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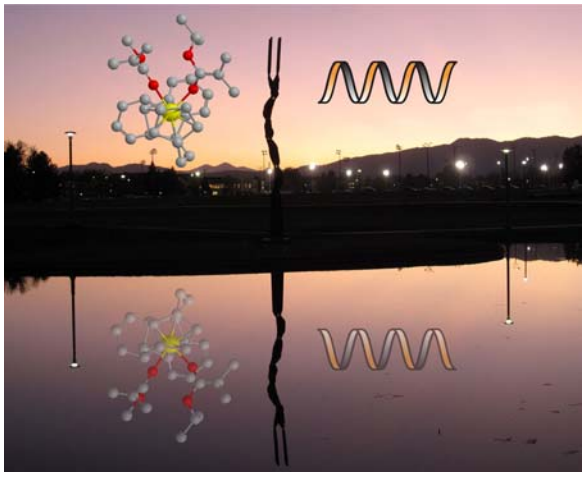

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Alternating ethylene-norbornene copolymerization catalyzed by cationic organopalladium complexes bearing hemilabile bidentate ligands of α-amino-pyridines†

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Cationic methylpalladium complexes with hemilabile bidentate ligands of α-amino-pyridines, in the form of {[$R^1HNCR^2H(o\text{-}C_6H_5N)$]Pd(Me)(NCMe)}($BF_4$) ($R^1$ = ^{i}Pr, ^{t}Bu, Ar R^2 = H, Me) have been found to be effective precursors for catalytic copolymerization of ethylene and norbornene under mild conditions. The copolymer products exhibit predominant alternating microstructures which are evidenced by NMR and mass spectrometry as well as a kinetic analysis according to the Finman-Ross relationship.

Introduction

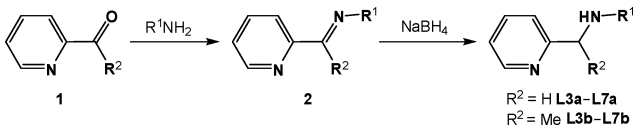
The cyclic-olefinic copolymers (COC) of ethylene and norbornene has acquired notice for their high transparency, low dielectric constants, bio-compatibility *etc.* for the practical purposes of materials.[1] Such copolymers with an alternating microstructure are of interest for their favorable high T_g values.[2] The *m*COCs are commercially available.[3] However, an industrial process using late transition metal catalysts remains unknown. The research in this aspect is worthy of investigation not only because the possibility of waiving the use of MAO cocatalyst,[4] but also for the potential in preparing functionalized polyolefins.[5]

On the other hand, design and synthesis of unsymmetrical bidentate ligands still remain a prevailing field, because their rich variation and potential for the control in homogeneous catalysis.[6] Herein we report that the combination of the hetero-functional ligands of α-amino-pyridines and square-planar methylpalladium cations can afford effective catalytic reactions of alternating copolymerization of ethylene and norbornene.

Results and discussion

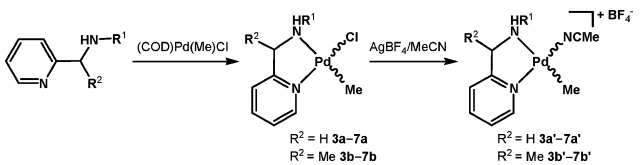
Synthesis and spectroscopic characterization

Hemilabile α-amino-pyridines in the form of $R^1HNCR^2H(o\text{-}C_6H_5N)$ (R^2 = H R^1 = ^{i}Pr (**L3a**), R^1 = ^{t}Bu (**L4a**), R^1 = Ph (**L5a**), R^1 = 2,6-$Me_2C_6H_3$ (**L6a**), R^1 = 2,6-$^i Pr_2C_6H_3$ (**L7a**) and R^2 = Me **L3b**–**L7b**) were synthesized *via* a route first by condensation of *o*-aldehyde-pyridine (**1**) with amine or aniline derivatives, first giving α-iminopyridines (**2**) whose reduction was then followed with the use of $NaBH_4$ (Scheme 1).[7]



Scheme 1 Synthesis of α-amino-pyridines.

The replacement of **L** for COD (1,5-cyclooctadiene) in (COD)Pd(Me)Cl generates the corresponding neutral complexes [$R^1HNCR^2H(o\text{-}C_6H_5N)$]Pd(Me)Cl ($R^2$ = H **3a**–**7a** and R^2 = Me **3b**–**7b**). Treating the complexes **3**–**7** with $AgBF_4$ in acetonitrile affords the cationic organopalladium [$R^1HNCR^2H(o\text{-}C_6H_5N)$]Pd(Me)(NCMe)]($BF_4$) ($R^2$ = H **3a′**–**7a′** and R^2 = Me **3b′**–**7b′**) as shown in Scheme 2.



Scheme 2 Synthesis of methylpalladium catalysts.

Both of the neutral and cationic organometallic complexes could show two isomers according to the NMR spectroscopy, which suggests such complexes are in a square-planar geometry. The 2D NMR-NOSEY techniques facilitate the assignments for the isomers. For instance in the spectrum of **3b**, Pd-Me at δ 0.17 of the *cis*-isomer shows correlated signal with isopropyl substituent on amino nitrogen, whilst Pd-Me at δ 0.90 of the *trans*-isomer correlates to *o*-hydrogen of pyridine. These spectra can also afford the thermodynamic ratios for the two geometrical isomers, which are collected in Table 1.

In general, conformationally bulky amino substituents tend to favor the *trans* configuration in which the coordination site *cis* to pyridine may accommodate a methyl better than the site *cis* to amino group.[8] The *ortho*-substituted aryl groups probably are

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† Electronic supplementary information (ESI) available: ORTEP drawings and crystallographic data of *trans*-**4a**, *trans*-**5a**, *cis*-**6a**, *cis*-**4b**, *cis*-**6b**, *cis*-**7b**, *cis*-**3a′**, *trans*-**4a′**, *trans*-**5a′** and *trans*-**4b′**, additional synthetic procedures, polymer characterization, 2D NMR spectrum, Fineman-Ross and variable temperature NMR data. CCDC reference numbers 736875–736888. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b912068h

Table 1 Relative percentage of *trans*/*cis* isomer of neutral and cationic palladium complexes in $CDCl_3$

Neutral complexes			Amino-pyridine		Cationic complexes		
Trans (%)	*Cis* (%)		R_2	R_1		*Trans* (%)	*Cis* (%)
48	52	**3a**	H	^{i}Pr	**3a′**	82	18
71	29	**4a**	H	^{t}Bu	**4a′**	100	0
62	38	**5a**	H	Ph	**5a′**	93	7
13	87	**6a**	H	2,6-$Me_2C_6H_3$	**6a′**	60	40
10	90	**7a**	H	2,6-$^i Pr_2C_6H_3$	**7a′**	62	38
54	46	**3b**	Me	^{i}Pr	**3b′**	45	54
65	35	**4b**	Me	^{t}Bu	**4b′**	100	0
76	24	**5b**	Me	Ph	**5b′**	89	11
18	82	**6b**	Me	2,6-$Me_2C_6H_3$	**6b′**	56	44
17	83	**7b**	Me	2,6-$^i Pr_2C_6H_3$	**7b′**	51	49

restrained to free rotation in **6** or **7**, particularly when a methyl is on the back-bone carbon. The relative yields of the isomers in the neutral and cationic species are in lack of good correlation. One supposes that the electronic effect should not be excluded.

X-ray structural analysis

Single crystals of *cis*-**3a**, *trans*-**4a**, *trans*-**5a**, *cis*-**6a**, *trans*-**3b**, *cis*-**4b**, *cis*-**6b**, *cis*-**7b** and *cis*-**3a′**, *trans*-**4a′**, *trans*-**5a′**, *cis*-**3b′**, *trans*-**4b′**, *cis*-**6b′** that are suitable for X-ray diffractions have been obtained. A crystallographic analysis provides solid evidence for the molecular structures of these complexes. None has been resolved for both geometrical isomers. The selected crystal data and the bond lengths and bond angles for **3a**, **3b**, **3b′**, **6b′** are collected in Tables 2 and 3 respectively. In Fig. 1, the ORTEP drawings of **3a**, **3b**, **3b′**, **6b′** are in square planar geometry. Other data are provided in the electronic supplementary information, ESI.†

In the neutral complexes, the *cis* derivatives have the bond lengths for Pd-N(Py) in the range of 2.115(2)–2.143(2) Å, and 2.086(3)–2.109(3) Å for Pd-N(am). The Pd-C bonds are 2.021(2)–2.075(2) Å, and the Pd-Cl bonds are 2.3124(7)–2.333(1) Å. Analogous data in the *trans* derivatives are: Pd-N(Py) 2.038(2)–2.055(2) Å, Pd-N(am) 2.202(2)–2.212(2) Å, Pd-C 2.015(3)–2.055(2) Å, Pd-Cl 2.3065(7)–2.3170(7) Å. Apparently, the methyl with good *trans*-influence can weaken its *trans* Pd-N bond in the ground state. A similar trend is observed in the cationic complexes too.

Table 2 X-ray crystal parameters and data collection

Compound	*cis*-**3a**	*trans*-**3b**	*cis*-**3b′**	*cis*-**6b′**
Formula	$C_{10}H_{17}ClN_2Pd$	$C_{11}H_{19}ClN_2Pd$	$C_{13}H_{22}BF_4N_3Pd$	$C_{18}H_{24}BF_4N_3Pd{\cdot}NC_2H_3$
Formula wt	307.11	321.13	413.55	516.67
Crystal size/mm	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20	0.30 × 0.25 × 0.20
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	*Pbca*	$P2_1/c$
a/Å	8.7000(4)	7.9040(2)	11.3568(4)	11.71270(10)
b/Å	9.7343(4)	8.4760(2)	13.8579(4)	15.1903(2)
c/Å	14.2066(7)	10.5230(2)	21.9950(7)	13.7906(2)
α/°	90	89.2210(10)	90	90
β/°	93.140(3)	86.4850(10)	90	112.3550(8)
γ/°	90	66.2490(10)	90	90
V/Å^3	1201.33(9)	644.01(3)	3461.60(19)	2269.21(5)
Z	4	2	8	4
ρ_{calcd}/Mg m^{-3}	1.698	1.656	1.587	1.512
F(000)	616	324	1664	1048
T/K	295(2)	295(2)	295(2)	295(2)
μ/mm^{-1}	1.732	1.620	1.108	0.863
Transmission	0.937–0.993	0.635–0.733	0.641–0.764	0.702–0.849
θ range/°	2.34–27.50	1.94–27.49	1.85–27.49	1.88–27.49
h, *k*, *l*	±	±	±	
	11, ±12, ±18	10, −10 to 11, ±13	14, −17 to 18, ±28	−15 to 14, ±19, ±17
Reflections collected	6926	4803	19197	17211
Independent reflections	2704	2863	3953	5135
R_{int}	0.0650	0.0251	0.0631	0.0473
Data/restraints	2704/0	2863/0	3953/0	5135/0
Parameters	128	141	204	276
R_1 [I>2σ(I)]	0.0440	0.0254	0.0514	0.0441
wR_2 [I>2σ(I)]	0.1091	0.0651	0.1313	0.1214
R_1 (all data)	0.0642	0.0273	0.0929	0.0555
wR_2 (all data)	0.1327	0.0663	0.1631	0.1381
Goodness of fit on F^2	1.153	1.073	1.060	1.125
Largest diff. peak and hole/e Å^{-3}	0.813 and −1.223	0.467 and −0.516	1.069 and −0.541	1.112 and −0.709

Table 3 Selected bond distances (Å) and angles (°)

[^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*cis*-**3a**)							
Pd-N1	2.141 (4)	Pd-N2	2.086 (3)	Pd-C1	2.026 (5)	Pd-Cl1	2.3325 (11)
N1-C6	1.348 (6)	N2-C7	1.474 (5)	C6-C7	1.496 (6)	N2-C9	1.504 (6)
N1-Pd-N2	81.3 (1)	C1-Pd-Cl1	91.6 (1)	Pd-N1-C6	112.5 (3)	Pd-N2-C7	108.9 (2)
N1-C6-C7	116.2 (3)	N2-C7-C6	113.4 (3)	C9-N2-Pd	117.4 (3)	C9-N2-C7	114.2 (3)
[^{i}PrHNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*trans*-**3b**)							
Pd-N1	2.049 (2)	Pd-N2	2.211 (2)	Pd-C1	2.055 (2)	Pd-Cl1	2.3170 (7)
N1-C6	1.349 (3)	N2-C7	1.474 (3)	C6-C7	1.521 (3)	N2-C9	1.498 (3)
N1-Pd-N2	78.78 (8)	C1-Pd-Cl1	87.72 (7)	Pd-N1-C6	114.0 (2)	Pd-N2-C7	101.4 (1)
N1-C6-C7	115.8 (2)	N2-C7-C6	108.3 (2)	C9-N2-Pd	112.7 (2)	C9-N2-C7	114.8 (2)
{[^{i}PrHNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (*cis*-**3b′**)							
Pd-N1	2.123 (4)	Pd-N2	2.061 (5)	Pd-C1	2.017 (6)	Pd-N3	2.013 (5)
N1-C6	1.348 (6)	N2-C7	1.498 (6)	C6-C7	1.506 (7)	N2-C9	1.506 (6)
N1-Pd-N2	80.2 (2)	C1-Pd-N3	88.8 (2)	Pd-N1-C6	112.4 (3)	Pd-N2-C7	107.5 (3)
N1-C6-C7	116.3 (4)	N2-C7-C6	110.1 (4)	C9-N2-Pd	114.7 (3)	C9-N2-C7	114.8 (4)
{[(2,6-Me$_2$C$_6$H$_3$)HNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (*cis*-**6b′**)							
Pd-N1	2.116 (3)	Pd-N2	2.075 (3)	Pd-C1	2.022 (4)	Pd-N3	2.003 (3)
N1-C6	1.338 (5)	N2-C7	1.512 (4)	C6-C7	1.513 (5)	N2-C9	1.460 (4)
N1-Pd-N2	81.0 (1)	C1-Pd-N3	89.8 (2)	Pd-N1-C6	114.5 (2)	Pd-N2-C7	110.4 (2)
N1-C6-C7	116.2 (3)	N2-C7-C6	110.9 (3)	C9-N2-Pd	120.5 (2)	C9-N2-C7	111.2 (3)

The N1-Pd-N2 angles are in the range of 80–82° when R_1 = H and 79–81° when R_1 = Me. The five-member metallacycles adopt envelope conformation with amino nitrogen lying off the Pd-N1-C6-C7 plane. In **3** or **4** which contains bulky amino substituent, the off-distance may be as large as 0.7–0.8 Å.

Mechanism of geometrical isomerization

Dissolution of crystals at 25 °C gives a geometrical isomerism in thermodynamic ratio as shown in Table 1 as soon as the first NMR spectra could be taken. Such results indicate that the isomerization is an instantaneous process. Attempts at dissolving a crystal of **3b** from −75 to −55 °C for the measurement of the isomer ratios have not been successful due to its poor solubility.

In the case of **5a** in $CDCl_3$ at 25–30 °C, there is one set of PyCH_2N that could be identified in the ^{1}H and ^{13}C NMR spectra. The diastereotopic hydrogen atoms of the α-amino-pyridine for the *trans* species were not observed. The spectra with a varied temperature in the range of 253–323 K in increments of 10 K are shown in Fig. 2 in which the methylene signals of the *trans* isomer clearly split to the doublet of doublets at δ 4.30 and 5.12 with germinal coupling J_{HH} = 16.3 Hz below 263 K, and the coalescence occurs at about 323 K. The free energy of activation $\Delta G_c‡$ is evaluated as 59 kJ mol^{-1} according to the Gutowsky-Holm and Eyring relationships.[9]

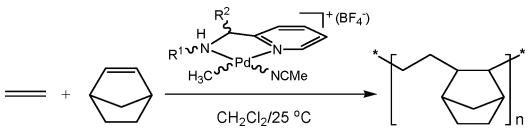
On the other hand, the *ortho*-methyl Hs of the aryl group in *trans*-**6b** also show dynamic properties. The ^{1}H NMR spectrum taken in $CDCl_3$ shows two singlets at δ 2.35 and 2.92 at 253 K, and one singlet at 328 K. The coalescence occurs at about 323 ± 5 K which affords a $\Delta G_c‡$ as 61 kJ mol^{-1}. A similar experiment for *trans*-**6a** and **6b′** gives $\Delta G_c‡$ as 58 and 59 kJ mol^{-1}, respectively.

Such phenomena may be attributed to the dissociation and recoordination of amine, which will facilitate pyramidal nitrogen inversion and aryl rotation, as well as isomerization. Previous work shows that the energy barrier for nitrogen inversion in the dithiolene zinc complex is about 50 kJ mol^{-1}.[10] The analogous sulfur inversion in pyridylthioether complexes is about 43–69 kJ mol^{-1}.[11]

The methylene hydrogen of *cis*-**5a** remains unchanged in the same temperature range, but appears to show a slight broadening above 323 K, indicating that a similar behavior might take place at higher temperature. One can conclude that the better lability for the amino functionality in the *trans* derivative is facilitated by the methyl ligand of good *trans*-effect and *trans*-influence as well.

Reactions of copolymerization

The neutral methylpalladium complexes **3**–**7** do not show reactivity toward the olefin polymerization. In contrast, the cationic complexes **3′**–**7′** can result in the formation of ethylene-norbornene COCs under mild conditions (Scheme 3).



Scheme 3 Ethylene-norbornene copolymerization catalyzed by a methyl–palladium cation bearing α-amino-pyridines.

The molecular weight M_w and M_n were determined by GPC, and the T_g were measured by DSC. Fitting T_g according to an empirical equation used by Fink *et al.*,[12] gives a molar fraction of norbonene in the COC products in the region of 50 ± 10%. The ^{13}C NMR integrations also afford consistent results for the norbornene content. In addition, the ^{13}C NMR spectra of COC as illustrated in Fig. 3 suggest that the microstructures of the COCs are of atactic alternating copolymers.[13] The data for the catalytic copolymerization of ethylene and norbornene with various cationic Pd(II) precursors are collected in Table 4. The yields, average molecular weights, and norbornene content as well as the polyads of norbonene for the COC products appear to increase with the norbornene feeding. With the calibration by using the molar fraction of norbonene in COC obtained from the ^{13}C NMR data in Table 5, the DSC measurements for the Tg may fit the ensuing linear equation, X_{NB}(mol %) = (0.22T_g) + 23 (Fig. S2†), which is somewhat different from an analogous approach in other COC studies.[14] The activity of such catalytic reactions also increased with ethylene pressure between 1–20 bar.

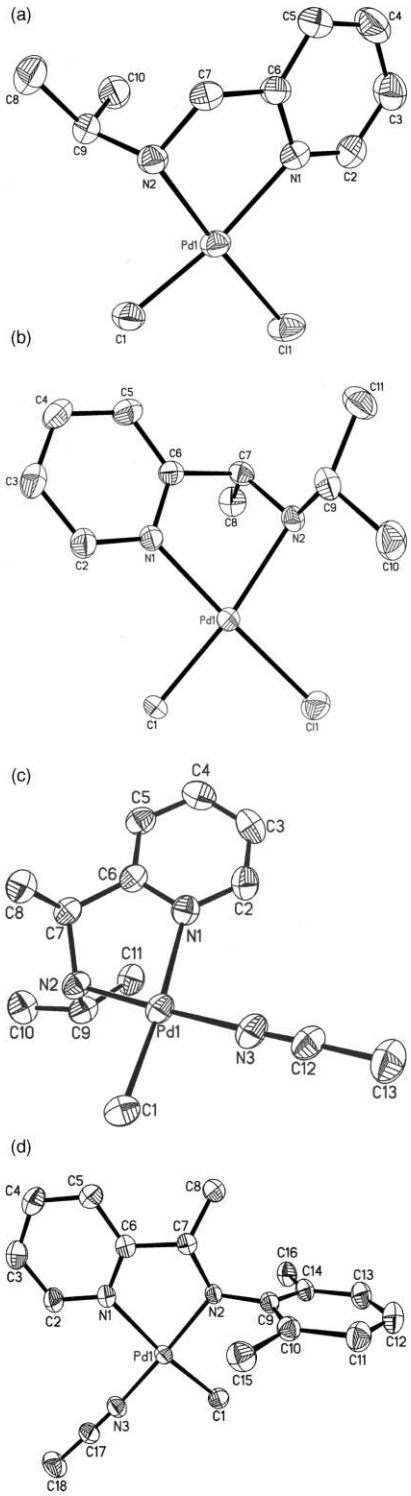


Fig. 1 ORTEP drawings of (a) [^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*cis*-**3a**), (b) [^{i}PrHNC(Me)H(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*trans*-**3b**), (c) [^{i}PrHNC(Me)H(*o*-C$_6$H$_5$N)Pd(Me)(NCMe)](BF$_4$) (*cis*-**3b′**), (d) [(2,6-Me$_2$C$_6$H$_3$)NC(Me)H(*o*-C$_6$H$_5$N)Pd(Me)(NCMe)](BF$_4$) (*cis*-**6b′**), all hydrogen atoms are omitted.

Further investigation for the E-NB copolymerization has been done using **3b′**. Variation of norbornene feeding between 0.5–30 g under 21 bar of ethylene led to the formation of COC with a differentiation of composition and microstructure for the

Table 4 Data for copolymerization of ethylene and norbornene[a]

	cat	Yield (g)	Activity[d]	Mw[e] ($\times 10^3$)	PDI[e]	Tg[f] (°C)	NB_{COC}[g] (mol %)
1	**3a′**	0.42	14	1.4	1.4	56	35
2	**4a′**	0.15	5	0.9	1.3	32	30
3	**5a′**	0.19	6	2.5	1.5	110	47
4	**6a′**	0.81	27	5.4	1.8	118	49
5	**7a′**	0.84	28	8.5	1.7	119	49
6	**7a′**[b]	1.47	49	23.0	2.1	156	57
7	**7a′**[c]	1.18	39	26.6	4.8	177	62
8	**3b′**	0.62	21	4.8	1.5	106	46
9	**4b′**	0.31	10	5.2	1.5	72	39
10	**5b′**	0.49	15	4.9	1.7	120	50
11	**6b′**	0.64	21	6.9	1.9	121	50
12	**7b′**	0.41	14	9.3	1.8	121	50

[a] Reaction conditions: 0.06 mmol of catalysts, 1 g of norbornene, 21 bar of ethylene, 50 mL of CH_2Cl_2, 30 min, room temperature. [b] 5 g of norbornene in the feed. [c] 10 g of norbornene in the feed. [d] Activity = kg (COC) mol^{-1}(Pd) h^{-1}. [e] Determined by GPC using polystyrene as standards. [f] Determined by DSC. [g] Calculated form Tg, norbornene mol % = Tg × 0.22 + 23.

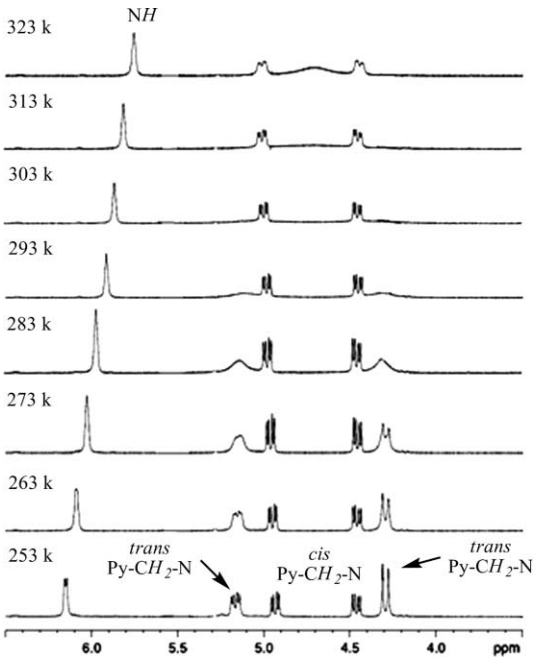


Fig. 2 Variable temperature ^{1}H NMR spectra of *trans*-**5a** in $CDCl_3$ recorded diastereotopic H-exchange.

products. A detailed analysis toward ^{13}C NMR integrations affords the evaluation of the abundance of norbornene block and the alternating component in mol % as listed in Table 5.[15] The diads are generated readily, but triads may be substantially formed only when norbornene feeding is over 20 g. The change of PDI however is rather limited. Attempts at analyzing the compositions for ethylene block and branching have not been successful because their NMR signals overlap with the polymer backbone data. Solvent fractionation experiments indicate that the products from the reactions of **3a′**, **5a′**, **6a′** with 1 g norbornene-feeding and of **3b′** with 0.5–5 g norbornene-feeding might contain miniature amounts of homopolymer impurities.

The relative contents of two monomers in the COCs and the feedings are linearly fairly good correlated according to

Table 5 Copolymerization of ethylene and norbornene at different comonomer ratios using catalyst **3b′**[a]

NB_{feed} (g)	NB_{feed}[b] (mol %)	Yield (g)	Activity (kg $mol^{-1}h^{-1}$)	Mw[c] ($\times 10^3$)	PDI[c]	Tg[d] (°C)	NBcoc[e] (mol %)	Single[f] (mol %)	Diads[f] (mol %)	Triads[f] (mol %)	Alternating[g] (mol %)
0.5	6	0.35	12	4.0	1.5	77	42.0	41.5	0.5	0	83.5
1	11	0.62	21	4.8	1.5	106	42.5	40.9	2.0	0	83.8
3	28	1.15	38	9.7	1.7	126	49.4	40.8	5.5	3.1	89.2
5	39	1.09	36	16.6	1.4	130	54.0	41.6	8.2	4.2	94.2
10	56	0.94	31	17.8	1.6	136	52.4	37.6	8.9	5.9	88.0
20	72	0.89	30	14.6	1.9	148	53.3	31.4	11.1	10.8	81.1
30	79	1.03	34	16.1	1.8	160	59.6	23.9	13.4	22.3	76.1

[a] Reaction conditions: 0.06 mmol of catalysts, 21 bar of ethylene, 50 mL of CH_2Cl_2, 30 min, room temperature. [b] Norbornene content in the feed. [c] Determined by GPC using polystyrene as standards. [d] Determined by DSC. [e] Norbornene content in the copolymer, determined by ^{13}C NMR. [f] Norbornene content of single norbornene unit or blocks in the copolymer, determined by ^{13}C NMR. [g] Determined by ^{13}C NMR, alternating mol % = 2 × single norbornene mol % + norbornene diads mol % + 2/3 × norbornene triads mol %.

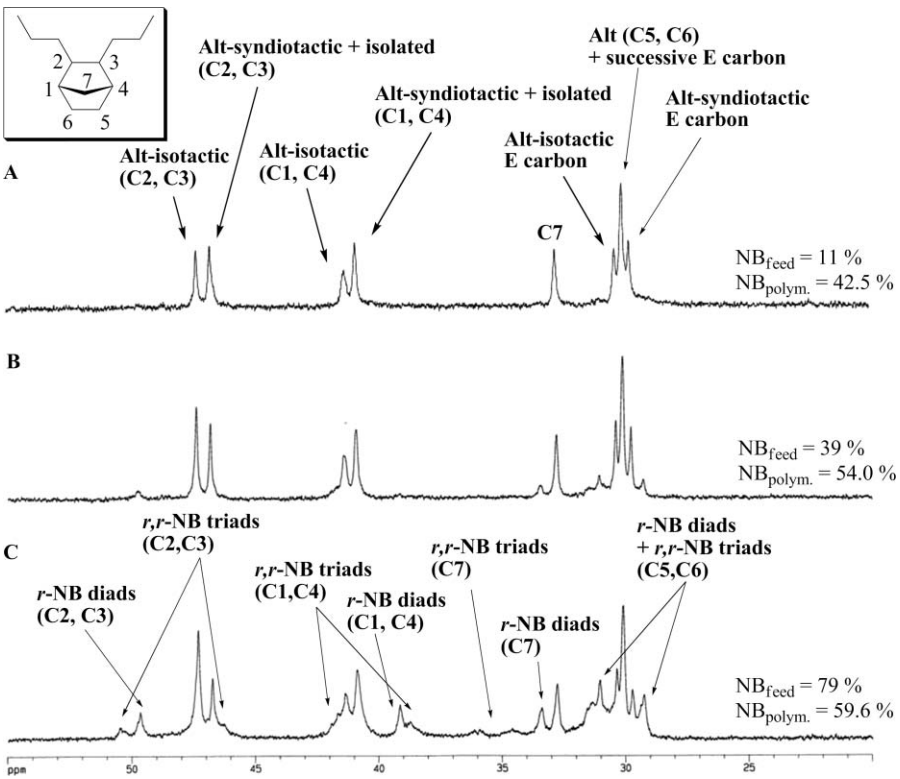


Fig. 3 ^{13}C NMR spectra of ethylene/norbornene copolymer produced by **3b′** with (A) 1 g, (B) 5 g, (C) 30 g of norbornene feeding.

the Fineman-Ross equation.[16] In the region of fed norbornene between 0.5 g and 30 g, the plot shows a linearity as illustrated in Fig. 4 which indicates that the formation of alternating COCs is due to a kinetic control in the steps of olefin insertion. The graph allows to evaluate the slope $r_1 = k_{NN}/k_{NE} = 0.11$ and the intercept $r_2 = k_{EE}/k_{EN} = 0.043$, wherein r_1 represents the ratio of the rate constants between the successive norbornene insertions and norbornene insertion followed by ethylene; and r_2 represents the ratio of the rate constants between the successive ethylene insertions and ethylene insertion followed by norbornene.[17] The product of $r_1 \times r_2$ is significantly smaller than 1.0, indicating the alternating microstructure is based on the kinetic control, *i.e.* the consecutive hetero-olefin insertions are faster than the consecutive homo-olefin insertions.

These reactions of E-N copolymerization are further examined with ESI-MS. In one we used 21.3 mM norbornene, 83 mM ethylene and 1.5 mM **3b′**, and the reaction was run in CH_2Cl_2 at 22 °C under ambient conditions. Aliquots of reaction solution were added into an excess of acetonitrile to quench the reaction, and then analyzed. The mass spectra for the reaction solutions analyzed at 15 and 66 min are shown in Fig. 5. At 15 min, two major signal sequences which are unequivocally disposed in alternating mode are assigned as (**L3b**)Pd[$(C_7H_{10})_N(C_2H_4)_E$-Me]$^+$ wherein E = 0 N = 1 – E = 9 N = 10, and E = 0 N = 2 – E = 9 N = 11. The species with maximum intensity is E = 4 N = 5 and E = 4 N = 6. At 66 min, the pattern could be generally kept and growing with the maxima at E = 7 N = 9 and E = 7 N = 10. Accordingly, the norbornene content tends to increase with the reaction time.

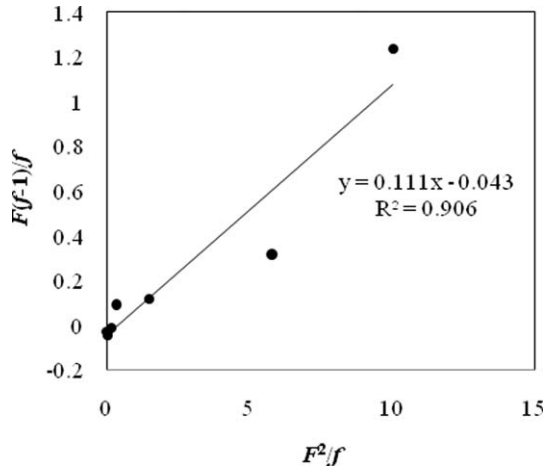


Fig. 4 Fineman-Ross relationship for E-NB copolymerization.

The slow rate of the investigated reaction may be ascribed to the low ethylene concentration. Under this circumstance, norbornene insertion appears to be more efficient than ethylene insertion at least at the early stage. Besides, the prominent intensity due to (**L3b**)Pd[$(C_7H_{10})_N$Me]$^+$ (N = 1–2) at 66 min might be owing to a distinguishable reactivity for the geometrical isomers toward olefin-insertion. Indeed, a preliminary stoichiometric study for the reaction of **3b′** and norbornene in 1:0.8 molar ratio at room temperature shows that the *cis* isomer appears to undergo norbornene insertion slightly faster than its *trans* analogue (Fig. S22†). A detailed mechanistic study is on under way.

Concluding remarks

Neutral and cationic methylpalladium complexes bearing bidentate ligands of α-amino-pyridines have been prepared and demonstrated geometrical isomerism. Cationic organometallic complexes can catalyze the copolymerization of ethylene and norbornene. The COC products show alternating microstructures which have been proved by NMR and ESI-MS. The Fineman-Ross correlation suggests that the alternating feature of the copolymerization is likely due to the kinetic control.

Experimental

General procedures

Commercially available reagents were purchased and used without further purification unless otherwise indicated. Diethyl ether was distilled from purple solutions of benzophenone ketyl under nitrogen prior to use, and dichloromethane was dried over P_2O_5 and distilled immediately prior to use. Acetonitrile was distilled over anhydrous CaH_2. Air-sensitive material was manipulated under a nitrogen atmosphere either in a glove box or by standard Schlenk techniques. The NMR spectra were measured on a Bruker AC-200, AC-300 or AC-400 spectrometers. The corresponding frequencies for ^{13}C NMR spectra were 50.3, 75.469, and 100.625 MHz, respectively. Values upfield of ^1H and ^{13}C data were given in δ (ppm) relative to chloroform in $CDCl_3$ (7.26, C*H*Cl_3; 77.0, *C*HCl_3) or to benzene in d_6-benzene (7.15, C_6H_6; 128.7, C_6H_6). To get good integration data, the ^{13}C NMR spectra of copolymers were obtained at 100.625 MHz in $CDCl_3$ or C_6H_6 using inverse gated proton decoupling with 30 degree pulse and 3 s delay between the pulses. FAB Mass spectrometric analyses were collected on a JEOL SX-102A mass spetrometer, and the electrospray ionization tandem mass spectrometric studies were taken on an LCQ ion-trap Finnigan mass spectrometer, San Jose, CA, USA. The elemental analysis was done on a Perkin-Elmer 2400 CHN analyzer. Gel permeation chromatography (GPC) was performed in toluene at 40 °C using a Kratos model spectroflow 400 equipped with PL-mixed D exclusion limit 400k columns, and the polystyrene calibration curve was used for analyses. Differential scanning calorimetry was measured under a continuous nitrogen purge (20 mL/min) on a Perkin-Elmer Pyris 6 DSC instrument. The data were gathered on the secondary heating cycle using a heating and cooling scan rate of 10 °C/min.

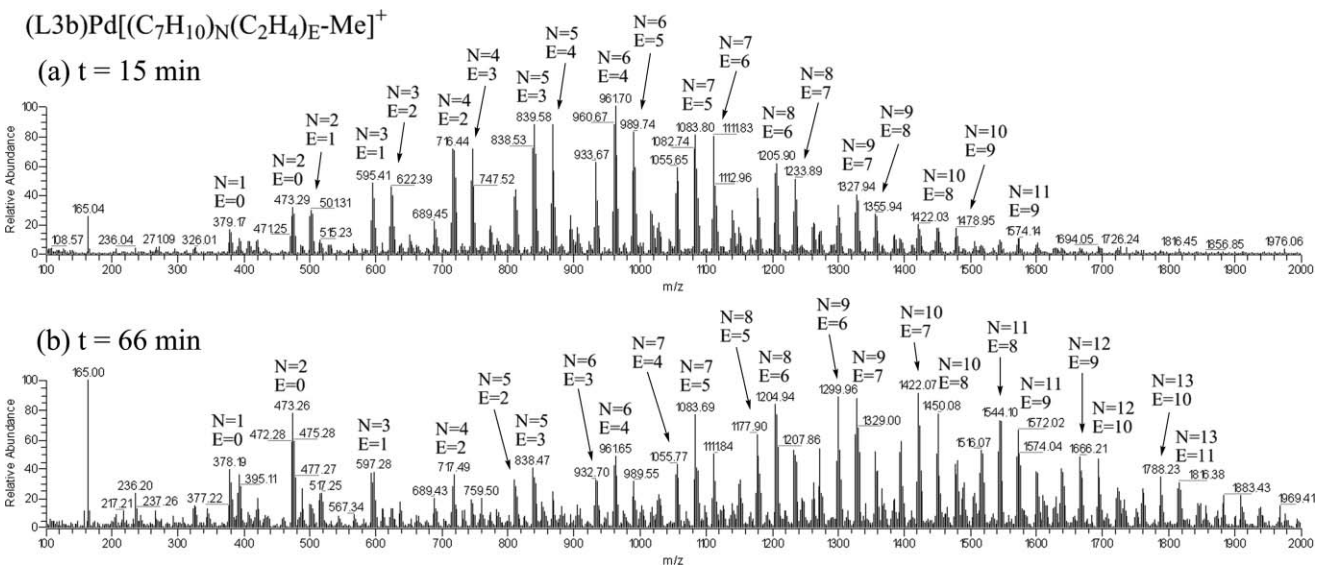


Fig. 5 ESI-MS data for E-NB copolymerization at (a) 15 min, (b) 66 min with **3b′** (1.5 mM), NB (21.3 mM), E (83 mM).

Synthesis and spectral characterization

***N*-(pyridin-2-ylmethylene)-propan-2-amine[18].** A 30 mL solution of dichloromethane that contained 2-pyridinecarboxaldehyde (2.40 mL, 25 mmol) and isopropylamine (2.20 mL, 25 mmol) was refluxed in the presence of catalytic amounts of sulfuric acid and 4 Å activated molecular sieves for 24 h. The reaction mixture was first filtrated, and the solvent was removed in *vacuo*. The product was collected as a yellow liquid by distillation (2.58 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.56 (d, J_{HH} = 5.0 Hz, 1H, Py H-6), 8.32 (s, 1H, C*H*=N), 7.91 (d, J_{HH} = 8.3 Hz, 1H, Py H-3), 7.64 (t, J_{HH} = 7.6 Hz, 1H, Py H-4) 7.22 (t, J_{HH} = 6.8 Hz, 1H, Py H-5), 3.56 (sept, J_{HH} = 6.1 Hz, 1H, NC*H*$(CH_3)_2$), 1.21 (d, J_{HH} = 5.9 Hz, 6H, NCH(C*H*$_3$)$_2$).

^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N) (L3a). To a solution of (pyridin-2-ylmethylene)-propan-2-amine (2.58 g, 17 mmol) in methanol (50 mL) was added excess $NaBH_4$ (1.00 g, 26 mmol). The reaction was stirred overnight at 25 °C, then quenched by water and extracted into dichloromethane. Then the solvent was removed under reduced pressure and the residue was distilled to give a yellow liquid product **L3a** in 74% yield (1.92 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, J_{H-H} = 4.0 Hz, 1H, Py H-2), 7.55 (dt, J_{H-H} = 2.0, 7.5 Hz, 1H, Py H-4), 7.20 (d, J_{H-H} = 7.9 Hz, 1H, Py H-5), 7.07 (t, J_{H-H} = 5.9 Hz, 1H, Py H-3), 3.82 (s, 2H, Py-C*H*$_2$N), 2.79 (sept, J_{H-H} = 6.1 Hz, 1H, NHC*H*$(CH_3)_2$), 1.04 (d, J_{H-H} = 6.5 Hz, 6H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 159.98 (Py C-2), 149.28 (Py C-6), 136.42 (Py C-4), 122.40 (Py C-5), 121.87 (Py C-3), 52.96 (Py-*C*H$_2$N), 48.46 (N*C*H$(CH_3)_2$), 22.94 (NCH(*C*H$_3$)$_2$).

(2,6-Me$_2$C$_6$H$_3$)HNCH$_2$(*o*-C$_6$H$_5$N) (L6a). A solution of 2-pyridinecarbox-aldehyde (2.40 mL, 25 mmol), 2,6-dimethyllaniline (3.10 mL, 25 mmol), catalytic amount of sulfuric acid and activated 4 Å molecular sieves in toluene (30 mL) were combined in a round-bottom flask. A condensation reaction was carried out by azeotropic removal of water using a Dean–Stark apparatus for 24 h. Then the reaction mixture was filtrated, and the solvent was removed in *vacuo*. The crude product of condensation was obtained in 68% yield (3.58 g). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.70 (d, J_{H-H} = 5.0 Hz, 1H, Py H-6), 8.33 (s, 1H, C*H*=N), 8.23 (d, J_{H-H} = 7.6 Hz, 1H, Py H-3), 7.83 (dt, J_{H-H} = 1.5, 7.7 Hz, 1H, Py H-4), 7.38 (ddd, J_{H-H} = 1.2, 4.9, 8.0 Hz, 1H, Py H-5), 6.90–7.15 (m, 5H, Ar), 2.17 (s, 6H, Ar-C*H*$_3$).

The successive reduction of 2,6-dimethyl-*N*-(pyridin-2-ylmethylene)aniline (3.58 g, 17 mmol) gave the product **L6a** in 81% yield (4.24 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (ddd, J_{H-H} = 0.9, 1.6, 4.8 Hz, 1H, Py H-6), 7.65 (dt, J_{H-H} = 1.8, 7.6 Hz, 1H, Py H-4), 7.27 (d, J_{H-H} = 7.7 Hz, 1H, Py H-3), 7.20 (ddd, J_{H-H} = 0.5, 5.0, 7.4 Hz, 1H, Py H-5), 7.02 (d, J_{H-H} = 7.3 Hz, 2H, m-Ar), 6.85 (t, J_{H-H} = 7.5 Hz, 1H, p-Ar), 4.31 (s, 2H, Py-C*H*$_2$N), 2.35 (s, 6H, Ar-C*H*$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 159.12 (Py C-2), 149.24 (Py C-6), 146.12 (ipso-Ar), 136.50 (Py C-4), 129.53 (o-Ar), 128.83 (m-Ar), 122.14 (Py C-5), 122.03 (Py C-3), 121.91 (p-Ar), 53.66 (Py-*C*H$_2$N), 18.69 (Ar-*C*H$_3$).

^{i}PrHNCMeH(*o*-C$_6$H$_5$N) (L3b). The synthesis was carried out according to the same procedure as for **L3a**, using 2-acetylpyridine (2.80 mL, 25 mmol) and isopropylamine (2.14 mL, 25 mmol) to give the product of condensation, *N*-(1-(pyridin-2-yl)ethylidene)propan-2-amine (3.56 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (ddd, J_{H-H} = 1.0, 1.8, 4.8 Hz, 1H, Py H-6), 8.06 (dt, J_{H-H} = 1.1, 8.0 Hz, 1H, Py H-3), 7.68 (dt, J_{H-H} = 1.8, 7.7 Hz, 1H, Py H-4), 7.25 (ddd, J_{H-H} = 1.3, 4.9, 7.4 Hz, 1H, Py H-5), 3.91 (sept, J_{H-H} = 6.3 Hz, 1H, NC*H*$(CH_3)_2$), 2.36 (s, 3H, Py-C(C*H*$_3$)N), 1.23 (d, J_{H-H} = 6.2 Hz, 6H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 163.62 (Py-*C*(CH_3)N), 158.41 (Py C-2), 148.16 (Py C-6), 136.30 (Py C-4), 123.84 (Py C-5), 121.09 (Py C-3), 51.56 (N*C*H$(CH_3)_2$), 23.42 (NCH(*C*H$_3$)$_2$), 13.63 (Py-C(*C*H$_3$)N).

The reductive reaction of *N*-(1-(pyridin-2-yl)ethylidene)propan-2-amine (3.56 g, 22 mmol) gave the product **L3b** in 73% yield (2.62 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (ddd, J_{H-H} = 0.9, 1.7, 4.8 Hz, 1H, Py H-6), 7.61 (dt, J_{H-H} = 1.8, 7.6 Hz, 1H, Py H-4), 7.26 (d, J_{H-H} = 8.0 Hz, 1H, Py H-3), 7.12 (ddd, J_{H-H} = 1.2, 4.8, 7.5 Hz, 1H, Py H-5), 3.96 (q, J_{H-H} = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 2.59 (sept, J_{H-H}= 6.2 Hz, 1H, NC*H*$(CH_3)_2$), 1.35 (d, J_{H-H} = 4.7 Hz, 3H, Py-CH(C*H*$_3$)N), 1.04, 0.98 (d, J_{H-H} = 6.2, 6.3 Hz, 6H, NCH(C*H*$_3$)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 165.01 (Py C-2), 149.29 (Py C-6), 136.33 (Py C-4), 121.72 (Py C-5), 121.28 (Py C-3), 56.19 (Py-*C*H(CH_3)N), 45.70 (N*C*H$(CH_3)_2$), 23.24 (Py-CH(*C*H$_3$)N), 23.81, 22.25 (NCH(*C*H$_3$)$_2$).

[^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (3a). To a solution of (COD)PdMeCl (50 mg, 0.19 mmol) in Et_2O (15 mL) was added **L3a** (28 mg, 0.19 mmol) which was dissolved in Et_2O (5 mL). The mixture was stirred for 1 h at room temperature. After filtration, the resulting precipitate was washed twice with Et_2O (2 × 5 mL) and dried in *vacuo*. The desired air-stable complex was obtained as a pale yellow powder in 96% yield (59 mg). Single crystals suitable for X-ray diffraction were grown by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of **3a**. ^{1}H NMR (400 MHz, $CDCl_3$) for *trans*-**3a**: δ 8.34 (d, J_{H-H} = 5.4 Hz, 1H, Py H-6), 7.82 (dt, J_{H-H} = 1.4, 7.7 Hz, 1H, Py H-4), 7.39 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.25–7.35 (m, 1H, Py H-5), 4.49 (dd, J_{H-H} = 6.6, 16.2 Hz, 1H, Py-C*H*′HN), 3.93 (dd, J_{H-H} = 3.1, 16.1 Hz, 1H, Py-CH′*H*N), 3.24 (bs, 1H, N*H*CH$(CH_3)_2$), 3.18 (sept, J_{H-H} = 6.9 Hz, 1H, NHC*H*$(CH_3)_2$), 0.79 (s, 3H, Pd-C*H*$_3$); *cis*-**3a**: δ 8.72 (d, J_{H-H} = 4.7 Hz, 1H, Py H-6), 7.71 (dt, J_{H-H} = 1.6, 7.7 Hz, 1H, Py H-4), 7.25–7.35 (m, 1H, Py H-3), 7.20 (t, J_{H-H} = 6.5 Hz, 1H, Py H-5), 4.75 (dd, J_{H-H} = 6.5, 16.0 Hz, 1H, Py-C*H*′HN), 4.56 (bs, 1H, N*H*CH$(CH_3)_2$), 4.05 (dd, J_{H-H} = 3.1, 16.1 Hz, 1H, Py-CH′*H*N), 3.20 (sept, J_{H-H} = 6.3 Hz, 1H, NHC*H*$(CH_3)_2$), 0.54 (s, 3H, Pd-C*H*$_3$); 1.27, 1.21, 1.25 (d, d, m, J_{H-H}= 6.2, 6.4 Hz, 12H, NHCH(C*H*$_3$)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *trans*-**3a**: δ 163.99 (Py C-2), 148.08 (Py C-6), 137.96 (Py C-4), 123.78 (Py C-5), 122.37 (Py C-3), 52.43 (Py-*C*H$_2$N), 51.34 (NH*C*H$(CH_3)_2$), 22.34, 21.47 (NHCH(*C*H$_3$)$_2$), -0.09 (Pd-*C*H$_3$); *cis*-**3a**: δ 159.12 (Py C-2), 148.13 (Py C-6), 138.12 (Py C-4), 123.27 (Py C-5), 120.61 (Py C-3), 54.49 (Py-*C*H$_2$N), 53.47 (NH*C*H$(CH_3)_2$), 22.00, 21.37 (NHCH(*C*H$_3$)$_2$), -8.87 (Pd-*C*H$_3$). Anal. Calcd for $C_{10}H_{17}N_2PdCl$: C, 39.10; H, 5.54; N, 9.12. Found: C, 38.52; H, 5.47; N, 9.29.

[(2,6-Me$_2$C$_6$H$_3$)HNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (6a). The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (283 mg, 1.07 mmol) and **L6a** (227 mg, 1.07 mmol) to give the pale white product **6a** (343 mg, 87%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for *cis*-**6a**: δ 8.72 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.70 (dt, J_{H-H} = 1.7, 7.8 Hz, 1H, Py H-4), 7.22 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), 7.00–7.16 (m, 1H, Py H-5; 2H, m-Ar; 1H, p-Ar), 6.68 (t, J_{H-H} = 7.5 Hz, 1H, N*H*-Ar), 5.07 (dd, J_{H-H} = 7.6, 17.3 Hz, 1H,

Py-C*H′*HN), 4.29 (dd, $J_{H\text{-}H}$ = 7.3, 17.3 Hz, 1H, Py-CH′*H*N), 2.91, 2.51 (s, 6H, Ar-CH_3), 0.10 (s, 3H, Pd-CH_3); *trans*-**6a**: δ 8.49 (d, $J_{H\text{-}H}$ = 6.4 Hz, 1H, Py H-6), 7.88 (dt, $J_{H\text{-}H}$ = 1.4, 7.8 Hz, 1H, Py H-4), 7.40 (t, $J_{H\text{-}H}$ = 7.0 Hz, 1H, Py H-5), 7.34 (d, $J_{H\text{-}H}$ = 7.3 Hz, 1H, Py H-3), 7.00–7.16 (2H, m-Ar; 1H, p-Ar), 1.00 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *cis*-**6a**: δ 158.37 (Py C-2), 147.80 (Py C-6), 143.21 (ipso-Ar), 137.58 (Py C-4), 130.82, 129.57 (o-Ar), 131.07, 123.29 (Py C-5 and p-Ar), 128.48, 125.97 (m-Ar), 120.16 (Py C-3), 59.87 (Py-*C*H_2N), 20.22, 18.96 (Ar-*C*H_3), -6.03 (Pd-*C*H_3); *trans*-**6a**: δ 147.96 (Py C-6), 138.10 (Py C-4), 125.30, 124.04, 122.13 (Py C-5, Py C-3 and p-Ar), 62.97 (Py-*C*H_2N), 0.15 (Pd-*C*H_3).

[^{i}PrHNCMeH(*o*-C_6H_5N)]Pd(Me)Cl (3b). The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (200 mg, 0.75 mmol) and **L3b** (124 mg, 0.75 mmol) to give the pale white product **3b** (214 mg, 89%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for *trans*-**3b**: δ 8.41 (d, $J_{H\text{-}H}$ = 5.2 Hz, 1H, Py H-6), 7.84 (dt, $J_{H\text{-}H}$ = 1.6, 7.7 Hz, 1H, Py H-4), 7.20–7.40 (1H, Py H-3; 1H, Py H-5), 4.14 (q, $J_{H\text{-}H}$ = 6.8 Hz, 1H, Py-C*H*(CH$_3$)N), 3.05 (sept, $J_{H\text{-}H}$ = 6.6 Hz, 1H, NHC*H*(CH$_3$)$_2$), 1.89 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(CH_3)N), 1.20–1.30 (m, 6H, NHCH(CH_3)$_2$), 0.90 (s, 3H, Pd-CH_3); *cis*-**3b**: δ 8.84 (d, $J_{H\text{-}H}$ = 5.2 Hz, 1H, Py H-6), 7.77 (dt, $J_{H\text{-}H}$ = 1.5, 7.7 Hz, 1H, Py H-4), 7.20–7.40 (m, 1H, Py H-3; 1H, Py H-5), 4.24 (q, $J_{H\text{-}H}$ = 6.7 Hz, 1H, Py-C*H*(CH$_3$)N), 3.09 (sept, $J_{H\text{-}H}$ = 6.5 Hz, 1H, NHC*H*(CH$_3$)$_2$), 1.89 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(CH_3)N), 1.20–1.30 (m, 6H, NHCH(CH_3)$_2$), 0.59 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *trans*-**3b**: δ 168.41 (Py C-2), 138.42 (Py C-4), 60.00 (Py-*C*H(CH$_3$)N), 52.26 (NH*C*H(CH$_3$)$_2$), 0.17 (Pd-*C*H_3); *cis*-**3b**: δ 162.65 (Py C-2), 138.42 (Py C-4), 62.77 (Py-*C*H(CH$_3$)N), 55.22 (NH*C*H(CH$_3$)$_2$), -11.21 (Pd-*C*H_3); 148.71, 148.30 (Py C-6) 123.94, 123.70, 121.99, 120.38 (Py C-5 and Py C-3), 25.04, 24.51(Py-CH(*C*H_3)N), 23.33, 22.97, 22.43, 22.28 (NHCH(*C*H_3)$_2$). Anal. Calcd for $C_{11}H_{19}N_2PdCl$: C, 41.18; H, 5.92; N, 8.73. Found: C, 40.89; H, 5.92; N, 8.53.

[(2,6-$Me_2C_6H_3$)HNCMeH(*o*-C_6H_5N)]Pd(Me)Cl (6b). The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (265 mg, 1.00 mmol) and **L6b** (226 mg, 1.00 mmol) to give the pale white product **6b** (332 mg, 87%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for *cis*-**6b**: δ 9.10 (d, $J_{H\text{-}H}$ = 4.9 Hz, 1H, Py H-6), 7.86 (dt, $J_{H\text{-}H}$ = 1.7, 7.7 Hz, 1H, Py H-4), 7.40 (t, $J_{H\text{-}H}$ = 7.3 Hz, 1H, Py H-5), 7.30 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Py H-3), 7.15 (m, 1H, p-Ar), 7.07 (m, 2H, m-Ar), 5.50 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, N*H*-Ar), 4.69 (m, 1H, Py-C*H*(CH$_3$)N), 2.91, 2.38 (s, 6H, Ar-CH_3), 1.62 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(CH_3)N), 0.13 (s, 3H, Pd-CH_3); *trans*-**6b**: δ 8.54 (d, $J_{H\text{-}H}$ = 5.8 Hz, 1H, Py H-6), 7.91 (dt, $J_{H\text{-}H}$ = 1.6, 7.8 Hz, 1H, Py H-4), 7.40 (1H, Py H-5), 7.34 (1H, Py H-3), 7.03 (m, 2H, m-Ar), 6.95 (m, 1H, p-Ar), 4.69 (1H, N*H*-Ar), 4.43 (m, 1H, Py-C*H*(CH$_3$)N), 2.51 (bs, 6H, Ar-CH_3), 1.75 (d, $J_{H\text{-}H}$ = 6.9 Hz, 3H, Py-CH(CH_3)N), 1.03 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *cis*-**6b**: δ 160.39 (Py C-2), 148.79 (Py C-6), 141.10 (ipso-Ar), 138.31 (Py C-4), 131.73 (p-Ar), 130.45, 129.20 (o-Ar), 128.58, 126.16 (m-Ar), 124.07 (Py C-5), 121.04 (Py C-3), 65.17 (Py-*C*H(CH$_3$)N), 20.42, 18.73 (Ar-*C*H_3), 19.79 (Py-CH(*C*H_3)N), -5.18 (Pd-*C*H_3); *trans*-**6b**: δ 167.23 (Py C-2), 147.89 (Py C-6), 138.31 (Py C-4), 128.60, 128.52, 128.29, 126.55, 124.90, 124.78 (Py C-5, m-Ar, o-Ar and p-Ar), 122.64(Py C-3), 63.05 (Py-*C*H(CH$_3$)N), 22.75 (Py-CH(*C*H$_3$)N), 17.80, 17.34 (Ar-*C*H_3), 0.19 (Pd-*C*H_3). Anal. Calcd for $C_{16}H_{21}N_2PdCl$: C, 50.15; H, 5.48; N, 7.31. Found: C, 49.50; H, 5.63; N, 7.12.

{[^{i}PrHNCH$_2$(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (3a′). A Schlenk flask was charged with complex **3a** (120 mg, 0.39 mmol) and $AgBF_4$ (76 mg, 0.39 mmol) in a glovebox, followed with CH_2Cl_2 (15 mL) and MeCN (1 mL). The mixture was stirred at 25 °C for 2 h. The residue of AgCl and Pd were removed by filtering through celite. The resulting pale yellow solution was concentrated in *vacuo* and then precipitated by addition of Et_2O (20 mL). After filtration, the crude product was washed with Et_2O (2 × 5 mL) and dried in *vacuo*. The desired air-sensitive complex was obtained as pale white powder in 56% yield (87 mg). Alternatively, one-pot reaction with (COD)PdMeCl, $AgBF_4$, **L3a**, CH_2Cl_2 and MeCN also provided the desired product. Single crystals were grown from $Et_2O/MeCN/CH_2Cl_2$ solution. ^{1}H NMR (400 MHz, $CDCl_3$) for *trans*-**3a′**: δ 8.26 (d, $J_{H\text{-}H}$= 5.6 Hz, 1H, Py H-6), 7.91 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, Py H-4), 7.50 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.37 (t, $J_{H\text{-}H}$ = 6.6 Hz, 1H, Py H-5), 4.51 (dd, $J_{H\text{-}H}$ = 6.3, 16.5 Hz, 1H, Py-C*H′*HN), 4.14 (bs, 1H, N*H*CH(CH$_3$)$_2$), 3.97 (d, $J_{H\text{-}H}$ = 16.5 Hz, 1H, Py-CH′*H*N), 2.89 (qd, $J_{H\text{-}H}$ = 6.3, 6.4 Hz, 1H, NHC*H*(CH$_3$)$_2$), 2.39 (s, 3H, NCCH_3), 1.22, 1.14 (d, $J_{H\text{-}H}$ = 6.3, 6.4 Hz, 6H, NHCH(CH_3)$_2$), 0.79 (s, 3H, Pd-CH_3); *cis*-**3a′**: δ 8.42 (d, $J_{H\text{-}H}$ = 4.9 Hz, 1H, Py H-6), 7.84 (t, $J_{H\text{-}H}$ = 7.8 Hz, 1H, Py H-4), 7.46 (d, $J_{H\text{-}H}$ = 6.4 Hz, 1H, Py H-3), 7.43 (t, $J_{H\text{-}H}$ = 7.6 Hz, 1H, Py H-5), 4.65 (bs, 1H, N*H*CH(CH$_3$)$_2$), 4.63 (dd, $J_{H\text{-}H}$ = 5.9, 16.7 Hz, 1H, Py-C*H′*HN), 4.12 (d, $J_{H\text{-}H}$= 16.6 Hz, 1H, Py-CH′*H*N), 3.03 (m, 1H, NHC*H*(CH$_3$)$_2$), 2.45 (s, 3H, NCCH_3), 1.17 (d, $J_{H\text{-}H}$ = 6.5 Hz, 3H, NHCH(CH_3)$_2$), 1.12–1.15 (3H, NHCH(CH_3)$_2$), 0.65 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *trans*-**3a′**: δ 164.80 (Py C-2), 148.28 (Py C-6), 139.66 (Py C-4), 124.12 (Py C-5), 122.09 (Py C-3), 53.85 (Py-*C*H$_2$N), 52.44 (NH*C*H(CH$_3$)$_2$), 22.48, 21.39 (NHCH(*C*H$_3$)$_2$), 3.25 (NC*C*H$_3$), 1.82 (Pd-*C*H_3); *cis*-**3a′**: δ 158.97 (Py C-2), 148.38 (Py C-6), 139.21 (Py C-4), 124.38 (Py C-5), 121.56 (Py C-3), 56.68 (Py-*C*H$_2$N), 55.37 (NHCH(CH$_3$)$_2$), 22.41, 21.78 (NHCH(*C*H$_3$)$_2$), 3.18 (NC*C*H$_3$), -7.32 (Pd-*C*H_3). Anal. Calcd for $C_{12}H_{20}N_3PdBF_4$: C, 36.07; H, 5.01; N, 10.52. Found: C, 35.89; H, 4.73; N, 10.52.

{[(2,6-$Me_2C_6H_3$)HNCH$_2$(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (6a′). The synthesis was carried out according to the same procedure as for **3a′**, using **6a** (200 mg, 0.54 mmol) and $AgBF_4$ (105 mg, 0.54 mmol) to give the pale white product **6a′** (207 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) for *trans*-**6a′**: δ 8.31 (d, $J_{H\text{-}H}$ = 5.8 Hz, 1H, Py H-6), 7.94 (dt, $J_{H\text{-}H}$ = 1.5, 7.8 Hz, 1H, Py H-4), 7.52 (1H, Py H-3), 7.41 (1H, Py H-5), 6.95–7.15 (m, 2H, m-Ar; 1H, p-Ar), 5.89 (t, $J_{H\text{-}H}$ = 7.6 Hz, 1H, N*H*-Ar), 4.82 (1H, Py-C*H′*HN), 4.48 (dd, $J_{H\text{-}H}$ = 9.3, 17.1 Hz, 1H, Py-CH′*H*N), 2.76 (bs, 6H, Ar-CH_3), 1.85 (s, 3H, NCCH_3), 0.98 (s, 3H, Pd-CH_3); *cis*-**6a′**: δ 8.49 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.87 (dt, $J_{H\text{-}H}$ = 1.6, 7.8 Hz, 1H, Py H-4), 7.51 (1H, Py H-5), 7.40 (1H, Py H-3), 6.95–7.15 (m, 2H, m-Ar; 1H, p-Ar), 6.48 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, N*H*-Ar), 4.82 (dd, $J_{H\text{-}H}$ = 6.5, 16.9 Hz, 1H, Py-C*H′*HN), 4.40 (dd, $J_{H\text{-}H}$ = 8.4, 16.6 Hz, 1H, Py-CH′*H*N), 2.90, 2.42 (s, 6H, Ar-CH_3), 2.45 (s, 3H, NCCH_3), 0.17 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *trans*-**6a′**: δ 163.47 (Py C-2), 147.75 (Py C-6), 141.55 (ipso-Ar), 139.62 (Py C-4), 125.60 (p-Ar), 124.24 (Py C-5), 123.40 (Py C-3), 55.00 (Py-*C*H$_2$N), 2.74 (NC*C*H$_3$), 2.15 (Pd-*C*H_3); *cis*-**6a′**: δ 157.36 (Py C-2), 148.33 (Py C-6), 141.63 (ipso-Ar), 139.09 (Py C-4), 131.20

(p-Ar), 124.60 (Py C-5), 121.44 (Py C-3), 60.51 (Py-*C*H$_2$N), 3.37 (NC*C*H$_3$), -1.35 (Pd-*C*H$_3$); 130.09, 129.99, 129.91, 129.82 (o-Ar), 128.92, 126.74 (m-Ar), 20.15, 19.70, 18.06, 18.00 (Ar-*C*H$_3$). Anal. Calcd for $C_{17}H_{22}N_3PdBF_4$: C, 44.24; H, 4.77; N, 9.11. Found: C, 43.93; H, 4.85; N, 9.20.

{[^{i}PrHNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (3b′). The synthesis was carried out according to the same procedure as for **3a′**, using **3b** (300 mg, 0.93 mmol) and $AgBF_4$ (182 mg, 0.93 mmol) to give the pale white product **3b′** (290 mg, 75%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for *trans*-**3b′**: δ 8.27 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.88 (dt, $J_{H\text{-}H}$ = 1.4, 7.7 Hz, 1H, Py H-4), 7.46 (d, $J_{H\text{-}H}$ = 7.8 Hz, 1H, Py H-3), 7.33 (dt, $J_{H\text{-}H}$ = 1.2, 7.2 Hz, 1H, Py H-5), 4.22 (q, $J_{H\text{-}H}$ = 6.7 Hz, 1H, Py-C*H*(CH$_3$)N), 2.83 (qd, $J_{H\text{-}H}$ = 6.4, 12.9 Hz, 1H, NHC*H*(CH$_3$)$_2$), 2.39 (s, 3H, NCC*H*$_3$), 1.87 (d, $J_{H\text{-}H}$ = 6.5 Hz, 3H, Py-CH(C*H*$_3$)N), 1.23, 1.16 (d, $J_{H\text{-}H}$ = 6.4, 6.5 Hz, 6H, NHCH(C*H*$_3$)$_2$), 0.81 (s, 3H, Pd-C*H*$_3$); *cis*-**3b′**: δ 8.42 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.88 (dt, $J_{H\text{-}H}$ = 0.8, 7.7 Hz, 1H, Py H-4), 7.46 (t, $J_{H\text{-}H}$ = 6.4 Hz, 1H, Py H-5), 7.43 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 4.32 (q, $J_{H\text{-}H}$ = 6.7 Hz, 1H, Py-C*H*(CH$_3$)N), 3.02 (qd, $J_{H\text{-}H}$ = 6.4, 11.6 Hz, 1H, NHC*H*(CH$_3$)$_2$), 2.44 (s, 3H, NCC*H*$_3$), 1.82 (d, $J_{H\text{-}H}$ = 6.7 Hz, 3H, Py-CH(C*H*$_3$)N), 1.52, 1.13 (d, $J_{H\text{-}H}$ = 6.5, 6.5 Hz, 6H, NHCH(C*H*$_3$)$_2$), 0.66 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *trans*-**3b′**: δ 168.69 (Py C-2), 148.38 (Py C-6), 139.61 (Py C-4), 124.05 (Py C-5), 122.68 (Py C-3), 60.86 (Py-*C*H(CH$_3$)N), 52.45 (NH*C*H(CH$_3$)$_2$), 23.80 (Py-CH(*C*H$_3$)N), 22.78, 21.50 (NHCH(*C*H$_3$)$_2$), 3.29 (NC*C*H$_3$), 1.58 (Pd-*C*H$_3$); *cis*-**3b′**: δ 162.99 (Py C-2), 148.55 (Py C-6), 139.61 (Py C-4), 124.54 (Py C-5), 121.52 (Py C-3), 64.08 (Py-*C*H(CH$_3$)N), 55.67 (NH*C*H(CH$_3$)$_2$), 24.68 (Py-CH(*C*H$_3$)N), 23.29, 22.23 (NHCH(*C*H$_3$)$_2$), 3.23 (NC*C*H$_3$), -8.20 (Pd-*C*H$_3$). Anal. Calcd for $C_{13}H_{22}N_3PdBF_4$: C, 37.83; H, 5.34; N, 10.19. Found: C, 37.54; H, 5.00; N, 9.93.

{[(2,6-Me$_2$C$_6$H$_3$)HNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (6b′). The synthesis was carried out according to the same procedure as for **3a′**, using (COD)PdMeCl (300 mg, 1.13 mmol), $AgBF_4$ (221 mg, 1.13 mmol) and **L6b** (255 mg, 1.13 mmol) to give the pale white product **6b′** (450 mg, 84%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) for *trans*-**6b′**: δ 8.37 (d, $J_{H\text{-}H}$ = 5.7 Hz, 1H, Py H-6), 8.04 (dt, $J_{H\text{-}H}$ = 1.5, 7.9 Hz, 1H, Py H-4), 7.54 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.47 (d, $J_{H\text{-}H}$ = 6.6 Hz, 1H, Py H-5), 6.95–7.20 (m, 2H, m-Ar; 1H, p-Ar), 5.20 (bs, 1H, N*H*-Ar), 4.82 (qd, $J_{H\text{-}H}$ = 6.7, 9.5 Hz, 1H, Py-C*H*(CH$_3$)N), 1.84 (NC*C*H$_3$), 0.95 (s, 3H, Pd-C*H*$_3$); *cis*-**6b′**: δ 8.62 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.95 (dt, $J_{H\text{-}H}$ = 1.6, 8.0 Hz, 1H, Py H-4), 7.60 (dt, $J_{H\text{-}H}$ = 1.1, 6.5 Hz, 1H, Py H-5), 7.42 (1H, $J_{H\text{-}H}$ = 7.9 Hz, Py H-3), 6.95–7.20 (m, 2H, m-Ar; 1H, p-Ar), 5.69 (d, $J_{H\text{-}H}$ = 9.0 Hz, 1H, Py-C*H*(CH$_3$)N), 4.71 (qd, $J_{H\text{-}H}$ = 7.1, 7.4 Hz, 1H, Py-C*H*(CH$_3$)N), 2.85, 2.36 (s, 6H, Ar-C*H*$_3$), 2.48 (NC*C*H$_3$), 0.09 (s, 3H, Pd-C*H*$_3$). 1.60 (m, 6H, Py-CH(C*H*$_3$)N). ^{1}H NMR (500 MHz, $CDCl_3$, 253K) for *trans*-**6b′**: δ 8.37 (d, $J_{H\text{-}H}$ = 5.7 Hz, 1H, Py H-6), 8.04 (dt, $J_{H\text{-}H}$ = 1.5, 7.9 Hz, 1H, Py H-4), 7.52 (m, 1H, Py H-3; 1H, Py H-5), 7.20–7.20 (m, 2H, m-Ar; 1H, p-Ar), 4.90 (d, $J_{H\text{-}H}$ = 10.8 Hz, 1H, N*H*-Ar), 4.84 (m, 1H, Py-C*H*(CH$_3$)N), 3.01, 2.34 (s, 6H, Ar-C*H*$_3$), 1.79 (NC*C*H$_3$), 0.92 (s, 3H, Pd-C*H*$_3$); *cis*-**6b′**: δ 8.62 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.95 (dt, $J_{H\text{-}H}$ = 1.6, 8.0 Hz, 1H, Py H-4), 7.60 (t, $J_{H\text{-}H}$ = 6.5 Hz, 1H, Py H-5), 7.43 (1H, $J_{H\text{-}H}$ = 8.0 Hz, Py H-3), 7.00–7.20 (m, 2H, m-Ar; 1H, p-Ar), 5.63 (d, $J_{H\text{-}H}$ = 9.2 Hz, 1H, N*H*-Ar), 4.72 (m, 1H, Py-C*H*(CH$_3$)N), 2.87, 2.33 (s, 6H, Ar-C*H*$_3$), 2.45 (NC*C*H$_3$), 0.04 (s, 3H, Pd-C*H*$_3$); 1.55 (d, $J_{H\text{-}H}$ = 6.6 Hz, 6H, Py-CH(C*H*$_3$)N). ^{13}C NMR (100.625 MHz, $CDCl_3$) for *trans*-**6b′**: δ 164.99 (Py C-2), 148.91 (Py C-6), 140.37 (ipso-Ar), 140.22 (Py C-4), 60.07 (Py-*C*H(CH$_3$)N), 20.13, 18.44 (Ar-*C*H$_3$), 18.32 (Py-CH(*C*H$_3$)N), 3.10 (NC*C*H$_3$), 2.00 (Pd-*C*H$_3$); *cis*-**6b′**: δ 159.71 (Py C-2), 148.32 (Py C-6), 140.02 (ipso-Ar), 139.65 (Py C-4), 66.57 (Py-*C*H(CH$_3$)N), 18.62, 18.44 (Ar-*C*H$_3$), 18.32 (Py-CH(*C*H$_3$)N), 3.35 (NC*C*H$_3$), -1.08 (Pd-*C*H$_3$); 131.88, 131.36, 129.32, 128.96, 126.85, 125.92 (m-Ar and p-Ar), 130.35, 130.19, 130.10, 129.90 (o-Ar), 125.35, 124.76, 123.95, 122.08 (Py C-3 and Py C-5). Anal. Calcd for $C_{18}H_{24}N_3PdBF_4$: C, 45.45; H, 5.05; N, 8.84. Found: C, 45.89; H, 4.57; N, 9.74.

General procedure for copolymerization of ethylene-norbornene

Into a 600 mL Parr autoclave equipped with a magnetic stirring bar was placed norbornene (0.5–30 g) in dried CH_2Cl_2 (50 mL). The autoclave was sealed. Upon flush with ethylene gas several times, the ethylene gas was pressurized. The solution was stirred for 20 min in order to be saturated with ethylene gas. After release of ethylene pressure, the palladium complexes (0.06 mmol) were added, and then refilled with ethylene gas up to 21 bar. The mixture was stirred for 30 min, and the ethylene pressure was kept constant during the copolymerization runs. The reaction was quenched with venting the autoclave followed by adding 100 mL MeOH–HCl in 4:1 v/v ratio. The precipitated polymers were filtered from solution, washed with methanol and dried in vacuum oven at 80 °C overnight.

X-ray crystallographic analysis

Diffraction data were measured on a Nonius CAD-4, SmartCCD, or Nonius KappaCCD diffractometer with graphite-monochromatized Mo K_α radiation (λ = 0.7103 Å). No significant decay was observed during the data collection. The data were processed on a PC using the SHELXTL refinement software package.[19] The structures were solved using the direct method and refined by full-matrix least-squares on the F^2 value.

All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were identified by calculation and refined using a riding mode, and their contributions to structure factors were included. Atomic scattering factors were taken from the International Tables of Crystallographic Data, Vol. IV. Computing programs are from the NRC VAX package.[20]

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