and with high yields. Preliminary observations indicate distinctly different properties of cationic species derived from them as norbornene polymerization catalysts.

Experimental Section

All complex preparation and polymerization reactions were performed under argon atmosphere using standard Schlenk techniques. *N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)diamine,^[31] the ligands **1**–**3**^[20] and dichloro(1,5-cyclooctadiene)palladium(II) [Pd(COD)Cl₂]^[32] were prepared as reported earlier. Solvents were dried prior to use by refluxing over and distillation from sodium (hydrocarbons), magnesium (alcohols), P₂O₅ (acetonitrile) or calcium hydride (dichloromethane). Deuterated solvents were dried over 4-Å molecular sieves. All other chemicals were purchased from commercial suppliers and used without further purification. Elemental analyses were performed with an EA 1110 CHNS-O CE instrument. NMR spectra were collected with a Varian Gemini 200 spectrometer. Polymer molar mass and molar mass distributions were measured by gel permeation chromatography (GPC) relative to polystyrene standards.

***N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine-PdCl₂ (1-PdCl₂):** A solution of ligand **1** (0.59 g, 1.52 mmol) and Pd(COD)Cl₂ (0.39 g, 1.38 mmol) in CH₂Cl₂ (25 mL) was stirred at 0 °C. The product started to precipitate as a light yellow powder after 1 h. After stirring for another 20 h at room temperature, the product was filtered, washed with diethyl ether and dried in vacuo. Yield 658 mg, 84%. ¹H NMR (200 MHz, [D₆]DMSO): δ = 1.82, 2.02 and 2.23 (3 lines, 6 H, CH₃), 7.02 (d, *J* = 8.0 Hz, 0.5 H, Ar-*H*), 7.25–7.39 (m, 3.5 H, Ar-*H*), 7.5 (m, 2 H, Ar-*H*), 7.71–7.94 (m, 3.5 H, Ar-*H*), 8.21–8.27 (m, 2.5 H, CH), 8.5 (s, 0.5 H, imine-CH), 8.64–8.71 (m, 1 H, CH), 8.83–8.97 (m, 1.5 H, CH), 8.88 ppm (s, 1 H, imine-CH); elemental analysis (%) calcd. for C₂₆H₂₂Cl₂N₄Pd (567.81): C 55.00, H 3.91, N 9.87; found: C 54.70, H 3.71, N 10.25.

***N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis[(6-methyl-2-pyridyl)methyl]diimine-PdCl₂ (2-PdCl₂):** This complex was prepared in the same manner as described above for complex **1**-PdCl₂. Yield 0.16 g, 50%. ¹H NMR (200 MHz, [D₆]DMSO): δ = 1.96 (s, 3 H, biaryl-CH₃), 2.05 (s, 3 H, biaryl-CH₃ on Pd-coordinated side), 2.47 (s, 3 H, pyridine-CH₃), 2.80 (s, 3 H, pyridine-CH₃ on Pd-side), 6.96 (d, *J* = 8 Hz, 1 H, pyridine-CH), 7.16 (d, *J* = 8 Hz, 1 H, pyridine-CH), 7.24–7.48 (m, 6 H, 1 pyridine-CH and 2 biaryl-CH on non-coordinated side, and 3 Ar-CH on Pd-coordinated side), 7.65–7.73 (m, 2 H, 1 pyridine-CH from Pd-free side and 1 Ar-*H* from Pd-coordinated side), 7.97–8.11 (br., 2 H, Ar-*H* on Pd-side), 8.21 (s, 1 H, imine-CH), 8.69 ppm (br., 1 H, Pd-coordinated imine-CH); elemental analysis (%) calcd. for C₂₈H₂₆Cl₂N₄Pd (595.86): C 56.44, H 4.40, N 9.40; found: C 55.85, H 4.34, N 9.21.

***N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis[(5-methyl-2-furyl)methyl]diimine-PdCl₂ (3-PdCl₂):** Ligand **3** (0.49 g, 1.25 mmol) and Pd(COD)Cl₂ (0.36 g, 1.25 mmol) were refluxed in CH₂Cl₂ (20 mL)

for 20 h. Diethyl ether (20 mL) was added to reaction mixture, which was then filtered and kept at –20 °C. The product was collected as orange crystals by filtration after 24 h. Yield 0.36 g, 50%. ¹H NMR (200 MHz, CDCl₃): δ = 1.88 (s, 6 H, furyl-CH₃), 2.18 (s, 6 H, biaryl-CH₃), 6.01 (d, *J* = 3.6 Hz, 2 H, furyl-CH), 6.16 (d, *J* = 3.2 Hz, 2 H, furyl-CH), 7.09 (d, *J* = 7.8 Hz, 2 H, biaryl-CH), 7.22 (d, *J* = 7.0 Hz, 2 H, biaryl-CH), 7.29 (pt, *J* = 7.6 Hz, 2 H, biaryl-CH), 8.32 ppm (s, 2H imine-CH). Minor isomer: 1.82 (s, biaryl-CH₃), 2.12 (s, furyl-CH₃), 8.29 ppm (s, imine-CH). ¹³C NMR (50 MHz, CDCl₃): δ = 13.9, 18.7, 109.9, 120.3, 124.5, 127.7, 129.3, 129.7, 138.5, 145.9, 146.4, 156.3, 159.5 ppm; elemental analysis (%) calcd. for C₂₆H₂₄Cl₂N₂O₂Pd·CH₂Cl₂ (658.75): C 49.23, H 3.98, N 4.25; found: C 48.26, H 4.57, N 4.06.

***N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine-PdCl₂ [1-(PdCl₂)₂]:** A solution of ligand **1** (0.43 g, 1.10 mmol) and Pd(COD)Cl₂ (0.63 g, 2.20 mmol) in CH₂Cl₂ (35 mL) was stirred at room temperature for 20 h. The product precipitated as a yellow powder, which was collected by filtration, washed with diethyl ether and dried in vacuo. Yield 0.80 g, 97%. ¹H NMR (200 MHz, [D₆]DMSO): δ = 2.02 (s, 3 H, CH₃), 2.12 (s, 3 H, CH₃), 7.31–7.38 (m, 3.5 H, Ar-*H*), 7.48–7.51 (m, 2.5 H, Ar-*H*), 7.80 (br., 3.5 H, Ar-*H*), 8.21 (m, 3.5 H, CH), 8.83 (d, *J* = 5.2 Hz, 1 H, CH), 8.88 (s, 1 H, imine-CH), 9.04 ppm (br., 1 H, pyridine-CH). ¹³C NMR (50 MHz, CDCl₃): δ = 19.30, 120.23, 128.90–130.16 (m), 131.39, 144.01, 150.91, 171.36 ppm; elemental analysis (%) calcd. for C₂₆H₂₂N₄Pd₂Cl₄ (745.14): C 41.91, H 2.97, N 7.51; found: C 41.25, H 2.78, N 7.67.

[*N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine-Pd]²⁺(BF₄)₂ {[1-Pd]²⁺(BF₄)₂}: A filtered solution of ligand **1 (0.29 g, 0.74 mmol) in acetonitrile (15 mL) was added to a solution of [Pd(NCCH₃)₄]²⁺(BF₄)₂ (0.33 g, 0.74 mmol) in acetonitrile (15 mL) and the reaction mixture stirred at room temperature for 5 h. Reaction was then evaporated and dried in vacuo. Yield 0.49 g, 98%. ¹H NMR (200 MHz, CD₃CN): δ = 1.67–1.81 (m, 6 H, CH₃), 7.16–7.45 (m, 7 H, Ar-*H*), 7.65–7.82 (m, 2 H, Ar-*H*), 7.93–7.97 (m, 2 H, Ar-*H*), 8.09–8.16 (m, 3 H, Ar-*H*), 8.37–8.39 ppm (m, 2 H, imine-CH); elemental analysis (%) calcd. for C₂₆H₂₂B₂F₈N₄Pd·CH₃CN (711.57): C 47.26, H 3.54, N 9.84; found: C 47.44, H 3.31, N 9.92.**

[*N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis[(5-methyl-2-furyl)methyl]diimine-Pd(NCCH₃)₂]²⁺(BF₄)₂ {[3-Pd(NCCH₃)₂]²⁺(BF₄)₂}: This complex was prepared in the same manner as described above for complex [1-Pd]²⁺(BF₄)₂. Yield 0.53 g, 94%. ¹H NMR (200 MHz, CD₃CN): δ = 2.08 (s, 6 H, NCCH₃), 2.20 (s, 6 H, biaryl-CH₃), 2.63 (s, 6 H, furyl-CH₃), 6.52–6.55 (m, 2 H, furyl-CH), 7.30–7.39 and 7.48–7.50 ppm (m, 10 H, Ar-*H*); elemental analysis (%) calcd. for C₂₈H₃₀B₂F₈N₄O₂Pd (734.60): C 45.78, H 4.11, N 7.62; found: C 45.62, H 3.97, N 7.66.

[*N,N'*-(6,6'-Dimethylbiphenyl-2,2'-diyl)bis(2-pyridylmethyl)diimine-Pd(NCCH₃)₂]⁴⁺(BF₄)₄ {[1-Pd(NCCH₃)₂]⁴⁺(BF₄)₄}: This complex was prepared in the same manner as described for complex [1-Pd]²⁺(BF₄)₂ above except for the use of only 0.15 g (0.37 mmol) of ligand **1 for reaction with 0.33 g (0.74 mmol) of [Pd(NCCH₃)₄]²⁺(BF₄)₂. Yield 0.41 g, 95%. ¹H NMR (200 MHz, CD₃CN): δ = 1.72 (s, 6 H, biaryl-CH₃), 2.05 (br., 12 H, NCCH₃), 7.35–7.37 (m, 8 H, Ar-*H*), 7.77 (t, 2 H, Ar-*H*), 7.97 (d, 2 H, Ar-*H*), 8.21 (t, 2 H, Ar-*H*), 8.58 ppm (d, 2 H, Ar-*H*); elemental analysis (%) calcd. for C₃₄H₃₄B₄F₁₆N₈Pd₂ (1114.75): C 36.63, H 3.07, N 10.05; found: C 36.00, H 3.16, N 10.74%.**

Crystal Structure Determinations: Single crystals of complexes **1**-PdCl₂, **1**-(PdCl₂)₂, [1-Pd]²⁺(BF₄)₂ and [3-Pd(NCCH₃)₂]²⁺(BF₄)₂ were obtained as yellow-orange blocks upon layering a filtered re-

Table 6. Details for the crystal structure determinations

	1-PdCl ₂ · 2 CH ₂ Cl ₂	3-PdCl ₂	3-PdCl ₂ · CH ₂ Cl ₂	1-(PdCl ₂) ₂ · 2 CH ₂ Cl ₂	[1-Pd] ²⁺ (BF ₄ ⁻) ₂ · (H ₂ O) _{0.5}	[3-Pd(NCCH ₃) ₂] ²⁺ (BF ₄ ⁻) ₂
CCDC number	243264	243267	243268	243265	243266	243269
Formula	C ₂₆ H ₂₂ Cl ₂ N ₄ Pd· (CH ₂ Cl ₂) ₂	C ₂₆ H ₂₅ Cl ₂ N ₂ O ₂ Pd	C ₂₆ H ₂₄ Cl ₂ N ₂ O ₂ Pd· (CH ₂ Cl ₂)	C ₂₅ H ₂₀ Cl ₄ N ₄ Pd ₂ · (CH ₂ Cl ₂) ₂	C ₂₆ H ₂₄ N ₄ Pd(BF ₄) ₂ · (H ₂ O) _{0.5}	C ₃₀ H ₃₀ N ₄ O ₂ Pd(BF ₄) ₂ · (C ₂ H ₅ N)
Formula mass	737.63	574.78	658.70	999.85	680.51	799.65
Temperature	173(2)K	173(2)K	173(2)K	173(2)K	173(2)K	173(2)K
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.003(2)	8.4180(8)	10.7960(7)	9.0280(12)	12.593(4)	12.023(2)
<i>b</i> (Å)	14.360(1)	15.2480(17)	17.573(2)	14.6330(17)	14.363(5)	12.9240(7)
<i>c</i> (Å)	17.917(2)	18.679(3)	17.484(2)	15.5050(19)	19.361(4)	14.341(3)
α (°)	90	90	90	113.074(11)	90	104.178(8)
β (°)	121.844(14)	99.244(8)	122.895(5)	98.359(13)	128.47(3)	99.756(11)
γ (°)	90	90	90	90.177(9)	90	117.483(6)
<i>V</i> (Å ³); <i>Z</i>	3060.5(6); 4	2366.5(5); 2	2785.2(5); 4	1860.4(4); 2	2741.6(14); 4	1810.4(5); 2
<i>d</i> _{calcd} [g/cm ³]	1.601	1.613	1.571	1.785	1.649	1.467
μ [mm ⁻¹], <i>F</i> (000)	1.156; 1480	1.037; 1164	1.078; 1328	1.713; 984	0.758; 1360	0.590; 808
Crystal size (mm)	0.25 × 0.15 × 0.12	0.30 × 0.25 × 0.20	0.25 × 0.18 × 0.12	0.20 × 0.05 × 0.05	0.18 × 0.04 × 0.02	0.20 × 0.20 × 0.20
Theta range (°)	5.03 to 27.51	5.03 to 27.51	5.01 to 27.53	2.66 to 27.57	3.04 to 25.25	3.10 to 27.50
Reflections collected/unique	24160 / 6960	16675 / 5352	29085 / 6210	28531 / 8435	39662 / 4875	26221 / 8243
<i>R</i> (int) = 0.0714]	[<i>R</i> (int) = 0.0714]	[<i>R</i> (int) = 0.1057]	[<i>R</i> (int) = 0.0456]	[<i>R</i> (int) = 0.0572]	[<i>R</i> (int) = 0.1233]	[<i>R</i> (int) = 0.0459]
<i>T</i> _{max} , <i>T</i> _{min}	0.8737, 0.7609	0.8194, 0.7461	0.8816, 0.7744	0.9193, 0.7258	0.9850, 0.8757	0.9127, 0.8932
Data/restraints/parameters	6960 / 0 / 352	5352 / 0 / 302	6210 / 0 / 325	8435 / 80 / 462	4875 / 74 / 416	8243 / 0 / 463
GoF(<i>F</i> ²)	0.989	0.963	0.628	1.050	1.033	1.030
Final <i>R</i> indices	<i>R</i> 1 = 0.0471,	<i>R</i> 1 = 0.0649,	<i>R</i> 1 = 0.0344,	<i>R</i> 1 = 0.0597,	<i>R</i> 1 = 0.0726,	<i>R</i> 1 = 0.0381,
[<i>I</i> > 2σ(<i>I</i>)]	<i>wR</i> 2 = 0.0883	<i>wR</i> 2 = 0.1009	<i>wR</i> 2 = 0.1232	<i>wR</i> 2 = 0.1530	<i>wR</i> 2 = 0.1781	<i>wR</i> 2 = 0.0823
<i>R</i> indices	<i>R</i> 1 = 0.0993,	<i>R</i> 1 = 0.1561,	<i>R</i> 1 = 0.0537,	<i>R</i> 1 = 0.0863,	<i>R</i> 1 = 0.1163,	<i>R</i> 1 = 0.0584,
(all data)	<i>wR</i> 2 = 0.1025	<i>wR</i> 2 = 0.1236	<i>wR</i> 2 = 0.1545	<i>wR</i> 2 = 0.1698	<i>wR</i> 2 = 0.1990	<i>wR</i> 2 = 0.0887
Largest diff. peak	0.671 eÅ ⁻³	0.539 eÅ ⁻³	0.997 eÅ ⁻³	1.136 eÅ ⁻³	1.047 eÅ ⁻³	0.572 eÅ ⁻³

action solution with diethyl ether at ambient temperature. Crystals of 3-PdCl₂ were obtained at 4 °C; at room temperature, 3-PdCl₂ gave crystals with a different unit cell. Crystals selected for X-ray measurements were mounted on a glass fiber using the oil-drop method. Data were collected on a Nonius-Kappa CCD diffractometer using Mo-*K* α radiation (71.073 pm) and a graphite monochromator. Structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically.^[33] Hydrogen atoms were introduced at calculated positions and refined with fixed geometry with respect to their carrier atoms. Cell parameters and data collection parameters are summarized in Table 6. CCDC-243264 (for 1-PdCl₂), CCDC-243267 and CCDC-243268 (for 3-PdCl₂, two crystals with different structures), CCDC-243265 (for 1-(PdCl₂)₂), CCDC-243266 (for [1-Pd]²⁺(BF₄⁻)₂) and CCDC-243269 (for [3-Pd(NCCH₃)₂]²⁺(BF₄⁻)₂) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Norbornene Polymerizations: The dichloro complexes 1-PdCl₂, 2-PdCl₂ and 3-PdCl₂ (20 μmol) were suspended in toluene (60 mL), MAO (4 mL, 20 mmol) and 2-norbornene (2.1 g, 22.3 mmol) were added and the reaction solution stirred at room temperature for 1 h. Conversions measured from the isolated products were 64, 71 and 38%, respectively. In the case of complexes [1-Pd]²⁺(BF₄⁻)₂ and [3-Pd(NCCH₃)₂]²⁺(BF₄⁻)₂ norbornene was added to a solution of the complex (50 mg, 66 μmol) in CH₂Cl₂ (50 mL), chlorobenzene (5 mL) and nitrobenzene (1 mL) and stirred at room tempera-

ture for 1 h. Conversions were 0 and 44%, respectively. After quenching the reaction by addition of methanol (200 mL), acidified with HCl (1 mL), the precipitate was collected by filtration, washed with methanol and dried at 60 °C. Decomposition points were determined with thermogravimetric balance under N₂ flow. ¹H NMR (200 MHz, CDCl₃): δ = 0.87–2.23 (br. m, 10 H) ppm. ¹³C NMR (50 MHz, CDCl₃): δ = 28–44 (br. m), 48–55 ppm (br. m).

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