

Pyrazolyl-pyrimidine based ligands in palladium catalyzed copolymerization and terpolymerization of CO/olefins

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Dedicated to Dr. Antonio Abad for his contributions in organometallic chemistry.

Abstract

Cationic palladium(II) complexes of the type $[\text{PdMe}(\text{NCMe})(N-N')][\text{BAR}'_4]$ containing bisnitrogen ligands with a pyrazole moiety were synthesized from the corresponding neutral derivatives $[\text{PdClMe}(N-N')]$. Their characterization by ^1H and ^{13}C NMR spectroscopy in solution evidences the presence of the Pd–Me group *cis* to the pyrazole ring. The catalytic behaviour of the cationic complexes in CO/4-*tert*-butylstyrene copolymerization and CO/ethylene/4-*tert*-butylstyrene terpolymerization was investigated. Productivity was greatly enhanced when the reaction was carried out in 2,2,2-trifluoroethanol (TFE). Molecular weights and polydispersity (M_w/M_n) of the obtained polyketones resulted among the best reported for C_s -bisnitrogen planar ligands.

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Keywords: Palladium; Nitrogen ligands; Polyketone; Carbon monoxide; Copolymerization; Terpolymerization

1. Introduction

The search for new polymers with high content of heteroatom functionalities that can provide materials with interesting engineering properties continues unabated ever since the rise of polyolefin production and of the plastics made from them for daily use. Whereas alternating ethene/CO copolymers are white crystalline high-melting solids, only poorly soluble and difficult to process, the corresponding terpolymers containing small amount of propene/CO units (5–10%) show reduced melting transitions and more favourable behaviour in blow-molding or extrusion applications. This thermoplastic material was commercialised by Shell under the trade name Carilon in the 1990s [1].

The research on polyketones prepared with late transition metal catalysts continues in academic and industrial laboratories around the world. It has been comprehensively reviewed [2–9]. The most thoroughly studied comonomers are ethene and propene, for which Pd complexes based on bisphosphine ligands and non-coordinating counterion have been by far the most widely used precatalysts [2,10]. Alternating copolymerization of ethene or propene with carbon monoxide has become an attractive option due to the readily available and inexpensive starting materials. Moreover, the resulting polymer, poly(1,4-ketone), has potential photo- and biodegradable properties owing to the repeating carbonyl units [11], which lend themselves to further chemical modifications [12]. Among the higher olefins, vinylarenes have gained most attention as comonomers. Most of the results with styrene and derivatives have been obtained with catalysts based on ligands developed for the stereocontrolled co- and terpolymerization [13–25], as for N–N [13–17], P–N [18,19], N–N' [25] and P–O [23].

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Furthermore, it has been shown that catalytic tests performed in 2,2,2-trifluoroethanol (TFE) as solvent, greatly improved catalyst lifetime leading to higher productivities and molecular weights [26].

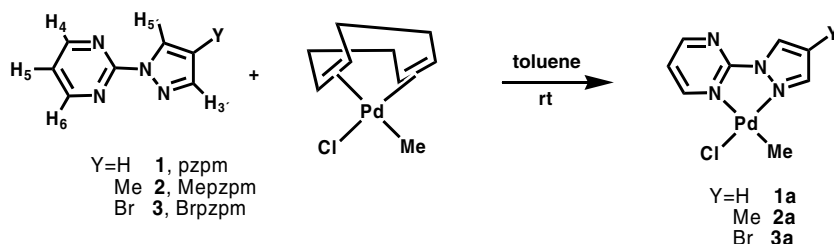
We have previously shown that in the CO/*tert*-butylstyrene/ethylene terpolymerization catalyzed by $[\text{Pd}(\text{Me})(\text{NCMe})(N-N')][\text{BAR}'_4]$ complexes $[\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3]$, where $N-N' =$ pyridine-imidazoline and pyrazolyl-pyrimidine ligands, the olefin preferentially inserted in the terpolymer chain is strictly related to the nature of the nitrogen ligand [27].

In this paper we extend this study to the synthesis and characterization of complexes of general formula $[\text{Pd}(\text{Me})(\text{NCMe})(N-N')][\text{BAR}'_4]$ from their corresponding chloro neutral complexes containing pyrazolyl-pyrimidine ligands. The catalytic behaviour of the cationic complexes in CO/4-*tert*-butylstyrene copolymerization and CO/ethylene/4-*tert*-butylstyrene terpolymerization has been studied. Furthermore, catalytic experiments have been carried out in 2,2,2-trifluoroethanol (TFE).

2. Results and discussion

2.1. Synthesis and characterization of neutral palladium complexes $[\text{PdClMe}(N-N')]$ (**1a–3a**)

New neutral complexes **2a** and **3a** were readily synthesized similarly to a procedure reported in the literature [28] for the synthesis of the neutral complex $[\text{PdClMe}(\mathbf{1})]$, (**1a**). Addition of 1 equiv. of the corresponding ligand to a solution of $[\text{PdClMe}(\text{cod})]$ in toluene gave the neutral complexes **2a** and **3a** (Scheme 1), which were fully characterized by elemental analysis, ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy in solution as well as by NOE and g-HSQC experiments. ^1H NMR shows the signals corresponding to coordinated pyrazolyl-pyrimidine ligands and the σ -bonded palladium methyl group. Spectroscopic data also suggested that H_6 is sensitive to coordination being the ^1H NMR signal considerably downfield shifted with respect to the corresponding one in the free ligand [29]. This suggests that chloride is *cis* coordinated [30] to the pyrimidine ring in all neutral complexes (**1a–3a**). This has been confirmed by NOE experiments at room temperature, that showed the interaction between the Pd–Me group and H_3' of the pyrazole ring.



Scheme 1. Synthesis and characterization of the neutral palladium derivatives $[\text{PdClMe}(N-N')]$ (**1a–3a**)

2.2. Synthesis and characterization of cationic palladium catalyst precursors $[\text{Pd}(\text{Me})(\text{NCMe})(N-N')][\text{BAR}'_4]$ (**1b–3b**)

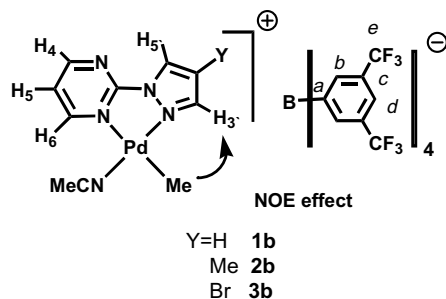
The cationic palladium catalyst precursors $[\text{Pd}(\text{Me})(\text{NCMe})(N-N')][\text{BAR}'_4]$ (Scheme 2) were synthesized by adding a CH_2Cl_2 solution of the neutral derivatives (**1a–3a**) to an equimolar solution of NaBAR'_4 in anhydrous MeCN. These palladium complexes were obtained as yellow pale solids, which resulted to be completely soluble in chlorobenzene and dichloromethane, solvents selected for copolymerization and terpolymerization, respectively. No crystals suitable for structural determination were obtained for complexes **1b–3b**. They were fully identified by means of elemental analysis, ^1H and ^{13}C $\{^1\text{H}\}$ NMR spectroscopy in solution. The resonances were assigned on the basis of selective decoupling experiments and on the multiplicity of the signals. The coordinated methyl group appear upfield as a singlet in the range between 1.2 and 1.3 ppm, showing irrelevant chemical shift differences of this Pd–Me proton signal, moving from **1b** to **3b**. This indicates that there is not a clear electronic influence of the substituents (Y) in position 4' of the pyrazole ring over these methyl groups.

Irradiation of the methyl group at room temperature produced a NOE difference signal on H_3' of the pyrazole ring. This reflects a *trans*-disposition with respect the pyrimidine moiety of the ligand (Scheme 2).

The relative disposition of the ligands found in complexes **1a–3a** and **1b–3b** is that expected considering electronic factors. The methyl group which has a higher *trans* influence than the chloride or acetonitrile is situated *trans* to the weaker donor heterocycle. Besides, on the basis of steric factors the stereochemistry predicted would be the same. The methyl in proximity of H_6 of the six-membered pyrimidine ring would give rise to a major steric repulsion than in the proximity of H_3' of the five-membered pyrazole moiety. ^1H NOESY NMR spectrum for cationic complexes **1b–3b** recorded at room temperature did not show any interionic contact. This is not surprising considering that $\text{B}(\text{3,5-(CF}_3)_2\text{C}_6\text{H}_3)_4$ is a weak coordinating anion [31].

2.3. Catalytic CO/TBS copolymerization

The CO/4-*tert*-butylstyrene (TBS) copolymerization reaction promoted by cationic palladium catalysts



Scheme 2. *trans*-Disposition of the Me group with respect to the pyrimidine moiety.

[Pd(Me)(NCMe)(*N-N'*)] $[BAR_4']$ (**1b–3b**) was investigated (Table 1). All catalytic experiments were carried out at 1 bar of CO and room temperature. Catalysts **1b–3b** were active towards 4-*tert*-butylstyrene/CO copolymerization leading in all cases to syndiotactic polyketones. The high stereochemical control attributed to chain-end control is due to the interaction of the growing chain with the incoming styrene unit, which inserts exclusively in the 2,1 fashion [20,22,32,33]. This trend is equivalent to what is generally reported in the literature for ligands possessing C_s symmetry. Analysis of the $^{13}C\{^1H\}$ spectra indicated high stereoregularity from the signals of the methylene carbon atoms. The resonance at 43.2 ppm (100% relative content) was assigned to the syndiotactic *uu*-triad by comparison with literature values [18,34].

The productivity and molecular weight of the catalytic systems for CO/TBS copolymerization carried out in chlorobenzene is influenced by the nature of the substituent in position 4' of the ligands coordinated to palladium. Thus, productivity and molecular weight for the cationic complex **2b** bearing a methyl group was lower than that found for complexes **1b** and **3b** containing hydrogen and bromide

in the same position, respectively (Table 1, entries 1–3). Surprisingly, for the catalytic system **3b** in chlorobenzene, when the TBS/Pd ratio was increased, higher molecular weight and productivity were obtained. GPC in THF revealed the formation of a mixture of copolymers with very different magnitude of molecular weight values (Table 1, entry 4). A polymeric fraction with M_n value in the order of 10^6 was only present in a concentration of 10% weight of the overall composition. 1H and ^{13}C NMR spectra showed no formation of TBS homopolymer. Decomposition to Pd(0) is observed for the catalytic system **3b** after 24 h at room temperature, under 1 bar CO pressure in chlorobenzene. The solution obtained with catalyst **1b** and **2b** in the same conditions, however, are yellow after 24 h, indicating the presence of Pd(II) species. Productivities were reasonably improved when the copolymerization reactions were carried out in 2,2,2-trifluoroethanol (entries 5 and 6). This effect has previously been observed for CO/styrene copolymerization using palladium systems containing bis-oxazoline, bipyridine and related ligands [26c]. Also in TFE when the TBS/Pd ratio was increased higher productivity was obtained (entries 7 and 8). Usually at room temperature TFE and TBS are not miscible thus a double phase system could be operating. An increase of the ratio TFE/TBS leads to the formation of a more homogeneous system that remarkably improves productivities (entries 8 and 9). Molecular weights for polyketones obtained in fluorinated media depend on the catalyst employed. In particular, catalyst **2b** gave higher M_n values in TFE (entries 2 and 5), while negligible solvent effects on M_n and polydispersity were observed for catalyst **3b** (entries 3 and 6).

2.4. Catalytic CO/TBS/E terpolymerization

Table 2 shows the results obtained in CO/4-*tert*-butylstyrene/ethylene terpolymerization using the cationic

Table 1
CO/TBS copolymerisation^a

Entry	Catalyst precursor	TBS/Pd	Productivity [g PK(gPd ⁻¹ h ⁻¹)] ^d	$M_n(M_w/M_n)^e$
1	1b	310	11.8	3.60×10^4 (1.3)
2	2b	310	7.5	1.50×10^4 (1.7)
3	3b	310	11.3	1.90×10^4 (1.3)
4	3b	2000	14.1	1.30×10^6 (1.1) 2.90×10^4 (1.4)
5 ^b	2b	310	24.6	3.49×10^4 (1.6)
6 ^b	3b	310	16.9	1.95×10^4 (1.4)
7 ^b	2b	2000	73.7	4.96×10^4 (1.8)
8 ^b	3b	2000	123.7	1.30×10^4 (1.7)
9 ^c	3b	2000	187.5	1.48×10^4 (1.6)

Effect of TFE as solvent. Catalyst precursor [Pd(Me)(NCMe)(*N-N'*)] $[BAR_4']$ (*N-N'* = 1–3).

^a Reaction conditions: n_{Pd} = 0.0125 mmol; P_{CO} = 1 bar; solvent: 5 mL of chlorobenzene; 24 h; room temperature.

^b Same conditions, except solvent: 5 mL of TFE.

^c Same conditions, except solvent: 15 mL of TFE.

^d Calculated from isolated polymer.

^e Determined by SEC-MALLS in THF.

Table 2

Terpolymerization of 4-*tert*-butylstyrene (TBS) and ethene with CO using [Pd(Me)(NCMe)(*N-N'*)] $[BAR_4']$ (*N-N'* = 1–3)^a

Entry	Catalyst precursor	TBS/Pd	PCO/E(1:1) (atm)	Productivity ^c [g PK(gPd ⁻¹ h ⁻¹)]	%E ^d	$M_n(M_w/M_n)^e$
1	1b	2000	10	31.2	28	6.1×10^4 (1.3)
2	2b	2000	10	37.5	24	4.0×10^4 (1.3)
3	2b	620	10	38.3	30	4.0×10^4 (1.2)
4	3b	2000	10	43.8	22	3.8×10^4 (1.2)
5	3b	2000	15	54.6	29	3.8×10^4 (1.3)
6 ^b	2b	2000	10	125	32	8.2×10^4 (1.1)
7 ^b	3b	2000	10	87.5	28	4.7×10^4 (1.1)

Effect of TFE as solvent.

^a Reaction conditions: n_{Pd} = 0.0125 mmol; solvent: 15 mL of CH_2Cl_2 ; 24 h; room temperature.

^b Same conditions, except solvent: 15 mL of TFE.

^c Calculated from isolated polymer.

^d Calculated by relative integration of the 1H NMR signals of the terpolymers.

^e Determined by SEC-MALLS in THF.

palladium catalytic precursors $[\text{Pd}(\text{Me})(\text{NCMe})(N-N')][\text{BAR}'_4]$ (**1b–3b**). When terpolymerization experiments were carried out in dichloromethane, as reaction medium, the productivities of all the complexes **1b–3b** are modest and do not exceed the value of 55 g PK/g Pd h, obtained with complex **3b** (Table 2, entries 1–5). The effect of the nature of the N–N ligand evidences increasing productivities going from **1** (pzpm) to **2** (Mepzpm) and **3** (Brpzpm) containing catalysts. On the other hand, M_n values significantly decreased going from unsubstituted **1** (pzpm) to **2** (Mepzpm) and **3** (Brpzpm) (entries 1, 2 and 4). Variation of the TBS/Pd ratio has not a significant influence on the productivity and molecular weight values, in the case of catalyst **2b** (entries 2 and 3). An increment of the CO/E pressure from 10 to 15 atm resulted in a better productivity for the catalyst precursor **3b**, indicating a positive dependency on the CO/E pressure of the catalytic experiment (entries 4 and 5), while almost no variation on the molecular weight and polydispersity was observed in this case. Productivities were significantly affected by the nature of the reaction medium as shown in Fig. 1. An increase in productivity from 1.5 to 3 times was observed for the terpolymerization reaction in TFE, even though the reaction was carried out in the absence of 1,4-benzoquinone as an oxidant for the catalytic system [35]. The differences appear reasonably pronounced, probably due to the high stability of catalysts **1b–3b** in TFE. These catalysts preserve their activity for up to 24 h without decomposition in the absence of an oxidant. Productivity as high as 125 g PK ($\text{gPd}^{-1} \text{h}^{-1}$) (Table 2, entry 6) was attained with the pre-catalyst **2b**. GPC analysis of the obtained terpolymers also revealed differences on the molecular weights for the terpolymers obtained in fluorinated medium compared to those in CH_2Cl_2 . CO/ethylene/4-*tert*-butylstyrene terpolymers with M_n values as high as 82,000 were obtained with TFE (Table 2, entry 6). The enhancement of the length of the polymeric chain indicates that the fluorinated alcohol

increase the ratio between the propagation and the termination rate which could give an evidence of a greater stability of the active species in solution. The incorporation degree of ethylene, [ethylene–CO] units, into the produced terpolymers, was calculated by ^1H NMR and resulted to be much lower than the incorporation of 4-*tert*-butylstyrene, [4-*tert*-butylstyrene–CO] units, due to a faster insertion of the aromatic olefin than ethylene into the Pd–acyl bond. Alkene insertion is the rate-determining step in the CO/alkene polymerization reaction [2,36,37] and the preferred coordination of the olefinic double bond is likely to depend on the steric characteristics of the alkene [38] together with the steric influence of the ligand coordinated to the palladium centre. Bulkier ligands could increase activation energies of the olefin double bond coordination step, making incorporation of small olefins particularly facile. The higher incorporation of 4-*tert*-butylstyrene over ethylene found for the cationic catalysts **1b–3b**, could therefore be ascribed to the modest steric hindrance offered from this class of C_s symmetrical ligands. Additional analysis by means of ^{13}C NMR of the CO/TBS/E terpolymers showed the signal of alternating CO/TBS copolymers together with two added signals at 36.3 and 35.3 ppm corresponding to the presence of CO/E units. Methylene carbons of *tert*-butylstyrene give two signals at 43.2 and 45.4 ppm. The former signal was attributed to the syndiotactic *uu*-triad by comparison with literature values [17,18,34,39] which indicates complete stereoregularity. The signal at 45.4 ppm was attributed to isolated CO/TBS units [19].

3. Conclusions

Cationic palladium(II) complexes of general formula $[\text{PdMe}(\text{NCMe})(N-N')][\text{BAR}'_4]$ containing bisnitrogen ligands of C_s -symmetry effectively promote CO/4-*tert*-butylstyrene copolymerization and CO/ethylene/4-*tert*-butylstyrene terpolymerization. The corresponding polyketones are obtained in high yield with a molecular weight up to 82,000 and polydispersities ranging between 1.3 and 1.7, which are in the order of the best ones reported for C_s -bis-nitrogen planar ligands using styrene derivatives [9]. Syndiotactic microstructure of CO/vinyl arene polyketones was produced. High yields as well as enhanced growth of the polymeric chain are observed when the reaction is carried out in trifluoroethanol.

4. Experimental

4.1. General remarks

Chemicals and solvents were purchased from commercial sources and were used as received unless otherwise stated. Reactions were carried out under inert atmosphere (nitrogen), using standard Schlenk techniques. Solvents were purified prior to use by conventional methods [40]. The ligands **1–3** [29,41], the palladium complexes [28,30,42] and the NaBAR'_4 [43] salt were prepared accord-

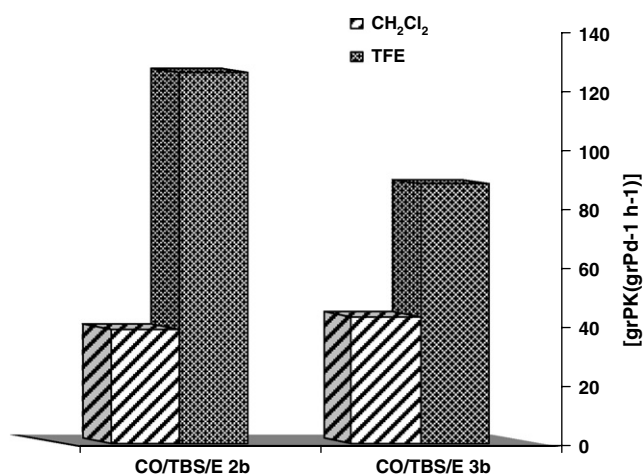


Fig. 1. CO/styrene/ethene terpolymerization: effect of the catalyst precursor $[\text{Pd}(\text{Me})(\text{NCMe})(N-N')][\text{BAR}'_4]$, **2b** and **3b**, and of the solvent on the productivity.

ing to reported methods. Carbon monoxide (CP grade 99.99%) was supplied by Air Liquide. The methylene chloride and chlorobenzene were used without further purification for the copolymerization and terpolymerization reactions. One and two-dimensional ^1H , ^{13}C $\{^1\text{H}\}$ NMR spectra were recorded on a 300 MHz Varian Gemini spectrometer and on a Varian Mercury VX 400 MHz spectrometer. Referencing is relative to TMS (^1H and ^{13}C). Samples were prepared dissolving about 20 mg of compound in 0.5 mL of the deuterated solvent. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet and br, broad. Unless specified the ^{13}C resonances are singlets. Chemical shifts are in ppm and coupling constants (J) in Hz. Some assignments in NMR spectra were determined by two-dimensional ^1H -NOESY techniques. ^1H - ^{13}C g-HSQC spectra: standard pulse sequence with an acquisition time of 0.1 s, pulse width 11 ms, relaxation delay 1 s, number of scans 8, number of increments 256. Fourier Transform Infrared (FT IR) spectra were recorded as Nujol mulls. Absorptions are reported in wavenumbers (cm^{-1}). Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. The molecular weight and molecular weight distributions of the obtained copolymers and terpolymers, were determined by gel-permeation chromatography (GPC-MALLS).

4.2. Synthesis of $[\text{PdClMe}(2-3)]$ (**2a**, **3a**)

In a 25 mL Schlenk flask, 0.5 mmol of the corresponding ligand **2-3**, were dissolved in 10 mL of distilled and degassed toluene, under a nitrogen atmosphere. To this solution were added 5 mL of a previously prepared toluene solution containing $[\text{PdClMe}(\text{cod})]$ (0.133 g, 0.5 mmol), $[\text{ligand}]/[\text{Pd}] = 1$. The solution was stirred at room temperature for 1 h. The yellow solid was filtered off, extensively washed with diethylether and dried under vacuum to constant weight.

4.2.1. $[\text{PdClMe}(2)]$ (**2a**)

Yield: (0.152 g, 96%). Anal. Calc. for $\text{C}_9\text{H}_{11}\text{ClN}_4\text{Pd}$: C, 34.09; H, 3.50; N, 17.67. Found: C, 33.82; H, 3.76; N, 17.08%. ^1H NMR (400 MHz, CD_2Cl_2 , RT): δ_{H} 8.93 (dd, $^3J = 5.2$ Hz, $^4J = 2.4$ Hz, 1H, H_6), 8.77 (dd, $^3J = 4.8$ Hz, $^4J = 2.4$ Hz, H_4), 8.31 (s, 1H, H_5), 7.66 (s, 1H, H_3), 7.38 (t, $^3J = 5.2$ Hz, 1H, H_5), 2.19 (s, 3H, $\text{CH}_3\text{-pz}$), 0.99 (s, 3H, Pd- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2) δ_{C} 160.3 (C_6), 157.3 (C_4), 143.4 (C_3), 128.8 (C_5), 121.8 (C_4'), 120.3 (C_5), 9.5 ($\text{CH}_3\text{-pz}$), -7.0 (Pd- CH_3).

4.2.2. $[\text{PdClMe}(3)]$ (**3a**)

Yield: (0.175 g, 92%). Anal. Calc. for $\text{C}_8\text{H}_8\text{BrClN}_4\text{Pd}$: C, 25.16; H, 2.11; N, 14.67. Found: C, 25.78; H, 2.24; N, 14.13%. ^1H NMR (400 MHz, CDCl_3 , RT): δ_{H} 9.11 (dd, $^3J = 5.2$ Hz, $^4J = 2.4$ Hz, 1H, H_6), 8.85 (dd, $^3J = 4.8$ Hz, $^4J = 2.4$ Hz, H_4), 8.63 (s, 1H, H_5), 7.85 (s, 1H, H_3), 7.50 (t, $^3J = 4.8$ Hz, 1H, H_5), 1.21 (3H, Pd- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, CDCl_3) δ_{C} 160.0 (C_6), 157.5 (C_4),

142.7 (C_3), 130.3 (C_5), 120.9 (C_5), 99.3 (C_4), -5.1 (Pd- CH_3).

4.3. Synthesis of $[\text{Pd}(\text{Me})(\text{NCCH}_3)(\mathbf{1-3})][\text{BAR}'_4]$ (**1b-3b**)

4.3.1. $[\text{Pd}(\text{Me})(\text{NCCH}_3)(\mathbf{1})][\text{BAR}'_4]$ (**1b**)

To a stirred solution of NaBAR'_4 ($\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$) (0.133 g, 0.15 mmol) in 3 mL of MeCN was added 3 mL of a previously prepared CH_2Cl_2 solution containing $[\text{PdClMe}(\mathbf{1})]$ (**1a**) (0.045 g, 0.15 mmol). The light yellow solution obtained was stirred for 1 h and filtered through celite to remove NaCl. The solvent was evaporated under reduced pressure to leave an oil which was then extensively washed with hexane, dissolved in a minimum amount of dry dichloromethane and the solvent evaporated under vacuum furnishing a yellow solid identified as the cationic complex **1b**, (0.150 g, 85%). Anal. Calc. for $\text{C}_{42}\text{H}_{24}\text{BF}_{24}\text{N}_5\text{Pd}$: C, 43.05; H, 2.06; N, 5.98. Found: C, 43.17; H, 2.24; N, 6.09%. ^1H NMR (400 MHz, CDCl_3 , RT): δ_{H} 8.74 (dd, $^3J = 4.8$ Hz, $^4J = 2.4$ Hz, 1H, H_6), 8.57 (dd, $^3J = 3.2$ Hz, $^4J = 0.8$ Hz, 1H, H_5), 8.33 (dd, $^3J = 5.2$ Hz, $^4J = 2.4$ Hz, 1H, H_4), 7.84 (dd, $^3J = 2.4$ Hz, $^4J = 0.8$ Hz, 1H, H_3), 7.71 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.15 (t, $^3J = 5.2$ Hz, 1H, H_5), 6.76 (dd, $^3J = 3.2$ Hz, $^4J = 2.4$ Hz, 1H, H_4), 2.32 (s, 3H, Pd- NCCH_3), 1.3 (s, 3H, Pd- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, CDCl_3 , RT) δ_{C} 161.9 (q, $J_{\text{C-B}} = 49.8$ Hz, C_a), 161.6 (C_6), 156.3 (C_4), 156.0 (C_2), 143.8 (C_3), 135.0 (C_b), 132.3 (C_5), 129.2 (m, C_c), 124.7 (q, $J_{\text{C-F}} = 272$ Hz, C_e), 123.3 (Pd- NCCH_3), 120.8 (C_5), 117.7 (C_d), 111.2 (C_4'), 3.2 (Pd- NCCH_3), -0.1 (Pd- CH_3).

4.3.2. $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{2})][\text{BAR}'_4]$ (**2b**)

Compound **2b** was obtained in a similar way as described for compound **1b** as a yellow solid, (0.158 g, 89%). Anal. Calc. for $\text{C}_{43}\text{H}_{26}\text{BF}_{24}\text{N}_5\text{Pd}$: C, 43.55; H, 2.21; N, 5.91. Found: C, 43.52; H, 2.24; N, 5.42%. ^1H NMR (400 MHz, CDCl_3 , RT): δ_{H} 8.69 (dd, $^3J = 4.8$ Hz, $^4J = 2.4$ Hz, 1H, H_6), 8.34 (dd, $^3J = 5.6$ Hz, $^4J = 2.4$ Hz, H_4), 8.31 (s, 1H, H_5), 7.71 (s, 8H, H_b), 7.65 (s, 1H, H_3), 7.53 (s, 4H, H_d), 7.15 (t, $^3J = 5.2$ Hz, 1H, H_5), 2.28 (s, 3H, Pd- NCCH_3), 2.18 (s, 3H, $\text{CH}_3\text{-pz}$), 1.23 (s, 3H, Pd- CH_3). ^{13}C $\{^1\text{H}\}$ NMR (100.5 MHz, CDCl_3 , RT) δ_{C} 161.9 (q, $J_{\text{C-B}} = 49.4$ Hz, C_a), 161.5 (C_6), 156.3 (C_4), 155.9 (C_2), 144.5 (C_3), 135.0 (C_b), 130.2 (C_5), 129.2 (m, C_c), 124.7 (q, $J_{\text{C-F}} = 272$ Hz, C_e), 122.4 (Pd- NCCH_3), 121.0 (C_4'), 120.3 (C_5), 117.8 (C_d), 9.2 ($\text{CH}_3\text{-pz}$), 3.0 (Pd- NCCH_3), -0.51 (Pd- CH_3).

4.3.3. $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{3})][\text{BAR}'_4]$ (**3b**)

Compound **3b** was obtained in a similar way as described for compound **1b** as a brownish solid, (0.156 g, 83%). ^1H NMR (400 MHz, CDCl_3 , RT): δ_{H} 8.71 (dd, $^3J = 4.8$ Hz, $^4J = 2.4$ Hz, 1H, H_6), 8.61 (s, 1H, H_5), 8.36 (dd, $^3J = 5.2$ Hz, $^4J = 2.4$ Hz, H_4), 7.82 (s, 1H, H_3), 7.70 (s, 8H, H_b), 7.52 (s, 4H, H_d), 7.19 (t, $^3J = 5.2$ Hz, 1H, H_5), 2.28 (s, 3H Pd- NCCH_3), 1.29 (s, 3H, Pd- CH_3). ^{13}C $\{^1\text{H}\}$

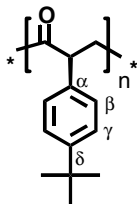
NMR (100.5 MHz, CDCl_3 , RT) δ_{C} 161.9 (q, $J_{\text{C-B}} = 49.7$ Hz, C_a), 161.7 (C_6), 156.6 (C_4), 156.1 (C_2), 144.3 (C_3'), 135.0 (C_b), 132.1 (C_3'), 129.1 (m, C_c), 124.7 (q, $J_{\text{C-F}} = 272.1$ Hz, C_e), 122.3 (s, Pd– NCCH_3), 121.24 (C_5), 117.8 (C_d), 100.2 (C_4'), 3.1 (Pd– NCCH_3), 0.53 (s, Pd– CH_3).

4.4. Copolymerization of 4-*tert*-butylstyrene with carbon monoxide

The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Chlorobenzene or TFE were used as purchased from Aldrich. The cationic precursors **1b–3b** (0.0125 mmol) were dissolved in 5 mL of chlorobenzene or TFE in a previously flushed Schlenk and the N_2 atmosphere replaced with CO, bubbling through the solution (5 min), 4-*tert*-butylstyrene was then introduced and the reaction was allowed to take place at r.t. and 1 bar of CO. Reaction time was 24 h. Work-up included filtration of the reaction mixture through Kieselghur and precipitation of the polymeric material by adding the reaction solution dropwise into 100 mL of rapidly stirring methanol. The off-white powder was collected by filtration, washed with methanol and dried in vacuum overnight. Productivities were calculated from the weight of the isolated polymeric material.

4.5. Copolymer characterization (obtained by using $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{3})][\text{BAR}'_4]$ (**3b**) precatalyst)

^1H NMR (400 MHz, CDCl_3 , RT): δ_{H} 2.92 (d, $^3J = 7.68$ Hz, 2H, H_β or H_γ), 6.50 (d, $^3J = 7.68$ Hz, 2H, H_γ or H_β), 4.03 (m, 1H, CH) 2.92 (dd, $^2J = 18.3$, $^3J = 7.3$ H, 1H, CH_2), 2.54 (dd, $^2J = 18.3$, $^3J = 7.3$ H, 1H, CH_2), 1.14 (s, 9H, $\text{C}(\text{CH}_3)$). ^{13}C { ^1H } NMR (100.5 MHz, CDCl_3 , RT) δ_{C} 206.9 (–CO–), 149.8 (C_δ), 134.3 (C_α), 128.2 (C_γ), 125.6 (C_β), 52.9 (CH), 43.2 (CH_2), 34.5 ($\text{C}(\text{CH}_3)$), 31.5 ($\text{C}(\text{CH}_3)$).



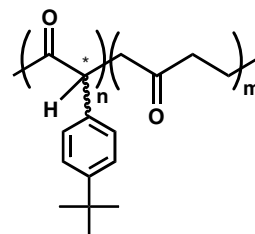
4.6. Terpolymerization of 4-*tert*-butylstyrene/ethylene/carbon monoxide

The 4-*tert*-butylstyrene was passed through a small column of Al_2O_3 prior to use. Distilled dichloromethane or TFE, as purchased from Aldrich, were used as the solvent. The reactions were carried out in a stainless steel Berghoff autoclave (150 mL), equipped with a teflon liner, magnetic

stirrer, heating mantle and temperature controller. After treating a solution of $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{1-3})][\text{BAR}'_4]$ in CH_2Cl_2 (15 mL) with bubbling CO (1 atm), 4-*tert*-butylstyrene was added, and the mixture immediately transferred into a 100 mL stainless steel Berghoff autoclave previously purged with a CO/E mixture. The reaction mixture was then pressurized at the desired level and stirred for 24 h before releasing unreacted gases. The resulting mixture was filtered through Kieselghur and successively added into 100 mL of rapidly stirred methanol to precipitate poly{ethylene; 4-*tert*-butylstyrene}-alt-CO}.

4.7. Terpolymer characterization (obtained by using $[\text{Pd}(\text{Me})(\text{NCMe})(\mathbf{3})][\text{BAR}'_4]$ (**3b**) precatalyst)

^1H NMR (400 MHz, CDCl_3 , RT): δ_{H} 7.41–7.15 (aromatic), 4.20 [bs, – $\text{CH}(\text{Ar})\text{CH}_2\text{C}(\text{O})$ –], 3.10 [bs, – $\text{CH}(\text{Ar})\text{CHH}\text{C}(\text{O})$ –], 2.51 [– $\text{CH}(\text{Ar})\text{CHH}\text{C}(\text{O})$ – and – $\text{CHH}\text{CHH}\text{C}(\text{O})$ –], 1.27 [bs, $\text{C}(\text{CH}_3)_3$]; ^{13}C { ^1H } NMR (100.5 MHz, CDCl_3 , RT) δ_{C} 206.9 (–CO–), 149.8 (C_δ), 134.6–134.2 (C_α), 128.2–127.5 (C_γ), 125.6–124.8 (C_β), 52.9 (CH), 45.3–43.3 (– $\text{CH}(\text{Ar})\text{CH}_2\text{C}(\text{O})$ –), 36.2 ($\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{E}$), 35.4[– $\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{TBS}$], 34.6 ($\text{C}(\text{CH}_3)$) 31.5 ($\text{C}(\text{CH}_3)$). IR (nujol, cm^{-1}): 1705($\text{C}=\text{O}$), 1459, 1375.



4.8. Molecular weight measurement

Before measuring the molecular weight, the CO/styrene polyketones were treated as follows: The copolymer (1.00 g) was stirred in ethyl acetate (50 mL) for 4 h. After filtration it was stirred with diethyl ether (25 mL) for 2 h. The solid was filtered and vacuum-dried. The copolymers' molecular weights (M_w) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography vs. polystyrene standards. The analyses were performed by gel-permeation chromatography (GPC-MALLS), measurements made in THF on a Waters 515 gel-permeation chromatography device using a lineal Waters Ultrastayragel column with a Waters 2410 refractive index detector vs. polystyrene standards. The CO/styrene copolymers were dissolved as follows: 42 mg of each sample were solubilized in 5 mL of THF.

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