# ORGANOMETALLICS

# Cationic Palladium(II) Complexes for CO/Vinyl Arene Copolymerization in the Presence of Carbon Dioxide

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Supporting Information

ABSTRACT: New dicationic and monocationic palladium complexes with **ABSTRACT:** New dicationic and monocationic palladium complexes with 2,2'-bipyridine ligands bearing perfluorinated ponytails have been prepared and  $n \in CO/4$ . tert-butylstyrene (TBS) and CO/styrene (ST) used as catalysts for CO/4-tert-butylstyrene (TBS) and CO/styrene (ST) copolymerization in supercritical carbon dioxide and in CO<sub>2</sub>-expanded liquids. Best catalytic performances were achieved carrying out the copolymerization in carbon dioxide expanded substrates in the presence of 2,2,2-trifluoroethanol. The dicationic systems with 5,5'-substituted ligands  $[Pd(N-N)_2][X]_2$ generated the most active and productive catalysts with up to 532 g copolymer CP/g Pd·h for CO/TBS and led to polyketones with high molecular weight and narrow polydispersity (molecular weight up to  $M_w = 692\,000$  for CO/ST;  $M_w/$ 



 $R = C_6H_5$ , 4-tert-BuC<sub>6</sub>H<sub>4</sub>

 $[cat] = [Pd(N-N)_2][X]_2, [Pd(CH_3)(NCCH_3)(N-N)][X]$ 

$$N-N = \bigvee_{N} \bigvee_{N$$

 $M_{\rm p} = 1.2-3.3$ ). MALDI-TOF mass spectrometry analysis of copolymer end groups revealed that the main initiation and termination steps involved the insertion of the alkene into the Pd-H bond and the  $\beta$ -H elimination on the Pd-alkyl bond, respectively.

# INTRODUCTION

The carbon monoxide/ $\alpha$ -olefin copolymerization leading to perfectly alternating polyketones (Scheme 1) is an interesting

Scheme 1. Alternating Copolymerization of Carbon Monoxide with  $\alpha$ -Olefins (R = H, CH<sub>3</sub>, Ar)

$$n R^{+} n CO \xrightarrow{[cat]} (CAT) R^{+}$$

reaction,<sup>1-7</sup> due to the peculiar properties of these polymers and to the presence of the carbonyl group, allowing for postfunctionalization along the polymer backbone.<sup>8</sup>

Special interest has been devoted to palladium(II) complexes with N,N-donor chelating ligands and weakly coordinating anions X (OTs<sup>-</sup> (tosylate), OTf<sup>-</sup> (triflate), TFA<sup>-</sup> (trifluoroacetate), BF<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup>, and tetraarylborates).<sup>2,4-9</sup> Palladium complexes based on nitrogen-donor ligands belonging to the family of 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen),<sup>10</sup> or pyridine-imidazoline<sup>11</sup> are benchmark catalysts for this reaction. The complexes generally used as precatalysts were dicationic species of general formula [Pd(N-N)2][X]2 or monocationic derivatives  $[Pd(CH_3)(NCCH_3)(N-N)]$ -[X]<sup>10b,11-14</sup> In particular, dicationic bischelated Pd complexes of general formula  $[Pd(3-R-phen)_2][PF_6]_2$  (3-R-phen = 3-alkylsubstituted phen) are very productive catalysts (up to 12 kg

CP/g Pd in 72 h; kg CP/g Pd = kilograms of copolymer per gram of palladium) for the synthesis of high molecular weight copolymers (up to  $M_{\rm w}$  = 300 000) when the polymerization is carried out in 2,2,2-trifluoroethanol (TFE).<sup>15</sup> A further remarkable improvement of the catalyst performances was realized by applying the monocationic Pd complexes with 5,5,6,6-tetrafluoro-5,6-dihydro-1,10-phenanthroline; the corresponding active species has a catalyst lifetime of at least 90 h, yielding the syndiotactic CO/styrene copolymer with a stereoregularity of 96% and an  $M_{\rm w}$  value of 1 000 000.<sup>1</sup>

During the last years, dense carbon dioxide (liquid or supercritical,  $scCO_2$ ) has found increasing use as an alternative medium for catalytic reactions because of its favorable environmental profile, lack of toxicity and flammability, and tunable solvent properties.<sup>17</sup> In particular, the tunable solvent properties of  $scCO_2^{18}$  and the partition behavior with other media permitted the design of advanced process schemes integrating catalyst retention and product separation for continuous flow catalysis.<sup>19</sup> Moreover, the formation of gasexpanded liquids<sup>20</sup> via addition of subcritical carbon dioxide to organic liquids (CXL) accounts for a myriad of different liquid phases, which can be useful media for catalysis too. The properties of the CXL (in particular polarity and gas solubility) can be adjusted by adding a proper amount of CO<sub>2</sub>. In some

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While several examples of free radical polymerization reactions in compressed carbon dioxide have been reported,<sup>23-26</sup> the catalytic polymerization in this medium has been less studied.<sup>27</sup> In 2006, we reported the first example of an active catalytic system for the CO/4-tert-butylstyrene (TBS) copolymerization in scCO<sub>2</sub> based on a monocationic palladium complex with a perfluorinated bipyridine ligand (1, Chart 1),

Chart 1. Perfluorinated Nitrogen-Donor Chelating Ligands 1 - 4



 $[Pd(CH_3)(NCCH_3)(N-N)][BArF]$  (N-N = 1, BArF<sup>-</sup> =  $B\{(3,5-C_6H_3(CF_3)_2\}_4^{-})$ , achieving a productivity of 234 g CP/ g Pd in copolymers of higher molecular weight ( $M_w$  = 87 800) and narrower polydispersities  $(M_w/M_n = 1.2)$  than in organic solvents under the same conditions.<sup>28</sup>

In the present work, we evaluate related, new catalysts for the same reaction both in scCO<sub>2</sub> and in CXL. To this aim, new bpy ligands 2-4 (Chart 1) bearing perfluorinated chains in 5 (2), 4,4' (3), and 5,5' (4) positions have been synthesized. This substitution pattern should greatly enhance the solubility of ligands and of the corresponding complexes in CO<sub>2</sub> and CXL, allowing to carry out catalytic reactions in these apolar media.<sup>29</sup> Moreover, the introduction of a substituent in the 5 or 5,5' positions should lead to more productive polymerization catalysts than those containing the unsubstituted bpy, as shown by Soro et al.<sup>30</sup> Ligands 2-4, together with the previously reported 1, were used to synthesize the corresponding monocationic  $[Pd(CH_3)(NCCH_3)(N-N)][X]$  (N-N = 2-4, X = BArF<sup>-</sup>,  $PF_6^-$ ,  $OTs^-$ ) and dicationic complexes  $[Pd(N-N)_2][X]_2$  (N-N = 1-4; X = BArF<sup>-</sup>, PF<sup>-</sup><sub>6</sub>, BF<sup>-</sup><sub>4</sub>) and to

study their catalytic activity in the CO/vinyl arene copolymerization in supercritical and liquid CO<sub>2</sub>.

## **RESULTS AND DISCUSSION**

Synthesis of Ligands 1–4. The fluorinated bpy ligand 1 was obtained according to a previously reported method via Calkylation of 4,4'-dimethyl-2,2'-bipyridine.<sup>28,31</sup> When the same procedure was applied to the synthesis of the 5,5'-perfluoralkylated bpy, the nonsymmetrical 5-[4-(perfluorooctyl)butyl]-5'methyl-2,2'-bipyridine was isolated (2, Chart 1), and all attempts to obtain the disubstituted compound were unsuccessful. Thus, we identified an alternative approach for introducing two perfluorinated chains at the bpy backbone through an ester function. Accordingly, ligands 3 and 4 (Chart 1) were obtained in a three-step reaction starting from 4,4'- and 5,5'-dimethyl-2,2'-bipyridine, respectively. After oxidation with sodium dichromate to the corresponding di(carboxylic)acids<sup>32</sup> and conversion into acyl chlorides, the latter compounds were reacted with 3-(perfluorooctyl)propanol, giving the bipyridines 3 and 4 as a cream powder (Scheme 2), the last step being a variation of the procedure described by Garelli and Vierling.<sup>33</sup> While 3 is soluble in most organic solvents, 4 is unexpectedly almost insoluble in common organic solvents at room temperature and precipitates from dichloromethane during the synthesis.

Bipyridines 2-4 were characterized by NMR and FTIR spectroscopy and mass spectrometry.<sup>34</sup> The <sup>1</sup>H and <sup>13</sup>C NMR spectra of 3 and 4 show the pattern corresponding to a  $C_2$ symmetric molecule. As a general trend, the <sup>1</sup>H NMR peaks of the aromatic protons of 4 were downfield shifted with respect to those of 3, likely due to the different experienced electronwithdrawing effect as a function of the substituent position. The presence of the ester group was confirmed by IR through the C–O stretching frequency  $\nu$ (CO) at 1731 and 1716 cm<sup>-1</sup> for 3 and 4, respectively.

In the aliphatic region of the <sup>1</sup>H NMR spectrum of **2** both the signals of the hydrocarbon chain attached to the fluorinated tail ( $\delta$  1.70–2.70 ppm) and the signal of the methyl group ( $\delta$ 2.40 ppm) were present, while in the aromatic region only three well-separated multiplets were observed. In the <sup>13</sup>C NMR spectrum distinct signals for all expected aromatic carbons, which were related to the corresponding protons in the  $HSQC-^{1}H-^{13}C$  spectrum (see Supporting Information), were observed, thus confirming the nonsymmetric structure of the ligand.

Palladium Monocationic Complexes [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)-(2-4)][X]. The monocationic palladium complexes [Pd(CH<sub>3</sub>)- $(NCCH_3)(2-4)$  [X] (Scheme 3) with counterions X = PF<sub>6</sub>, OTs<sup>-</sup> were synthesized by reaction of the neutral derivatives  $[Pd(CH_3)Cl(2-4)]$  (see Supporting Information) with the corresponding silver salt and acetonitrile.<sup>16,35</sup> Derivatives with





i) NaCr<sub>2</sub>O<sub>7</sub>; ii) SOCl<sub>2</sub>; iii) C<sub>8</sub>F<sub>17</sub>(CH<sub>2</sub>)<sub>3</sub>OH / NEt<sub>3</sub> / CH<sub>2</sub>Cl<sub>2</sub>

Article

Scheme	3.	Synthetic	Pathway	for	the	Palladium	Complexes
2a-c to	4a	i-c					

$[Pd(CH_3)(Cl)(N-N)] \xrightarrow{AgX}$	[Pd(CH <sub>3</sub> )(NCCH <sub>3</sub> )(N-N)][X]
- AgCl	2, 3, 4
	$X = (a) PF_6^{-}, (b) OTs^{-}$

[Pd(CH <sub>3</sub> )(NCCH <sub>3</sub> )(N-N)][OTs] <u>NaBArF</u> - NaOTs	[Pd(CH <sub>3</sub> )(NCCH <sub>3</sub> )(N-N)][BArF]
2b, 3b, 4b	2c, 3c, 4c

	[Pd(CH <sub>3</sub>	[Pd(CH <sub>3</sub> )(NCCH <sub>3</sub> )(N-N)][X]			
N-N	$X = PF_6$	$X = OTs^{-}$	X = BArF		
2	2a	2b	2c		
3	3a	3b	3c		
4	4a	4b	4c		

BArF<sup>-</sup>, 2c-4c, were obtained by counterion exchange reaction from tosylate complexes  $2b-4b^{36}$  (Scheme 3).

All complexes were isolated as pale yellow or pale brown solids and fully characterized by infrared spectroscopy (IR), mass spectrometry (MALDI-TOF), and mono- and bidimensional <sup>1</sup>H, <sup>15</sup>N, and <sup>19</sup>F NMR spectroscopy. The <sup>1</sup>H NMR spectra of the cationic complexes **2a**-**c** to **4a**-**c** showed the signals of the coordinated acetonitrile ( $\delta$  2.35–2.60 ppm; free acetonitrile  $\delta$  2.10 ppm<sup>37</sup>) and the singlet due to the methyl group bonded to palladium ( $\delta$  0.90–1.25 ppm). The <sup>1</sup>H NMR spectra of these complexes were different depending on the

counterion (see for example for complexes 4a-c in Figure 1). In particular, in the aromatic region of the <sup>1</sup>H NMR spectra of these complexes, the signals of H<sup>6'</sup> (that is, the proton close to the nitrogen atom of the pyridine ring *trans* to Pd-CH<sub>3</sub> (*trans*-py ring, Figure 1) were the most affected by the nature of the counterion, and especially for complexes with OTs<sup>-</sup> (Figure 1b) it was remarkably downfield shifted with respect to both the same signal in the complexes with the other counterions and the signal of H<sup>6</sup>. No evidence of counterion coordination was observed.

Complexes 2a-c showed broad signals at room temperature that might suggest the presence of cis/trans isomers (see Supporting Information). This was confirmed for complex 2b, having the tosylate as counterion. Even though only one signal was clearly evident for the Pd-CH<sub>3</sub> group, four signals (at  $\delta$  8.68, 8.57, 8.33, and 8.32 ppm) were observed for the protons in ortho position to the nitrogen-donor atoms. One strong NOE was observed between the Pd-CH<sub>3</sub> singlet and the signal at  $\delta$  8.33–8.32 ppm, which was assigned to H<sup>6</sup> of the *cis* and H<sup>6'</sup> of the trans isomer. In the NOESY spectrum clear cross-peaks were observed among the singlet of the methyl group in position 5 (indicated as  $(CH_3)^{1''}$  in the Supporting Information) and the two resonances at  $\delta$  8.57 and 8.32 ppm, indicating that they were due to H<sup>6</sup> of the *trans* and the *cis* isomer, respectively, and among the multiplet of  $(CH_2)^{1''}$  in position 5' and the signals at  $\delta$  8.68 and 8.33 ppm, which, therefore, were assigned to H<sup>6'</sup> of the cis and trans isomer, respectively (see Supporting Information). For complex 2c, spectra at low temperature, up to -80 °C, were recorded, resulting in further broadening of the signals, without reaching any decoalescence.



Figure 1. <sup>1</sup>H NMR spectra in the aromatic region of complexes [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(4)][X] (4a-c) (CD<sub>2</sub>Cl<sub>2</sub>, 500 MHz).

<sup>15</sup>N–<sup>1</sup>H HMBCAD NMR experiments at natural abundance of the <sup>15</sup>N isotope were performed for the ligands and complexes soluble in CD<sub>2</sub>Cl<sub>2</sub> (Experimental Section). The signals of ligand 3 appeared downfield shifted with respect to those of **2**, in agreement with the electronegativity of the substituent.<sup>38</sup> The <sup>15</sup>N chemical shifts of N<sub>cis</sub> (*cis* to the Pd-CH<sub>3</sub>) and N<sub>trans</sub> (*trans* to the Pd-CH<sub>3</sub>) were attributed by their correlations with the resonances of H<sup>6</sup> and H<sup>6</sup>, respectively. In particular, the chemical shift values of N<sub>cis</sub> were in the range –140 to –170 ppm, and those of N<sub>trans</sub> were in the range –110 to –125 ppm (Experimental Section). The difference of chemical shift between free ligand and the complex ( $\Delta \delta = \delta_{complex} - \delta_{ligand}$ ) for N<sub>cis</sub> was larger (ca. –80 ppm) than that of N<sub>trans</sub> (ca. –40 ppm), in agreement with the *trans* influence of the Pd-CH<sub>3</sub> group.<sup>39,40</sup>

The <sup>15</sup>N resonance for the Pd-NCCH<sub>3</sub> was observed in the NMR spectra of some complexes via the <sup>3</sup> $J(^{15}N,^{1}H)$  coupling. Even for this signal a remarkable  $\Delta\delta$  value (ca. – 70 ppm) was observed (considering the <sup>15</sup>N chemical shift of free acetonitrile at –137.1 ppm).<sup>40</sup>

lon Pairing Studies (Diffusion Data and Overhauser Studies). NMR diffusion methods (pulse gradient spin-echo, PGSE) in combination with heteronuclear Overhauser spectroscopy ( $^{1}H-^{1}H$  NOESY and  $^{1}H-^{19}F$  HOESY experiments) were run in order to analyze the existence and degree of ion pairing in CD<sub>2</sub>Cl<sub>2</sub>.<sup>41-53</sup>

<sup>1</sup>H<sup>-1</sup>H NOESY NMR experiments in CD<sub>2</sub>Cl<sub>2</sub> were examined for complexes containing BArF<sup>-</sup> and OTs<sup>-</sup> and <sup>1</sup>H<sup>-19</sup>F HOESY NMR experiments for complexes containing PF<sub>6</sub><sup>-</sup>. No correlation was observed in the <sup>1</sup>H<sup>-1</sup>H NOESY NMR spectra for complexes with BArF<sup>-</sup>, **2c**-4c. These results are in agreement with the literature<sup>41,47,48</sup> and supported by the fact that BArF<sup>-</sup> is a noncoordinating anion<sup>41,54</sup> and its size makes it difficult to have ion pairs.<sup>48,55</sup> Instead, OTs<sup>-</sup> (**2b** and **3b**)<sup>56</sup> and PF<sub>6</sub><sup>-</sup> (**2a**-4a) complexes showed cross-peaks connecting the signals of the anion with the aromatic signals of the pyridine ring *trans* to the Pd–CH<sub>3</sub> bond and also with the signals of the coordinated acetonitrile, suggesting the presence of an interionic interaction (Figure 2) as reported for other complexes.<sup>47,50,57</sup>



Figure 2. Representation of the localization of the counterion in solution for complexes 2a-4a, 2b, and 3b.

The degree of ion pairing and the molecular volume were estimated by the diffusion coefficient, *D*, and the hydrodynamic radii,  $r_{\rm H\nu}$  obtained by pulse gradient spin–echo (PGSE) NMR diffusion measurements<sup>41–44</sup> (see Supporting Information Table S1). For complexes with BArF<sup>-</sup>, **2c**–**4c**, the diffusion coefficient of the anions was different, pointing to different translation ratios for both cation and anion, confirming the lack of interaction<sup>45,49</sup> evidenced in the <sup>1</sup>H–<sup>1</sup>H NOESY experiments. Concerning the complexes containing OTs<sup>-</sup>, the obtained  $r_{\rm H}$  and D values for complex **2b** (Supporting Information Figure S43) indicated that both cation and anion

diffuse at very similar rates, suggesting an almost 100% ion pairing.

Palladium Dicationic Complexes  $[Pd(N-N)_2][X]_2$ . The dicationic bischelated palladium complexes  $[Pd(N-N)_2][X]_2$  (N-N = 1-4, Scheme 4) with different counterions

Scheme 4. Synthetic Pathway for the Palladium Complexes 1d–4d, 1d', and 1d''

[PdCl <sub>2</sub> (N	N-N)] CH <sub>2</sub> NaX o N-	$\frac{Cl_2}{\operatorname{pr} \operatorname{AgX}}  [\operatorname{Pd}(N-N)_2][X]_2 + 2 \operatorname{NaCl} \operatorname{or} 2 \operatorname{AgCl} \\ -N \qquad X = \operatorname{BArF}, \operatorname{PF}_6, \operatorname{BF}_4^-$
	N-N	$[Pd(N-N)_2][X]_2$
	1	$   \begin{array}{l}     1d (X = BArF) \\     1d' (X = PF_6) \\     1d'' (X = BF_4)   \end{array} $
	2	2d
	3	3d
	4	4d

X = BArF<sup>-</sup>, PF<sub>6</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> were synthesized by reaction of  $[PdCl_2(N-N)]$  (see Supporting Information) with one equivalent of N–N ligand and two equivalents of the corresponding sodium or silver salts (1d–4d, 1d', 1d", Scheme 4).<sup>58</sup>

Complexes 1d-4d, 1d', and 1d'' were isolated as pale brown or yellow solids and fully characterized by mass spectrometry and NMR and FTIR spectroscopy. The <sup>1</sup>H NMR spectrum of 1d at room temperature in acetone- $d_6$  is highly symmetric, and the number of signals is consistent with equivalence of the two halves of both coordinated ligands. In contrast to the corresponding monocationic derivatives, no variation in the <sup>1</sup>H NMR spectra of 1d-1d'' due to the different counterion was observed.

For complex 2d, *syn* and *anti* isomers can be expected according to the relative coordination of the two nonsymmetric bpy ligands The <sup>1</sup>H NMR spectrum of 2d displayed only one set of signals in the aliphatic region, while the aromatic protons gave one signal for  $H^{6,6'}$  and one overlapped multiplet for  $H^{3,3'}$  and  $H^{4,4'}$ . On the basis of the NMR analysis it was not possible to identify if one isomer or both of them were present.

The <sup>1</sup>H NMR spectrum in CDCl<sub>3</sub> at room temperature of **3d** showed two sets of rather broad signals both for the aromatic protons and for the methylenic group bonded to the oxygen atom (Figure 4b), while the other methylenic protons gave one broad resonance. The assignment of the signals was based on a COSY experiment (see Supporting Information). No signals due to free ligand were present, and all the signals, with the exception of that due to  $H^{5,5'}$ , were upfield shifted with respect to the same signals in the free ligand. These NMR data indicated the presence of two species, I and II, in 1:1 ratio at room temperature. A NOESY experiment performed at room temperature evidenced that the two species were interconverting (see Supporting Information). In each of them, both the ligands bonded to palladium and the two halves of each ligand were equivalent.

NMR experiments at variable temperature showed that at -55 °C only the set of broad signals corresponding to species I was present (Figure 4e). Increasing the temperature, the signals of species II together with new signals at 40 °C (species III) appeared, in a ratio of I:II:III = 1.0:1.0:0.5 (Figure 4a). The NMR spectrum of 4d at room temperature showed also two



Figure 4. Variable-temperature <sup>1</sup>H NMR spectra of 3d (1) aromatic region and (2)  $-O-CH_2-$  region at (a) 40 °C, (b) room temperature, (c) 0 °C, (d) -40 °C, and (e) -55 °C.

sets of signals in the aromatic and methylenic regions (see Supporting Information).

One possible hypothesis is that the different observed species are due to the two conformers *twist* and *bow-step* (Figure 5)



Figure 5. Conformational geometries of  $[Pd(N\!-\!N)_2]^{2+}$  cations: (a) twist conformation, (b) bow-step conformation.

arising from a geometrical distortion from ideal square-planar geometry. These two conformers were observed in solid state for analogous bischelated compounds  $[Pd(N-N)_2]^{2+}$  with bpy, phen, and their alkyl-substituted derivatives, <sup>10c,59</sup> while in

solution an average situation was always observed. The fact that in the <sup>1</sup>H NMR spectrum of  $[Pd(L1)_2][BArF]_2^{60}$  (L1 = 4,4'dimethyl-2,2'-bipyridine) (prepared by a similar procedure) only one set of signals was observed (Figure 6a), similarly to  $[Pd(1)_2][BArF]_2$ , suggests that this equilibrium, if present, is not responsible for the different species observed for complexes 3d and 4d.

Another possibility to take into account is that the species differ in the relative positions of the carbonyl group in the bipyridine ligands. To substantiate this hypothesis, the model compound  $[Pd(L3)_2][BArF]_2$  (L3 = dimethyl-2,2'-bipyridine-4,4'-dicarboxylate) was prepared. The corresponding <sup>1</sup>H NMR spectrum showed signals belonging to three species (ratio 1.0:0.2:0.3, Figure 6b), suggesting that the conformers for complexes  $[Pd(L3)_2][BArF]_2$ ,  $[Pd(3)_2][BArF]_2$ , and  $[Pd(4)_2]-[BArF]_2$  (vide infra) differ only in the relative orientation of the carbonyl groups.

To confirm this assumption, a theoretical study was carried out. DFT calculations were run on the model complexes  $[Pd(L1)_2]^{2+}$  and  $[Pd(L3)_2]^{2+}$  in chloroform, using the B3LYP and M06 functionals (see Supporting Information for



Figure 6. Aromatic region of the <sup>1</sup>H NMR spectra at room temperature of (a)  $[Pd(L1)_2][BArF]_2$  (CDCl<sub>3</sub>/acetone-d<sub>6</sub>); (b)  $[Pd(L3)_2][BArF]_2$  (CDCl<sub>3</sub>).

computational details). The optimized geometries of the *twist* and *bow-step* conformers and of all possible symmetric isomers were obtained (**IS1–IS5** for example for complex  $[Pd(L3)_2]^{2+}$  in Figure 7), and the relative populations of all the minima of



Figure 7. Relative positions of the carbonyl groups in symmetric rotamer complex  $[Pd(L3)_2]^{2+}$ .

each compound assuming a Boltzmann distribution (at T = 298 K) were calculated (Supporting Information Table S8).

For complex  $[Pd(L1)_2]^{2+}$  the *twist* conformation was substantially more stable than the *bow-step* one, which is in agreement with the NMR spectra (Figure 6a) and crystal structure (only one species observed).<sup>59</sup>

For the  $[Pd(L3)_2]^{2+}$  complex (species IS1–IS5 in Figure 7) exploratory calculations performed with a small basis set showed that also the *bow-step* conformation was less stable; therefore, only the geometries and energies of the *twist*- $[Pd(L3)_2]^{2+}$  species were recalculated with a larger basis set. The results (Supporting Information, Table S8) show that, of the five possible rotamers, three have large populations (IS1, IS2, IS3), but the other two are not negligible. The energy of the barrier for the rotation of a carbonyl group, calculated with the smaller basis set, was estimated as 4.6 kcal·mol<sup>-1</sup> relative to the most stable isomer IS1, small enough to allow a fast equilibrium between species, as observed by NMR NOESY experiments (*vide supra*). This could be the reason for the observation of only three signals in the <sup>1</sup>H NMR spectra (instead of 5), if some of the species give an averaged signal.

To sum up, according to theoretical DFT calculations on model complexes, the signals observed in the <sup>1</sup>H NMR spectra for bischelated complexes **3d** and **4d** could be attributed to isomers corresponding to different relative positions of the carbonyl groups, although the theoretical calculations do not give enough information to assign the signals to specific rotamers.

**Catalysis.** Both the monocationic  $[Pd(CH_3)(NCCH_3)(2-4)][X]$  and dicationic  $[Pd(1-4)_2][X]_2$  bipyridine complexes were tested as precatalysts in the copolymerization of CO/ styrene and CO/4-*tert*-butylstyrene in compressed carbon dioxide and 2,2,2-trifluoroethanol as a reference medium. Both series of precatalysts were soluble in liquid carbon dioxide at room temperature. It is well-known from the literature that

the two series of precatalysts require different reaction conditions (pressure and temperature) to generate active species for the studied copolymerization. Thus, for this reason only a relative comparison can be made between both systems.

CO/Styrene and CO/4-tert-Butylstyrene Copolymerization Using [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(2–4)][X] in TFE. Initially, we studied the catalytic behavior of complexes  $2\mathbf{a}-\mathbf{c}$  to  $4\mathbf{a}-\mathbf{c}$  in the copolymerization of CO/styrene (styrene = ST) using 2,2,2-trifluoroethanol at reference conditions reported in the literature:<sup>61</sup> 1 atm of CO pressure, 30 °C, 4.1 × 10<sup>-4</sup> M catalyst, and 10 mL of styrene. The comparison of the catalytic activity of complexes  $2\mathbf{a}-\mathbf{c}$  to  $4\mathbf{a}-\mathbf{c}$  with that of a model complex such as [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(bpy)][PF<sub>6</sub>] (5) provides evidence that most of the catalysts with the fluorinated bpys were more productive than the one with simple bpy (entries 1– 4, Table 3). In addition, in the absence of 1,4-benzoquinone

Table 3. CO/Styrene Copolymerization with 2a–4a and 5 in TFE  $^a$ 

entry	catalyst	[BQ]/[Pd]	productivity, g CP/g Pd
1	2a	0	530
2	3a	0	610
3	4a	0	3310 <sup>b</sup>
4	5	0	580
5	2a	5	1010
6	3a	5	4650 <sup>c</sup>
7	4a	5	720
9	2a	40	1530
10	3a	40	1310
11	4a	40	1010
12	3b	5	1060
13	3c	5	960

<sup>*a*</sup>Reaction conditions:  $n_{\rm Pd} = 1.27 \times 10^{-5}$  mol, styrene V = 10 mL ([ST]/[Pd] = 6823), TFE V = 20 mL,  $p_{\rm CO} = 1$  atm, T = 30 °C, time = 24 h. BQ = benzoquinone.  $M_{\rm w}$  determined by GPC vs polymethylmethacrylate standards.  ${}^{b}M_{\rm w} = 486500 \ (M_{\rm w}/M_{\rm n} = 1.3)$ .

(BQ, used as an oxidant), no decomposition was observed with complexes 2a-4a, while palladium metal was formed in the case of complex 5.

The highest productivity, 4.65 kg CP/g Pd (kg CP/g Pd = kilograms of copolymer per gram of palladium), was achieved with precatalyst 3a at [BQ]/[Pd] = 5 (entry 6, Table 3). The synthesized polyketone had  $M_w = 580\,000$  (1.3), and it was syndiotactic (content of *uu* triad = 93%). In agreement with the literature,<sup>10c</sup> the increase of the [BQ]/[Pd] ratio resulted in an enhancement of productivity in most of the cases, but for instance for complex 4a the highest productivity was obtained with no addition of BQ (entry 3, Table 3) or for complex 3a it was reached at [BQ]/[Pd] = 5 (entry 6, Table 3). Under these conditions, the catalysts with counterions OTs<sup>-</sup> (3b) or BArF<sup>-</sup> (3c), showed a lower productivity than the catalyst with  $PF_6^-$ (entries 12 and 13, Table 3). In the case of tosylate derivatives this behavior might be ascribed to the proximity of the counterion to the catalytic center, although also decomposition of the catalyst might account for the low productivity. In the case of the BArF<sup>-</sup> complexes the catalytic behavior is difficult to rationalize.

CO/Styrene and CO/4-*tert*-Butylstyrene Copolymerization in Compressed Carbon Dioxide. Complexes 2a-c, 3a-c, and 4a-c were tested as precatalysts in the copolymerization of CO/styrene and *tert*-butylstyrene using supercritical carbon dioxide or  $CO_2$ -expanded substrate as solvent at reference conditions (5 atm of CO pressure and 37 °C).<sup>28</sup> The catalytic reactions were carried out in a 11 mL window-equipped high-pressure reactor. After introducing the monocationic palladium complex and the degassed substrate the reactor was pressurized with CO and carbon dioxide and heated to the desired temperature. After the proper time, the reactor was cooled to 0 °C and slowly depressurized. The polymers were isolated by precipitation with methanol.

Complexes with BArF<sup>-</sup> as counterion (2c-4c), which usually provides the most soluble systems in CO<sub>2</sub>, were initially tested in the CO/TBS copolymerization. The results obtained in supercritical conditions (250 atm of total pressure and 37 °C) are represented in Figure 8. Almost all the



**Figure 8.** CO/TBS copolymerization in scCO<sub>2</sub>: effect of the ligand. Precatalyst = [Pd(CH<sub>3</sub>)(NCCH<sub>3</sub>)(N-N)][BArF], **1c** -4**c**. Reaction conditions:  $n_{\text{Pd}} = 1.27 \times 10^{-5}$  mol, TBS V = 0.51 mL ([TBS]/[Pd] = 620),  $p_{\text{CO}} = 5$  atm,  $p_{\text{tot}} = 250$  atm; T = 37 °C, time = 24 h.

investigated catalytic systems showed better results than the model complex  $[Pd(CH_3)(NCCH_3)(1)][BArF]$  (1c) under the same conditions.<sup>28</sup> The catalytic systems with ligands containing a chain in position 5 gave better productivities (339 and 276 g CP/g Pd with 2c and 4c, respectively) and higher molecular weight (75 200 and 197 900 with 2c and 4c, respectively) than the ones with the substituents at position 4. The stereoregularity of the synthesized copolymers ranged between 85% and 90% *uu* triads, for the syndiotactic polyketones.

Reaction conditions were optimized by focusing the attention on complex 4c (Table 4). An increase in the

Table 4. CO/Vinyl Arene Copolymerization in Liquid  $CO_2$  with Precatalyst  $4c^a$ 

entry	p <sub>CO</sub> (atm)	time (h)	[subs]/ [Pd]	productivity, g CP/g Pd (g CP/g Pd·h) <sup>b</sup>	% ии	$M_{ m w} \ (M_{ m w}/M_{ m n})^4$
1	5	24	620	$736(110^d)$	83	82 600 (2.1)
2	10	6	620	789 (132)	82	102 300 (1.6)
3 <sup>e</sup>	10	6	3100	1554 (259)	85	149 500 (2.4)
$4^{e,f}$	10	6	3100	1418 (236)	85	120 700 (2.5)
$5^{e_g}$	10	24	3100	1092 (46)	84	914 100 (1.2)

<sup>*a*</sup>Catalytic conditions:  $n_{\rm Pd} = 1.27 \times 10^{-5}$  mol 4c, [subs] = TBS,  $p_{\rm tot} = 70$  atm, T = 37 °C. <sup>*b*</sup>Averaged values. <sup>*c*</sup>Determined by GPC vs polystyrene standards in TBS copolymers and vs polymethylmethacrylate standards in ST copolymers. <sup>*d*</sup>TOF after 6 h. <sup>*e*</sup> $p_{\rm tot} = 65$  atm to maintain liquid phase. <sup>*f*</sup> $V_{\rm TFE} = 52 \ \mu L \ ([TFE]/[Pd] = 300)$ . <sup>*g*</sup>[subs] = styrene.

productivity of 2.6 times was found moving from  $scCO_2$  to liquid  $CO_2$  (entry 1, Table 4) but with the contemporary

decrease in the molecular weight. A contribution to this improvement may be the increase of catalyst concentration, since the volume of the liquid phase is lower than the volume of the vessel. Moreover, after 6 h the magnetic stirring bar was blocked due to the amount of precipitated polyketone. At this reaction time, the productivity was high, corresponding to an average TOF of 110 g CP/g Pd·h. A slight increase in the productivity and in the molecular weight was observed by doubling the CO pressure from 5 to 10 atm (entry 2, Table 4). At this pressure, an increase of the [TBS]/[Pd] ratio from 620 to 3100 resulted in a further enhancement of productivity (entry 3, Table 4). Addition of a small amount of TFE ([TFE]/ [Pd] = 300) did not result in a positive effect on the productivity (entry 4, Table 4).

Finally, when styrene was used as comonomer at the best conditions obtained for CO/TBS copolymerization, the productivity decreased, with a contemporary remarkable increase in the molecular weight (entry 5, Table 4), in agreement with the literature data.<sup>15a</sup>

Complexes with  $PF_6^-$  or  $OTs^-$  provided less productivity (see Supporting Information). In the case of  $OTs^-$ , decomposition of the catalyst was observed and homopolymer was also detected. Thus, this trend might be related to the ionpairing phenomenon and suggests that the anion (in particular the tosylate) might play a role in catalyst decomposition.

The synthesized polyketones have a prevailingly syndiotactic microstructure with a different percentage of the uu triad depending on the position of the fluorinated tail in the ligand and being around 93–96% when bpy's substituted in position 4 are used and around 76–83% in the case of bpy's substituted in position 5.

These catalytic results evidence that in compressed  $CO_2$  good values of productivities were obtained, even though they were lower than the values obtained in TFE, thus pointing out that compressed  $CO_2$  is a potential suitable medium for this reaction.

**CO/Vinyl Arenes Copolymerization in Compressed CO<sub>2</sub> Using [Pd(N–N)<sub>2</sub>][X]<sub>2</sub>.** The dicationic Pd(II) complexes with BArF<sup>-</sup> as counteranion, **1d**–**4d**, were tested as precatalysts for alternating CO/TBS copolymerization in expanded liquid and supercritical carbon dioxide. Initially, the CO<sub>2</sub> phase was optimized. Under fully homogeneous conditions (CO pressure 30 atm, CO<sub>2</sub> 11.1 g, total pressure 320 atm, T = 60 °C) complex **1d** catalyzed the formation of a perfectly alternating highly syndiotactic polyketone with a productivity of 260 g CP/ g Pd and a molecular weight of 96 200 g/mol (entry 1, Table 5).

Table 5. CO/TBS Copolymerization Using Precatalysts 1d and L1d: Effect of Total Pressure<sup>a</sup>

entry	g CO <sub>2</sub>	total pressure, atm	productivity, g CP/g Pd	$M_{ m w} \; (M_{ m w}/M_{ m n})^b$
1	11	320	260	96 200 (1.5)
2	8.5	200	816	134 000 (1.8)
3	5.1	115	1008	106 800 (1.6)
4	1.8	69	1379	167 000 (1.9)
5	0	30	528	277 000 (2.3)
6 <sup><i>c</i></sup>	1.8	69	820	117 200 (1.7)

<sup>*a*</sup>CO/TBS copolymerization: effect of total pressure. Precatalyst: **1d**. Reaction conditions:  $n_{\text{Pd}} = 2.42 \times 10^{-3}$  mmol, TBS = 1.3 mL, [TBS]/ [Pd] = 4843, TFE = 47  $\mu$ L, [TFE]/[Pd] = 300, *V* vessel = 11 mL, p(CO) = 30 atm, T = 60 °C, t = 24 h. <sup>*b*</sup> $M_{\text{w}}$  determined by GPC. <sup>c</sup>Precatalyst: [Pd(L1)<sub>2</sub>][BArF]<sub>2</sub>(L1d). By reducing the amount of added  $CO_2$  from 11.1 to 8.5 g (total pressure 200 atm), a biphasic system was obtained consisting of an upper supercritical phase and a bottom liquid expanded phase,<sup>20</sup> as assessed by visual inspection. Under these conditions, a 3-fold increase in the productivity with the contemporary enhancement of the molecular weight of the synthesized polyketones to 134 000 g/mol was achieved (entry 2, Table 5). By further lowering the  $CO_2$  amount to 1.8 g (total pressure 69 atm) even higher productivity was obtained in this expanded liquid system (1379 g CP/g Pd, 167 000 g/mol) (entries 3 and 4, Table 5). These results are in agreement with the catalytic data obtained with the monocationic complexes (Table 4), and, as suggested in that case, the higher concentration of catalyst and monomers in the expanded liquid as compared with the homogeneous scCO<sub>2</sub> phase may account for the observed enhancement of productivity. When the reaction was carried out in the absence of CO<sub>2</sub>, i.e., in a liquid (TBS/TFE)/gas CO system (total pressure 30 atm), the catalyst productivity dropped, while the molecular weight of the resulting polymer was significantly higher (277 000 g/mol) (entry 5, Table 5). The comparison of the results obtained in this last experiment and those in the expanded liquid phase shows that the availability of CO seems to play a very important role for the reaction efficiency and the CO2-induced high solubility of CO in the expanded liquid phase<sup>20</sup> has a remarkable positive effect.

When the complex with no fluorinated substituents,  $[Pd(L1)_2][BArF]_2$  (L1d),<sup>59</sup> which is soluble in CO<sub>2</sub>, was tested (entry 6, Table 5), a remarkable decrease of productivity and  $M_w$  was observed, indicating a positive effect of the perfluorinated tails.

Furthermore, the variation of other reaction parameters was studied using 1d as precatalyst (Table 6). Under fully

Table 6. CO/TBS Copolymerization Using 1d As Precatalysts: Effect of CO Pressure, Temperature, and Alcohol<sup>a</sup>

entry	$p_{\rm CO} \ ({\rm atm})$	$p_{\rm CO2} \ ({\rm atm})$	[ROH]/ [Pd]	productivity, g CP/gPd	$M_{ m w}~(M_{ m w}/M_{ m n})^b$
1	10	187	300	120	68 200 (1.9)
2	30	270	300	264	80 800 (1.5)
3	50	240	300	360	134 900 (1.4)
4 <sup><i>c</i></sup>	30	200	300	408	122 400 (1.2)
$5^d$	30	200	300	192	38 500 (1.7)
6 <sup>e</sup>	30	180	0	69	
7	30	120	1800	628	112 000 (1.7)
$8^{f}$	30	200	300	192	83 800 (1.6)
<sup>a</sup> Cataly	tic cond	litions: <i>n</i> <sub>Pd</sub>	= 2.42 ×	10 <sup>-3</sup> mmol, [TB	S]/[Pd] = 4843,

TBS = 1.3 mL, [TFE]/[Pd] = 300, TFE = 47  $\mu$ L, T = 60 °C, time = 24 h. <sup>b</sup>Determined by GPC. <sup>c</sup>T = 45 °C. <sup>d</sup>T = 80 °C, 12 h. <sup>e</sup>Homopolymer formed. <sup>f</sup>MeOH as the alcohol.

homogeneous supercritical conditions, the increase of the CO partial pressure from 10 to 50 atm resulted in an enhancement of productivity and molecular weight (entries 1–3, Table 6). By raising the temperature from 45 to 80 °C a progressive decrease of productivity and molecular weight was observed (entry 2 Table 5 vs entries 4 and 5, Table 6), the latter trend being in agreement with the more rapid increase of the termination rate with respect to the propagation rate observed when the temperature is enhanced.<sup>10c</sup> TFE is an essential component of the catalytic system. When no alcohol was added, a very low

activity was observed, and poly(TBS) was formed instead. In this case a considerable amount of Pd(0) was detected at the end of the reaction (entry 6, Table 6). On the other hand, an increase of the [TFE]/[Pd] ratio to 1800 resulted in a remarkable decrease of productivity, while no effect on the molecular weight was observed (entry 7, Table 6 vs entry 3, Table 5). When methanol was used instead of TFE, the productivity decreased together with the formation of a considerable amount of Pd(0) (entry 8, Table 6 vs entry 2, Table 5), thus confirming that, even in  $scCO_2$ , methanol is not a suitable component for the catalytic system based on nitrogen-donor ligands and that TFE plays a crucial role in increasing the stability of the catalyst. Rather surprisingly, a copolymer with an  $M_{\rm w}$  value higher than 80 000 was obtained even in the presence of MeOH, which is known from the literature to lead to polyketones with a maximum  $M_w$  value of 20 000.62-66

Both productivity and molecular weight increased by prolonging the reaction time, and after 48 h the catalyst was still active, reaching a value of 960 g CP/g Pd in a copolymer of  $M_{\rm w} = 161\,800$  (Figure 9). In general, traces of Pd(0) were detected at the end of the reaction.



**Figure 9.** CO/TBS copolymerization: effect of reaction time. Reaction conditions: Precatalyst 1d,  $n_{\rm Pd} = 2.42 \times 10^{-3}$  mmol, [TBS]/[Pd] = 4843, TBS = 1.3 mL, [TFE]/[Pd] = 300, TFE = 47  $\mu$ L, T = 60 °C, time = 24 h, and  $p_{\rm tot} = 200$  atm.  $M_{\rm w}/M_{\rm n} = 1.6$  (12 h), 1.8 (24 h), 1.7 (48 h).

The catalytic behavior of complexes 2d-4d was evaluated under the optimized reaction conditions for complex 1d ( $p_{tot} =$ 69 atm, [TFE]/[Pd] = 300,  $T = 60 \,^{\circ}C$ ,  $p_{CO} = 30$  atm,  $t = 24 \, \text{h}$ ) in expanded liquid phase (Table 7). The lowest productivity was obtained with complex 2d, with the nonsymmetric ligand having only one fluorinated tail (entry 2, Table 7). Catalyst 3d vielded a substantial amount of homopolymer (53%), which may be due to catalyst decomposition, since palladium black was observed at the end of the reaction. Catalyst containing ligand 4 was thus far the best performing, in terms of both productivity (6155 g CP/g Pd, average TOF after 6 h 532 g  $CP/g Pd \cdot h$ ) and molecular weight (222 000) (entry 4, Table 7). This result is in agreement with the literature data on 5substituted bpy's<sup>30</sup> and on 3-substituted phenanthrolines<sup>15</sup> and confirms that the presence of substituents in meta position with respect to the nitrogen donor is relevant for achieving excellent performing catalysts in combination with electron-withdrawing substituents.

Following this trend, the nonfluorinated complex with the ligand L4, dimethyl-2,2'-bipyridine-5,5'-dicarboxylate, [Pd- $(L4)_2$ ][BArF]<sub>2</sub> (L4d), showed a productivity of almost 5.5 kg CP/g Pd, not so far from that of complex 4d, suggesting that the major contribution to the improved productivity might be

Table 7. CO/TBS Copolymerization Using Precatalysts 1d-4d and  $L4d^a$ 

productivity g CP/g Pd (gCP/	$M_{ m w} \ (M_{ m w}/M_{ m n})^b$
entry catalyst substrate g Pd·h)	W ( W/ II/
1 1d TBS 1379 (57)	167 000 (1.9)
2 2d TBS 466 (19)	187 700 (3.3)
3 <sup>c</sup> 3d TBS 1535 (64)	
4 4d TBS $6155(532^d)$	222 000 (4.3)
5 L4d TBS 5490 (228)	197 200 (3.2)
$6^e$ 4d TBS 222 (9)	25 100 (2.0)
7 4d ST 2294 (95)	692 600 (1.3)
8 L4d ST 2235 (93)	374 200 (1.4)
$9^{f}$ 4d ST 10(-)	n.d.
$10^{g}$ 4d ST 2004 (83)	n.d.

<sup>a</sup>Reaction conditions:  $n_{Pd} = 2.42 \times 10^{-3}$  mmol, *V* vessel = 11 mL, TBS V = 2.2 mL, ST V = 1.3 mL ([substrate]/[Pd] = 4843), TFE V = 47  $\mu$ L ([TFE]/[Pd] = 300),  $p_{CO} = 30$  atm,  $p_{tot} = 70$  atm, T = 60 °C, time = 24 h. <sup>b</sup>Determined by GPC. <sup>c</sup>Homopolymer formed (53%). <sup>d</sup>Average TOF after 6 h. <sup>e</sup> $n_{Pd} = 6.6 \times 10^{-3}$  mmol, solvent TFE V = 30 mL, TBS V = 5.9 mL ([TBS]/[Pd] = 4843). <sup>f</sup>Solvent TFE,  $n_{Pd} = 6.6 \times 10^{-3}$  mmol catalyst, TFE V = 30 mL, styrene V = 3.7 mL, [styrene]/[Pd] = 4843. <sup>g</sup>Solvent TFE,  $n_{Pd} = 5.4 \times 10^{-3}$  mmol, TFE V = 30 mL, styrene V = 3.7 mL, [styrene]/[Pd] = 4843.

related to the electron properties of the ester group and only a minor part might be associated with the fluorinated tails (entry 5, Table 7). The catalytic activity of 4d in TFE as a solvent, in the absence of  $CO_2$ , decreased dramatically (entry 6, Table 7).

The copolymerization of CO/styrene with precatalysts 4d and L4d in compressed CO<sub>2</sub> proceeded with lower productivities than the CO/TBS copolymerization (entries 7 and 8, Table 7) but remarkable high  $M_{w}$ . Again the results obtained in compressed CO<sub>2</sub> with 4d for the CO/ST copolymerization were lower than those obtained in net TFE (entry 9, Table 7), even at optimized conditions from the literature (entry 10, Table 7).

Mechanism of the Catalytic Reaction. Mass spectrometry (MALDI-TOF) has been used to analyze the end groups of the polyketones, to obtain information about the initiation and termination steps of the catalytic cycle.<sup>60-65</sup> Therefore, to investigate the influence of the reaction media, MALDI-TOF mass spectra of the CO/TBS polyketones obtained in the CO<sub>2</sub>expanded liquid with precatalyst 2d were recorded and compared with those obtained in TFE (Figure 10). The mass spectra were characterized by several series of peaks that correspond to fragments containing chains a-c (Scheme 5) cationized with K<sup>+</sup> or Na<sup>+</sup>. The macromolecules differ in the end groups, while the repetitive unit (132 Da for CO/ST and 188 Da for CO/TBS) is that expected for this kind of copolymerization reaction. The mass spectra of the polymers obtained with catalyst 2d in  $CO_2$ -expanded liquid (Figure 10a) revealed that the main fragment corresponded to a species in which the initiation step involves the insertion of the alkene into the Pd-H bond and termination by  $\beta$ -H elimination (chain a, Scheme 5). Therefore, TFE should not be involved in the initiation.<sup>61</sup> Minor peaks that may correspond to a doublecarbonylation process were also observed for the polyketones synthesized in  $CO_2$  (chain c + CO, Scheme 5, Figure 10a). In contrast, although the mass spectra of the polyketone obtained in TFE (Figure 10b) showed also the peak corresponding to chain a, there were also peaks corresponding to chain b (Scheme 5), containing trifluoroethanol as an initiator. Therefore, as observed in the literature,<sup>61,67</sup> the fluorinated alcohol does not rise to termination through alcoholysis, and  $\beta$ -H elimination should be the main chain transfer process. This is also the prevailing termination process when the copolymerization is run in scCO<sub>2</sub> in the presence of methanol, instead of TFE (entry 8 Table 6). The MALDI-TOF mass spectrum of this polymer confirmed that methanol was the initiator, but the termination step involved the  $\beta$ -elimination from the alkyl group, accounting for the higher molecular weight of the polymer obtained in scCO<sub>2</sub> than of those reported in the literature obtained in net methanol.

Finally, there are no substantial differences between the composition of the polymers obtained with precatalyst 4d in the same medium,  $CO_2$  (see Supporting Information). Similar mass spectra were observed in the case of the polymers obtained with styrene as comonomer (see Supporting Information).

In conclusion, according to the mass spectra of the CO/TBS polyketones obtained in  $CO_2$ -expanded liquid, the mechanism did not involve trifluoroethanol as an initiator but as a stabilizing agent, since without TFE considerable catalyst decomposition was observed. When a less reactive substrate such as styrene was used, species deriving from double carbonylation increased considerably when  $CO_2$ -expanded liquid was used.

### CONCLUSION

We have synthesized new bipyridine ligands bearing one or two perfluorinated ponytails and studied their coordination chemistry with palladium(II) precursors by synthesizing two series of complexes, one involving monocationic complexes and the other dicationic derivatives with different counterions, such as tosylate, hexafluorophosphate, and BArF<sup>-</sup>. In ligands 3 and 4 the perfluorinated ponytails have been introduced through esterification of the carboxylic groups at the 4,4' and 5,5' positions, respectively. The characterization of the monocationic complexes in solution evidenced that the tosylate and the hexafluorophosphate interact with the cation, while BArF<sup>-</sup> did not. In the case of the dicationic derivatives 3d and 4d different conformers were detected in solution at room temperature via <sup>1</sup>H NMR. DFT calculations suggested that they differ in the relative orientation of the carboxylate groups.

Both series of complexes were tested as precatalysts for the CO/vinyl arene copolymerization by carrying out the reaction in scCO<sub>2</sub> and in CO<sub>2</sub>-expanded substrate. For both series of complexes, by far the best results were obtained by carrying out the polymerization in CO2-expanded substrate. The catalyst precursors based on ligand 4 yielded up to 1.5 kg CP/g Pd and 6.1 kg CP/g Pd of prevailingly syndiotactic polyketones with  $M_{\rm w}$  of 149 500 and 222 000 for the monocationic and the dicationic precatalysts, respectively. The very good catalytic data obtained in CO<sub>2</sub> point out that compressed CO<sub>2</sub> is a potential suitable medium for this reaction. In addition, the study of different reaction parameters evidenced that trifluoroethanol, even in a small amount, is an essential component of the catalytic system, playing a crucial role as catalyst stabilizer. Indeed, MALDI-TOF analysis of the synthesized polyketones using compressed carbon dioxide reveals that TFE is not involved either in the initiation or in the termination steps of the catalytic process.



Figure 10. MALDI-TOF mass spectra of the CO/TBS polyketones synthesized using precatalyst 2d: (a) in CO2-expanded liquid and (b) in TFE.

#### EXPERIMENTAL SECTION

**General Comments.** Commercially available Na<sub>2</sub>[PdCl<sub>4</sub>] (Johnson Matthey), ligand L1 (Aldrich), and methanol (Merck) were used without further purification for synthetic and spectroscopic purposes. L3<sup>68,69</sup> and L4<sup>68</sup> were prepared following the procedure described by Shan et al.<sup>68</sup> 2,2,2-Trifluoroethanol (Alfa-Aesar) for the catalytic reactions was purified by distillation with CaH<sub>2</sub>. Dichloromethane was purified through distillation over CaH<sub>2</sub> and stored under an inert atmosphere. Carbon monoxide (CP grade, 99.0%) was supplied by Westfalen and Air Liquide. Carbon dioxide (CO<sub>2</sub>, CP grade 5.3 and SCF grade, 99.995%) was supplied by Praxair and Air Products. IR spectra (range 4000–400 cm<sup>-1</sup>) were recorded on a Midac Grams/ 386 spectrometer in KBr pellets or dichloromethane solution (when indicated). NMR spectra were recorded on a 400 MHz Varian with tetramethylsilane (<sup>1</sup>H NMR and <sup>13</sup>C NMR) and fluoroform (<sup>19</sup>F NMR) as the internal standards. MALDI-TOF measurements of complexes and polymers were performed on a Voyager-DE-STR (Applied Biosystems, Framingham, MA, USA) instrument equipped

with a 337 nm nitrogen laser. All spectra were acquired in the positive ion reflector mode. 2,5-Dihydroxybenzoic acid (DHB) was used as matrix for complexes. The matrix was dissolved in MeOH at a concentration of 10 mg·mL<sup>-1</sup>. The complex was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mg· $L^{-1}$ ). The matrix and the samples were premixed in a 2:1 ratio (matrix:sample), and then the mixture was deposited  $(1 \ \mu L)$  on the stainless steel sample holder and allowed to dry before introduction into the mass spectrometer. Three independent measurements were made for each sample. For each spectrum 100 laser shots were accumulated. The molecular weights  $(M_w)$  of copolymers and the molecular weight distributions  $(M_w/M_n)$  were determined by gel permeation chromatography versus polystyrene standards (CO/TBS) or polymethylmethacrylate (PMMA) standards (CO/ST). Measurements for CO/TBS were made in THF on a Millipore-Waters 510 HPLC pump device using a three-serial column system (MZ-Gel 100 Å, MZ-Gel 1000 Å, MZ-Gel 10000 Å linear columns) with UV detector (ERC-7215) and IR detector (ERC-7515a). The software used to get the data was NTeqGPC 5.1. Samples were prepared as Scheme 5. Polyketone Chains a–c and the Proposed Catalytic Cycles for the Copolymerization Carried Out in Compressed  $CO_2$ 



follows: 5 mg of the copolymer was solubilized with 2 mL of tetrahydrofuran (HPLC grade) stabilized with toluene (HPLC grade). Measurements for CO/ST copolymers were made in hexafluoroisopropanol on an Alliance-Waters 2695 HPLC pump device using a PSS PFG analytical 1000 Å rigid column with IR detector (Waters-2414). The software used to get the data was Empower supplied by Waters. Samples were prepared as follow: 2.0 mg of the copolymer was solubilized in 2 mL of hexafluoroisopropanol (HPLC grade).

**Copolymerization Reactions in CO<sub>2</sub> As Solvent.** The catalytic experiments were performed in an 11 mL stainless steel autoclave. The catalyst was weighed and introduced into the purged autoclave. Then a solution of substrate and the alcohol was added under an argon atmosphere. The autoclave was pressurized with CO and CO<sub>2</sub> and heated to the temperature desired. After the reaction time, the autoclave was cooled to 0 °C and depressurized and the product was redissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. The copolymer was precipitated by pouring the reaction solution into rapidly stirred methanol (70 mL). The polymer was filtered, washed with methanol, and dried.

**Copolymerization Reactions in TFE As Solvent.** Copolymerization reactions were carried out in a 100 mL Bergoff reactor equipped with a magnetic stirrer at 30 atm of CO. After introduction of the catalyst precursor into the purged autoclave, the solvent and substrate were added under an argon atmosphere. The autoclave was pressurized with carbon monoxide and heated to the desired temperature. After 24 h, the reactor was vented out and the reaction mixture was poured into stirred methanol (100 mL). The polymer was filtered off, washed with methanol, and dried under vacuum.



Synthesis of Ligands and Complexes. 5-[4-(Perfluorooctyl)butyl]-5'-methyl-2,2'-bipyridine (2). A solution of *n*-butyllithium 1.6 M in hexane (6 mL, 9.5 mmol, 3.5 equiv) was added via a syringe to a solution of diisopropylamine (1.47 mL, 20.5 mmol) in tetrahydrofuran (3 mL) at -78 °C. The solution was stirred for 10 min at -78 °C, and 5,5'-dimethyl-2,2'-bipyridine (0.5 g, 2.7 mmol) in 40 mL of tetrahydrofuran was then added dropwise. The dark brown solution was stirred at -78 °C for 1 h. Then, 3-perfluorooctyl-1-iodopropane (3.77 g, 6.42 mmol) in 25 mL of tetrahydrofuran was added slowly via syringe at -78 °C. The brown solution was stirred for 5 h at -78 °C and at room temperature overnight. The solvent was removed under reduced pressure, and the solid was purified by Soxhlet extraction in methanol. The methanolic solution was evaporated to obtain a light brown solid, 0.81 g (yield 46%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  1.71 (4H, m, (CH<sub>2</sub>)<sup>2<sup>7,3</sup></sup>), 2.11 (2H, m, (CH<sub>2</sub>)<sup>4<sup>\*</sup></sup>), 2.40 (3H, s, CH<sub>3</sub>), 2.73 (2H, t, (CH<sub>2</sub>)<sup>1<sup>\*</sup></sup>, *J* = 7.35 Hz), 7.64 (1H, d, (CH)<sup>4<sup>\*</sup></sup>, *J* = 8.1 Hz), 8.28 (1H, d, (CH)<sup>3<sup>\*</sup></sup>, *J* = 8.1 Hz), 8.51 (2H, s, (CH)<sup>66</sup>). <sup>13</sup>C NMR (75.43 MHz, CDCl<sub>3</sub>):  $\delta$  18.6 (CH<sub>3</sub>), 20.3 (C<sup>3<sup>\*</sup></sup>H<sub>2</sub>), 30.9 (C<sup>2<sup>\*</sup></sup>H<sub>2</sub>), 31.1 (C<sup>4<sup>\*</sup></sup>H<sub>2</sub>), 32.9 (C<sup>1<sup>\*</sup></sup>H<sub>2</sub>), 110–120 (CF<sub>2</sub>–CF<sub>3</sub>), 120.6 (C<sup>4</sup>H), 120.7 (C<sup>4</sup>H), 137.3 (C<sup>3</sup>H), 134.0 (C<sup>2<sup>\*</sup></sup>), 154.5 (C<sup>4</sup>). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>):  $\delta$  –126.58 (CF<sub>2</sub>), –123.97 (CF<sub>2</sub>), –123.19 (CF<sub>2</sub>), –122.40 (CF<sub>2</sub>), –122.2 (CF<sub>2</sub>), –114.82 (CF<sub>2</sub>), –81.19 (CF<sub>3</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –76.8 (N<sub>cis</sub> N<sub>trans</sub>). MALDI-TOF: *m*/*z* calcd for C<sub>23</sub>H<sub>17</sub>F<sub>17</sub>N<sub>2</sub> 644.1115 [M]; found 644.6413.



Bis[3-(perfluorooctyl)propyl]-2,2'-bipyridine-4,4'-dicarboxylate (3). 2,2'-Bipyridine-4,4'-dicarboxylic acid (525 mg, 2.15 mmol) was suspended in tionyl chloride (8 mL, 43 mmol, 20 equiv) and refluxed (78 °C) under nitrogen until complete solubilization of the diacid (about 24 h). The excess of tionyl chloride was removed by reducing the pressure. The resulting white powder was dissolved in dry dichloromethane (10 mL) and was added dropwise to a solution of 3-(perfluorooctyl)propanol (2.6 mg, 5.4 mmol, 2.5 equiv) and triethylamine (1.2 mL, 8.6 mmol, 4 equiv) in 30 mL of dichloromethane. The mixture was refluxed for 6 h and stirred at room temperature for 12 h. After removal of dichloromethane, the obtained powder was washed with water, filtered under suction, recrystallized from dichloromethane, and washed three times with pentane to afford a pale white powder, 0.57 g (yield 23%). <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ :  $\delta$  (ppm) 2.18 (4H, m,  $(CH_2)^{3"}$ ), 2.30 (4H, m,  $(CH_2)^{2"}$ ), 4.49  $(4H, t, (CH_2)^{1''}, J = 6 Hz), 7.90 (2H, d, (CH)^{5,5'}, J = 4 Hz), 8.88 (2H, CH)^{5,5'}$ (41, c, (C1)), J = 0 (12), J = 0 (21, c, (C1)), J = 0 (12),  $\delta = 0$  (21, c, (C1)), J = 0 (12),  $\delta = 0$  (21, c, (C1)),  $\delta = 0$  (21, c, (C1)), \delta = 0 (21, c, (C1)),  $\delta = 0$  (21 C<sup>6,6'</sup>), 156.7 (s, C<sup>4,4'</sup>), 165.2 (s, CO). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) -126.5 (s, CF<sub>2</sub>), -123.7 (s, CF<sub>2</sub>), -123.1 (s, CF<sub>2</sub>), -122.3 (s, CF<sub>2</sub>), -122.1 (s, CF<sub>2</sub>), -114.7 (s, CF<sub>2</sub>), -81.1 (s, CF<sub>3</sub>). <sup>15</sup>N NMR (40 MHz,  $CD_2Cl_2$ ):  $\delta$  -61.6. HR MALDI-TOF: m/z calcd for C<sub>34</sub>H<sub>18</sub>F<sub>34</sub>N<sub>2</sub>O<sub>4</sub> 1164.0718 [M]; found 1164.4781. IR ν(COO) 1731  $cm^{-1}$ 

Bis[3-(perfluorooctyl)propyl]-2,2'-bipyridine-5,5'-dicarboxylate (4). 4 was prepared following the same procedure as 3, affording a white powder, 1.42 g (yield 52%).



<sup>1</sup>H NMR (400 MHz, toluene-*d*<sub>8</sub>, 80 °C): δ 1.71 (4H, m, (CH<sub>2</sub>)<sup>3°</sup>), 1.91 (4H, m, (CH<sub>2</sub>)<sup>2°</sup>), 3.99 (4H, t, (CH<sub>2</sub>)<sup>1°</sup> *J* = 6.2 Hz), 8.13 (2H, d, (CH)<sup>3,3′</sup> *J* = 8 Hz), 8.54 (2H, d, (CH)<sup>4,4′</sup> *J* = 8 Hz) 9.29 (2H, s, (CH)<sup>6,6′</sup>). <sup>19</sup>F NMR (376.3 MHz, toluene-*d*<sub>8</sub>, 80 °C): δ –126.5 (CF<sub>2</sub>), –123.6 (CF<sub>2</sub>), –123.5 (CF<sub>2</sub>), –123.0 (CF<sub>2</sub>), –122.2 (CF<sub>2</sub>), –122.9 (CF<sub>2</sub>), –114.3 (CF<sub>2</sub>), –81.1 (CF<sub>3</sub>). MALDI-TOF: *m*/*z* calcd for C<sub>34</sub>H<sub>18</sub>F<sub>34</sub>N<sub>2</sub>O<sub>4</sub> 1165.0796 [M + H]; found 1165.1724. IR *ν*(COO) 1716 cm<sup>-1</sup>.

 $[Pd(CH_3)(NCCH_3)(N-N)][X] X = PF_6^-$ , OTs<sup>-</sup> (**2a**-**4a**, **2b**-**4b**). A 1.2 equiv amount of the silver hexafluorophosphate or silver tosylate salt (6.6 × 10<sup>-2</sup> mmol) dissolved in 1 mL of dry acetonitrile was added to a solution of  $[Pd(CH_3)Cl(2-4)]$  (5.5 × 10<sup>-2</sup> mmol) in 4 mL of dry dichloromethane, kept in the dark, under magnetic stirring, at room temperature and in an argon atmosphere. After 5 h the solution was filtered over Celite to remove the silver chloride salt. The solution was concentrated, and diethyl ether was added, giving a precipitate, which was filtered off, washed with diethyl ether, and dried under vacuum.

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(2)][*PF*<sub>6</sub>] (2*a*). Pale brown solid (yield 84%). MALDI-TOF: calcd for (C<sub>26</sub>H<sub>23</sub>F<sub>23</sub>N<sub>3</sub>PPd) *m*/*z* 938.0223 [M<sup>+</sup> – CH<sub>3</sub> + 2H<sup>+</sup>], 954.0537 [M<sup>+</sup> + 3H<sup>+</sup>], 974.0200 [M<sup>+</sup> + Na<sup>+</sup>]; found *m*/*z* 938.7144 [M<sup>+</sup> – CH<sub>3</sub> + 2H<sup>+</sup>], 954.7755 [M<sup>+</sup> + 3H<sup>+</sup>], 974.7293 [M<sup>+</sup> + Na<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.07 (s, 3H, Pd-CH<sub>3</sub>), 1.72 (m, 2H, (CH<sub>2</sub>)<sup>3°</sup>), 1.78 (m, 2H, (CH<sub>2</sub>)<sup>2°</sup>), 2.17 (m, 2H, (CH<sub>2</sub>)<sup>4°</sup>), 2.48 (s, 3H, Pd-NCCH<sub>3</sub>), 2.53 (s, 3H, (CH<sub>3</sub>)<sup>1″</sup>), 2.80 (t, 1H, (CH<sub>2</sub>)<sup>1″</sup>, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz), 2.85 (t, 1H, (CH<sub>2</sub>)<sup>1″</sup>, <sup>3</sup>J<sub>H-H</sub> = 7.5 Hz), 7.96 (m, 2H, (CH)<sup>44'</sup>), 8.07 (m, 2H, (CH)<sup>3.3'</sup>), 8.32 (s, 1H, (CH)<sup>6'</sup>), 8.34 (s, 1H, (CH)<sup>6</sup>). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -73.4 (PF<sub>6</sub><sup>-</sup>, J<sub>P-F</sub> = 712 Hz), -81.6 (CF<sub>3</sub>), -115.0 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -122.6 (CF<sub>2</sub>), -123.4 (CF<sub>2</sub>), -124.2 (CF<sub>2</sub>), -126.8 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -204.7 (NCCH<sub>3</sub>), -159.2 (N<sub>cis</sub>), -121.1 (N<sub>trans</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(2)][*OTs*] (2*b*). Yellow brownish powder (yield 74%). MALDI-TOF: calcd for (C<sub>33</sub>H<sub>30</sub>F<sub>17</sub>N<sub>3</sub>O<sub>3</sub>PdS) *m/z* 938.0668 [M<sup>+</sup> – NCCH<sub>3</sub> + 2H<sup>+</sup>], 977.0778 [M<sup>+</sup>]; found *m/z* 938.7320 [M<sup>+</sup> – NCCH<sub>3</sub> + 2H<sup>+</sup>], 977.7690 [M<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  0.94 (s, 3H, Pd-CH<sub>3</sub>), 1.58 (s, 3H, CH<sub>3</sub>-OTs), 1.67–1.74 (m, 4H, (CH<sub>2</sub>)<sup>3′,2′</sup>), 2.15 (m, 2H, (CH<sub>2</sub>)<sup>4′</sup>), 2.37 (s, 3H, (CH<sub>3</sub>)<sup>1″</sup>), 2.42 (s, 3H, CH<sub>3</sub>CN-Pd), 2.73 (m, 2H, (CH<sub>2</sub>)<sup>1″</sup>), 7.21 (d, 2H, *m*-CH-OTs, <sup>3</sup>*J*<sub>Hm-Ho</sub> = 5 Hz), 7.79 (br, 3H, *o*-CH-OTs, (CH)<sup>4′</sup> overlapped), 7.84 (d, 1H, (CH)<sup>4′, 3</sup>*J*<sub>H4-H3</sub> = 8.5 Hz), 7.91–8.00 (m, 2H, (CH)<sup>3/3</sup>), 8.31 (psd, 2H, (CH)<sup>6cis,6′trans</sup>), 8.58 (s, 1H, (CH)<sup>6′trans</sup>), 8.68 (s, 1H, (CH)<sup>6′cis</sup>). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –81.5 (CF<sub>3</sub>), −115.1 (CF<sub>2</sub>), −122.4 (CF<sub>2</sub>), −122.6 (CF<sub>2</sub>), −123.3 (CF<sub>2</sub>), −124.1 (CF<sub>2</sub>), −126.8 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –162.4 (N<sub>cis</sub>), −115.9 (N<sub>trans</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(**3**)][*PF*<sub>6</sub>] (**3***a*). Bright yellow solid (yield 70%). IR (KBr): 1736 cm<sup>-1</sup> ν(COO). MALDI-TOF: calcd for (C<sub>37</sub>H<sub>24</sub>F<sub>40</sub>N<sub>3</sub>O<sub>4</sub>PPd) *m*/z 1439.0118 [M<sup>+</sup> – PF<sub>6</sub><sup>-</sup> + CF<sub>3</sub>COO<sup>-</sup>], 1473.0066 [M<sup>+</sup> + 2H<sup>+</sup>]; found *m*/z 1438.9903 [M<sup>+</sup> – PF<sub>6</sub><sup>-</sup> + CF<sub>3</sub>COO<sup>-</sup>], 1472.9887 [M<sup>+</sup> + 2H<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.21 (*s*, 3H, Pd-CH<sub>3</sub>), 2.20 (m, 4H, (CH<sub>2</sub>)<sup>2</sup><sup>°</sup>), 2.32 (m, 4H, (CH<sub>2</sub>)<sup>3</sup><sup>°</sup>), 2.58 (*s*, 3H, Pd-NCCH<sub>3</sub>), 4.56 (*t*, 4H, (CH<sub>2</sub>)<sup>1°</sup>, <sup>3</sup>J<sub>H-H</sub> = 5.5 Hz), 8.17 (dd, 1H, (CH)<sup>5</sup>, <sup>3</sup>J<sub>H5-H6</sub> = 5.75 Hz, <sup>4</sup>J<sub>H5-H3</sub> = 1.25 Hz), 8.33 (dd, 1H, (CH)<sup>5'</sup>, <sup>3</sup>J<sub>H5'-H6'</sub> = 5.5 Hz, <sup>4</sup>J<sub>H5'-H6'</sub> = 1.5 Hz), 8.78 (m, 3H, (CH)<sup>3,3',6</sup>), 8.91 (d, 1H, (CH)<sup>6'</sup>, <sup>3</sup>J<sub>H6'-H5'</sub> = 5.5 Hz). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –72.9 (PF<sub>6</sub><sup>-</sup>, J<sub>P-F</sub> = 712 Hz), -81.1 (CF<sub>3</sub>), -114.5 (CF<sub>2</sub>), -121.9 (CF<sub>2</sub>), -122.2 (CF<sub>2</sub>), -122.9 (CF<sub>2</sub>), -123.6 (CF<sub>2</sub>), 126.4 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –207.6 (NCCH<sub>3</sub>), -148.9 (N<sub>cik</sub>), -111.9 (N<sub>trans</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(**3**)][*OTs*] (**3b**). Green brownish powder (yield 72%). IR (KBr): 1729 cm<sup>-1</sup>  $\nu$ (COO). MALDI-TOF: calcd for (C<sub>44</sub>H<sub>31</sub>F<sub>34</sub>N<sub>3</sub>O<sub>7</sub>PdS) *m/z* 1497.0381 [M<sup>+</sup>], 1521.0361 [M<sup>+</sup> + Na<sup>+</sup>]; found *m/z* 1497.1564 [M<sup>+</sup>], 1521.1980 [M<sup>+</sup> + Na<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.09 (s, 3H, Pd-CH<sub>3</sub>), 1.41 (br, 3H, CH<sub>3</sub>-OTs), 2.19 (m, 4H, (CH<sub>2</sub>)<sup>3°</sup>), 2.31 (m, 4H, (CH<sub>2</sub>)<sup>2°</sup>), 2.40 (s, 3H, CH<sub>3</sub>CN-Pd), 4.53 (s, 4H, (CH<sub>2</sub>)<sup>1°</sup>), 7.25 (br, 2H, *m*-CH-OTs), 7.81 (br, 2H, *o*-CH-OTs), 8.06 (d, 1H, (CH)<sup>5</sup>, <sup>3</sup>J<sub>H5-H6</sub> = 4.5 Hz), 8.18 (d, 1H, (CH)<sup>5′</sup>, <sup>3</sup>J<sub>H5-H6</sub> = 4.5 Hz), 8.18 (d, 1H, (CH)<sup>5′</sup>, <sup>3</sup>J<sub>H5-H6</sub> = 4.5 Hz), 9.22 (d, 1H, (CH)<sup>6′</sup>, <sup>3</sup>J<sub>H6-H5′</sub> = 4.5 Hz). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -81.5 (CF<sub>3</sub>), -115.0 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -122.6 (CF<sub>2</sub>), -123.3 (CF<sub>2</sub>), -124.0 (CF<sub>2</sub>), -126.8 (CF<sub>2</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(*4*)][*PF*<sub>6</sub>] (*4a*). Pale yellow solid (yield 57%). IR (KBr): 1733 cm<sup>-1</sup> ν(COO<sup>-</sup>). MALDI-TOF: calcd for (C<sub>37</sub>H<sub>24</sub>F<sub>40</sub>N<sub>3</sub>O<sub>4</sub>PPd) *m/z* 1419.9080 [M<sup>+</sup> - CH<sub>3</sub> - PF<sub>6</sub><sup>-</sup> + Ag<sup>+</sup>], 1473.0066 [M<sup>+</sup> + 2H<sup>+</sup>]; found *m/z* 1419.1599 [M<sup>+</sup> - CH<sub>3</sub> - PF<sub>6</sub><sup>-</sup> + Ag<sup>+</sup>], 1472.9887 [M<sup>+</sup> + 2H<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.25 (s, 3H, Pd-CH<sub>3</sub>), 2.18 (m, 4H, (CH<sub>2</sub>)<sup>2'</sup>), 2.32 (m, 4H, (CH<sub>2</sub>)<sup>3'</sup>), 2.55 (s, 3H, Pd-NCCH<sub>3</sub>), 4.53 (t, 4H, (CH<sub>2</sub>)<sup>1\*</sup>, *J* = 6.25 Hz), 8.45 (pst, 2H, (CH)<sup>3,3'</sup>), 8.77 (pst, 2H, (CH)<sup>4,4'</sup>), 9.08 (s, 1H, (CH)<sup>6'</sup>), 9.15 (s, 1H, (CH)<sup>6</sup>). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -73.1 (PF<sub>6</sub>, *J*<sub>P-F</sub> = 712 Hz), -81.1 (CF<sub>3</sub>), -114.5 (CF<sub>2</sub>), -121.9 (CF<sub>2</sub>), -122.1 (CF<sub>2</sub>), -122.9 (CF<sub>2</sub>), -123.5 (CF<sub>2</sub>), 126.3 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -205.6 (NCCH<sub>3</sub>), -156.6 (N<sub>cis</sub>), -119.0 (N<sub>trans</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(*4*)][*OTs*] (*4b*). Brownish-green powder (yield 52%). IR (KBr): 1730 cm<sup>-1</sup> ν(COO<sup>-</sup>). MALDI-TOF: calcd for (C<sub>44</sub>H<sub>31</sub>F<sub>34</sub>N<sub>3</sub>O<sub>7</sub>PdS) *m/z* 1419.9080 [M<sup>+</sup> – CH<sub>3</sub> – OTs<sup>-</sup> + Ag<sup>+</sup>], 1474.0462 [M<sup>+</sup> – NCCH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>]; found *m/z* 1419.1079 [M<sup>+</sup> – CH<sub>3</sub> – OTs<sup>-</sup> + Ag<sup>+</sup>], 1474.2297 [M<sup>+</sup> – NCCH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.15 (s, 3H, Pd-CH<sub>3</sub>), 1.27 (s, 3H, CH<sub>3</sub>-OTs), 2.16 (m, 4H, (CH<sub>2</sub>)<sup>1</sup>), 7.24 (d, 2H, *m*-CH-OTs, <sup>3</sup>*J*<sub>Hm-Ho</sub> = 9 Hz), 7.81 (d, 2H, *o*-CH-OTs, <sup>3</sup>*J*<sub>Ho-Hm</sub> = 9 Hz), 8.26 (d, 1H, (CH)<sup>3</sup>, <sup>3</sup>*J*<sub>H3-H4</sub> = 8.5 Hz), 8.30 (d, 1H, (CH)<sup>3</sup>, <sup>3</sup>*J*<sub>H3-H4</sub> = 8.5 Hz), 8.67 (m, 2H, (CH)<sup>4,4</sup>), 9.18 (d, 1H, (CH)<sup>6</sup>, <sup>4</sup>*J*<sub>H6-H4</sub> = 2 Hz), 9.71 (d, 1H, (CH)<sup>6</sup>, <sup>4</sup>*J*<sub>H6'H4'</sub> = 2 Hz). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ -81.5 (CF<sub>3</sub>), -115.0 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -122.5 (CF<sub>2</sub>), -123.3 (CF<sub>2</sub>), -123.0 (N<sub>trans</sub>).

 $[Pd(CH_3)(NCCH_3)(N-N)][BArF]$  (2c-4c). Two drops of dry acetonitrile were added to a suspension of 2b-4b ( $3.4 \times 10^{-2}$  mmol) and 1.1 equiv of NaBArF (33 mg,  $3.7 \times 10^{-2}$  mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL). The mixture was stirred for 0.5 h at 0 °C and then for 1 h at room temperature. The resulting suspension was filtered off to remove the precipitated NaOTs, which was washed with dry dichloromethane. The filtrate was evaporated under vacuum to yield an oil, which was triturated with pentane, yielding a foam.

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(2)][*BArF*] (2*c*). Pale brown foam (yield 97%). MALDI-TOF: calcd for  $(C_{58}H_{35}BF_{41}N_3Pd) m/z \ 1600.1373 [M<sup>+</sup> - CF_3], 1643.1613 [M<sup>+</sup> - CF_3 + Na<sup>+</sup> + NH_4<sup>+</sup>]; found <math>m/z \ 1599.1922$ [M<sup>+</sup> - CF<sub>3</sub>], 1643.1685 [M<sup>+</sup> - CF<sub>3</sub> + Na<sup>+</sup> + NH\_4<sup>+</sup>]. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta \ 1.09$  (*s*, 3H, Pd-CH<sub>3</sub>), 1.71 (m, 2H, (CH<sub>2</sub>)<sup>2°</sup>), 1.78 (m, 2H, (CH<sub>2</sub>)<sup>3°</sup>), 2.16 (m, 2H, (CH<sub>2</sub>)<sup>4°</sup>), 2.48 (*s*, 3H, Pd-NCCH<sub>3</sub>), 2.55 (*d*, 3H, (CH<sub>3</sub>)<sup>1°</sup>), 2.81 (m, 2H, (CH<sub>2</sub>)<sup>1°</sup>), 7.54 (*s*, 4H, BArF), 7.71 (*s*, 8H, BArF), 7.90–8.10 (m, 4H, (CH)<sup>4,4′</sup>, (CH)<sup>3,3′</sup>), 8.23 (*d*, 1H, (CH)<sup>6</sup>), 8.33 (*s*, 1H, (CH)<sup>6′</sup>). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta \ -63.3$  (CF<sub>3</sub>, BARF), -81.5 (CF<sub>3</sub>), -115.1 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -122.6 (CF<sub>2</sub>), -123.4 (CF<sub>2</sub>), -124.2 (CF<sub>2</sub>), -126.8 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta \ -165.9$  (N<sub>dis</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>(**3**)][*BArF*] (**3c**). Brownish-yellow foam (Yield 65%). IR (KBr): 1744 cm<sup>-1</sup>  $\nu$ (COO). MALDI-TOF: calcd for (C<sub>69</sub>H<sub>36</sub>BF<sub>58</sub>N<sub>3</sub>O<sub>4</sub>Pd) *m/z* 1393.9049 [M<sup>+</sup> – NCCH<sub>3</sub> – BArF + Ag<sup>+</sup>], 1419.9080 [M<sup>+</sup> – CH<sub>3</sub> – BArF + Ag<sup>+</sup>]; found *m/z* 1393.0875 [M<sup>+</sup> – NCCH<sub>3</sub> – BArF + Ag<sup>+</sup>], 1419.1705 [M<sup>+</sup> – CH<sub>3</sub> – BArF + Ag<sup>+</sup>]. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.23 (s, 3H, Pd-CH<sub>3</sub>), 2.20 (m, 4H, (CH<sub>2</sub>)<sup>2°</sup>), 2.30 (m, 4H, (CH<sub>2</sub>)<sup>3°</sup>), 2.52 (s, 3H, Pd-NCCH<sub>3</sub>), 4.56 (t, 4H, (CH<sub>2</sub>)<sup>1°</sup>, <sup>3</sup>J<sub>H-H</sub> = 6 Hz), 7.55 (s, 4H, BArF), 7.71 (s, 8H, BArF), 8.18 (dd, 1H, (CH)<sup>5</sup>, <sup>3</sup>J<sub>H5-H6</sub> = 5.5 Hz, <sup>4</sup>J<sub>H5-H3</sub> = 1 Hz), 8.21 (d, 1H, (CH)<sup>5′</sup>, <sup>3</sup>J<sub>H5'+H6′</sub> = 3.5 Hz), 8.66 (d, 1H, (CH)<sup>6′</sup>, <sup>3</sup>J<sub>H6-H5</sub> = 5.5 Hz), 8.76 (d, 1H, (CH)<sup>6′</sup>, <sup>3</sup>J<sub>H6'+H5′</sub> = 5.5 Hz), 8.82 (s, 2H, (CH)<sub>3/3</sub>). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –63.3 (CF<sub>3</sub>, BArF), -81.6 (CF<sub>3</sub>), -114.9 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -122.6 (CF<sub>2</sub>), -123.4 (CF<sub>2</sub>), -124.1 (CF<sub>2</sub>), -126.8 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –204.3 (NCCH<sub>3</sub>), -149.3 (N<sub>ci</sub>), -111.5 (N<sub>tran</sub>).

[*Pd*(*CH*<sub>3</sub>)(*NCCH*<sub>3</sub>)(*4*)][*BArF*] (*4c*). Pale brown foam (yield 47%). IR (KBr): 1741 cm<sup>-1</sup>  $\nu$ (COO). MALDI-TOF: calcd for (C<sub>69</sub>H<sub>36</sub>BF<sub>58</sub>N<sub>3</sub>O<sub>4</sub>Pd) *m*/*z* 1419.9080 [M<sup>+</sup> - CH<sub>3</sub> - BArF + Ag<sup>+</sup>], 1477.9755 [M<sup>+</sup> - BArF + CF<sub>3</sub>COO<sup>-</sup> + K<sup>+</sup>]; found *m*/*z* 1419.0966 [M<sup>+</sup> - CH<sub>3</sub> - BArF + Ag<sup>+</sup>], 1477.1439 [M<sup>+</sup> - BArF + CF<sub>3</sub>COO<sup>-</sup> + K<sup>+</sup>]. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.27 (s, 3H, Pd-CH<sub>3</sub>), 2.18 (m, 4H, (CH<sub>2</sub>)<sup>2<sup>\*</sup></sup>), 2.30 (m, 4H, (CH<sub>2</sub>)<sup>3<sup>\*</sup></sup>), 2.53 (s, 3H, Pd-NCCH<sub>3</sub>), 4.52 (psq, 4H, (CH<sub>2</sub>)<sup>1<sup>\*</sup></sup>), 7.55 (s, 4H, BArF), 7.71 (s, 8H, BArF), 8.30 (pst) 2H, (CH)<sup>3,3'</sup>), 8.71 (dd, 1H, (CH)<sup>4'</sup>, <sup>3</sup>*J*<sub>H4'H3'</sub> = 8.5 Hz, <sup>4</sup>*J*<sub>H4'H6'</sub> = 1 Hz), 8.75 (dd, 1H, (CH)<sup>4</sup>, <sup>3</sup>*J*<sub>H4-H3</sub> = 8.5 Hz, <sup>4</sup>*J*<sub>H4-H6</sub> = 1 Hz), 9.07 (s, 1H, (CH)<sup>6'</sup>), 9.18 (s, 1H, (CH)<sup>6</sup>). <sup>19</sup>F NMR (376.3 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$ -63.3 (CF<sub>3</sub>, BARF), -81.6 (CF<sub>3</sub>), -114.9 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -122.6 (CF<sub>2</sub>), -123.4 (CF<sub>2</sub>), -124.1 (CF<sub>2</sub>), -126.8 (CF<sub>2</sub>). <sup>15</sup>N NMR (40 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  -204.8 (NCCH<sub>3</sub>), -155.9 (N<sub>cis</sub>), -118.2 (N<sub>trans</sub>).

 $[Pd(N-N)_2][BArF]_2$  (1d-4d). To a suspension of  $[PdCl_2(N-N)]$ (0.072 mmol) in 20 mL of dichloromethane was slowly added a solution of the ligand 1-4 (0.076 mmol) and sodium tetrakis(3,5-(trifluoromethyl)phenyl)borate (128.4 mg, 0.145 mmol) in 10 mL of dichloromethane. The mixture was heated for 1 h at 40 °C. The product was filtered off over Celite, and the solvent was removed under reduced pressure. The product obtained as an oil was triturated in pentane, and a solid was obtained.

[*Pd*(1)<sub>2</sub>][*BArF*]<sub>2</sub> (1*d*). Pale yellow solid (yield 34%). <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ 1.77 (m, 8H; (CH<sub>2</sub>)<sup>-4\*</sup>), 2.04 (m, 8H; (CH<sub>2</sub>)<sup>3\*</sup>), 2.32 (m, 8H, (CH<sub>2</sub>)<sup>2\*</sup>), 3.14 (t, 8H, (CH<sub>2</sub>)<sup>1\*</sup>, *J* = 7.2 Hz); 7.66 (s, 8H<sup>para</sup>, BArF), 7.79 (d, 16H<sup>ortho</sup>, BArF), 8.04 (d, 4H, H<sup>5.5</sup>), 8.82 (s, 4H, H<sup>3.3\*</sup>), 9.18 (d, 4H, H<sup>6.6\*</sup>, *J* = 5.6 Hz); <sup>19</sup>F NMR (376.3 MHz, (CD<sub>3</sub>)<sub>2</sub>CO): δ -63.7 (CF<sub>3</sub>, BArF), -81.2 (CF<sub>3</sub>), -114.2 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -123.2 (CF<sub>2</sub>), 0.123.9 (CF<sub>2</sub>), -126.6 (CF<sub>2</sub>). EIMS: m/z calcd for C<sub>132</sub>H<sub>68</sub>B<sub>2</sub>F<sub>116</sub>N<sub>4</sub>Pd 2314.1 [M - 2BArF]; found 2314.4.

[*Pd*(**2**)<sub>2</sub>][*BArF*]<sub>2</sub> (**2d**). Pale brown solid (yield 53%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 1.63 (4H, m, (CH<sub>2</sub>)<sup>2\*</sup>), 1.71 (4H, m, (CH<sub>2</sub>)<sup>3\*</sup>), 2.13 (4H, m, (CH<sub>2</sub>)<sup>4\*</sup>), 2.40 (6H, s, CH<sub>3</sub>), 2.72 (4H, m, (CH<sub>2</sub>)<sup>1\*</sup>), 7.64 (1H, d, CH<sup>4\*</sup>, *J* = 8.1 Hz), 7.65 (1H, d, CH<sup>4</sup>, *J* = 8.1 Hz), 8.24 (1H, d, CH<sup>3\*</sup>, *J* = 8.1 Hz), 8.28 (1H, d, CH<sup>3</sup>, *J* = 8.1 Hz), 8.51 (2H, s, CH<sup>66\*</sup>), 7.55 (s, 8H<sup>para</sup>, BArF), 7.73 (d, 16H<sup>ortho</sup>, BArF); <sup>19</sup>F NMR (376.3 MHz, DMSO-*d*): δ -126.2 (CF<sub>2</sub>), -123.5 (CF<sub>2</sub>), -122.9 (CF<sub>2</sub>), -122.2 (CF<sub>2</sub>), -113.7 (CF<sub>2</sub>), -80.7 (CF<sub>3</sub>), -62.0 (CF<sub>3</sub>, BArF). MALDI-TOF: *m*/*z* calcd for C<sub>110</sub>H<sub>58</sub>B<sub>2</sub>F<sub>82</sub>N<sub>4</sub>Pd 1397.1521 [M - 2BArF]; found 1397.3773.

[*Pd*(**3**)<sub>2</sub>][*BArF*]<sub>2</sub> (**3***d*). Pale brown solid (yield 92%). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>): ratio I:II = 1:1; δ (ppm) 2.17 (16H, m, (CH<sub>2</sub>)<sup>2',3'</sup>, I and II), 4.51 (4H, t, (CH<sub>2</sub>)<sup>1''</sup>, *J* = 6.4 Hz, II), 4.57 (4H, t, (CH<sub>2</sub>)<sup>1''</sup>, *J* = 6.2 Hz, I), 8.03 (2H, dd, CH<sup>5</sup>, *J* = 5.6 Hz, *J* = 1.6 Hz, II), 7.46 (16H, br, H<sup>para</sup> BArF), 7.66 (32H, br, H<sup>ortho</sup> BArF), 8.20 (2H, dd, CH<sup>5</sup>, *J* = 5.2 Hz, *J* = 1.6 Hz, I), 8.52 (2H, d, CH<sup>6</sup>, *J* = 5.2 Hz, I), 8.77 (2H, d, CH<sup>6</sup>, *J* = 5.2 Hz, II), 8.77 (2H, s, CH<sup>3</sup>, I); <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>): δ (ppm) -127.5 (CF<sub>2</sub>'), -126.7 (CF<sub>2</sub>), -124.6 (CF<sub>2</sub>'), -123.9 (CF<sub>2</sub>), -123.2 (CF<sub>2</sub>), -124.8 (CF<sub>2</sub>), -82.4 (CF<sub>3</sub>'), -81.2 (CF<sub>3</sub>), -63.4 (CF<sub>3</sub>', BArF), -62.9 (CF<sub>3</sub>, BArF). MALDI-TOF: *m*/*z* calcd for C<sub>132</sub>H<sub>60</sub>B<sub>2</sub>F<sub>116</sub>N<sub>4</sub>O<sub>8</sub>Pd 2434.0499 [M - 2BArF]; found 2434.2235. IR: ν(COO) 1742 and 1713 cm<sup>-1</sup>.

[*Pd*(**4**)<sub>2</sub>][*BAF*]<sub>2</sub> (**4d**). Pale brown solid (yield 61%). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>): ratio I:II = 1:1; δ (ppm) 2.08 (16H, m, (CH<sub>2</sub>)<sup>2<sup>\*,3<sup>\*</sup></sup></sup> I and II), 2.25 (16H, m, (CH<sub>2</sub>)<sup>2<sup>\*,3<sup>\*</sup></sup></sup> 4.42 (8H, t, (CH<sub>2</sub>)<sup>1<sup>\*</sup></sup>, *J* = 6.2 Hz, II), 4.52 (8H, t, (CH<sub>2</sub>)<sup>1<sup>\*</sup></sup>, *J* = 9.6 Hz, II) 7.48 (16H, br, H<sup>para</sup> BArF), 7.68 (32H, br, H<sup>ortho</sup> BArF), 7.82 (2H, d, CH<sup>3</sup>, *J* = 8 Hz, II), 7.96 (2H, m, CH<sup>3</sup>, I), 8.52 (4H, d, CH<sup>4</sup>, *J* = 8 Hz, II), 8.63 (4H, d, CH<sup>4</sup>, *J* = 8 Hz, I), 9.15 (4H, s, CH<sup>6</sup>, II) 9.20 (4H, s, CH<sup>6</sup>, I). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>): δ (ppm) -126.7 (CF<sub>2</sub>), -123.9 (CF<sub>2</sub>), -123.3 (CF<sub>2</sub>), -122.5 (CF<sub>2</sub>), -122.3 (CF<sub>2</sub>), -114.9 (CF<sub>2</sub>), -81.3 (CF<sub>3</sub>), -62.9 (CF<sub>3</sub>, BArF). MALDI-TOF: *m/z* calcd for C<sub>132</sub>H<sub>60</sub>B<sub>2</sub>F<sub>116</sub>N<sub>4</sub>O<sub>8</sub>Pd 2434.0499 [M - 2BArF]; found 2434.2408. IR: ν(COO) 1741 cm<sup>-1</sup>.

 $[Pd(N-N)_2][X]_2$  (1d-1d"). To a suspension of  $[PdCl_2(N-N)]$ (0.030 mmol) in 10 mL of dichloromethane was slowly added a solution of the ligand 1 (0.0318 mmol) and the corresponding silver salt (0.0618 mmol) in 5 mL of dichloromethane. The mixture was heated for 1 h at 40 °C. The product was filtered off over Celite, and the solvent was removed under reduced pressure. The product obtained as an oil was triturated in pentane, and pale yellow solids were formed.

 $[Pd(1)_2][PF_6]_2$  (1d'). Pale yellow solid (yield 30%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.70 (m, 8H; (CH<sub>2</sub>)<sup>-4</sup>"), 1.81 (m, 8H; (CH<sub>2</sub>)<sup>3</sup>"), 2.10 (m, 8H, (CH<sub>2</sub>)<sup>2</sup>"), 2.76 (t, 8H, (CH<sub>2</sub>)<sup>1"</sup>, J = 7.2 Hz); 7.16 (d, 4H, H<sup>5.5"</sup>), 8.26 (s, 4H, H<sup>3.3"</sup>), 8.59 (d, 4H, H<sup>6.6"</sup>, J = 4.4 Hz). <sup>19</sup>F NMR

(376.3 MHz, CDCl<sub>3</sub>):  $\delta$  –72.7 (PF<sub>6</sub><sup>-</sup>, J<sub>P-F</sub> = 712 Hz), –81.2 (CF<sub>3</sub>), –114.2 (CF<sub>2</sub>), –122.2 (CF<sub>2</sub>), –122.4 (CF<sub>2</sub>), 123.2 (CF<sub>2</sub>), –124.0 (CF<sub>2</sub>), –126.6 (CF<sub>2</sub>). EIMS: *m*/*z* calcd for C<sub>68</sub>H<sub>44</sub>F<sub>80</sub>N<sub>4</sub>P<sub>2</sub>Pd 2604.0 [M + H]; found 2606.0.

[*Pd*(1)<sub>2</sub>][*BF*<sub>4</sub>]<sub>2</sub> (1*d*"). Pale yellow solid, 7.5 mg (yield 10%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.70 (m, 8H; (CH<sub>2</sub>)<sup>-4'</sup>), 1.83 (m, 8H; (CH<sub>2</sub>)<sup>3'</sup>), 2.14 (m, 8H, (CH<sub>2</sub>)<sup>2'</sup>), 2.79 (t, 8H, (CH<sub>2</sub>)<sup>1'</sup>, *J* = 7.2 Hz); 7.22 (d, 4H, H<sup>5,5'</sup>), 8.22 (s, 4H, H<sup>3,3'</sup>), 8.56 (d, 4H, H<sup>6,6'</sup>, *J* = 4.8 Hz). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>):  $\delta$  -28.1 (CF<sub>3</sub>, BF<sub>4</sub>), -81.2 (CF<sub>3</sub>), -114.2 (CF<sub>2</sub>), -122.2 (CF<sub>2</sub>), -122.4 (CF<sub>2</sub>), -123.2 (CF<sub>2</sub>), -123.9 (CF<sub>2</sub>), -126.6 (CF<sub>2</sub>). EIMS: *m/z* calcd for C<sub>68</sub>H<sub>44</sub>B<sub>2</sub>F<sub>76</sub>N<sub>4</sub>Pd 2488.16 [M]; found *m/z* 2488.02.

[*Pd*(*L3*)<sub>2</sub>][*BArF*]<sub>2</sub> (*L3d*). Pale orange solid (yield 57%). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>): ratio I:II:III = 1.0:0.2:0.3; δ (ppm), integral ratio relative to each isomer: 4.02 (24H, s, CH<sub>3</sub>, I and III), 4.07 (12H, s, CH<sub>3</sub>, II), 7.45 (24H, br, BArF), 7.65 (48H, br, BArF), 8.05 (4H, d, (CH)<sup>5</sup>, *J* = 5.2 Hz, I and II), 8.09 (4H, br, (CH)<sup>5</sup>, III), 8.15 (4H, d, (CH)<sup>5</sup>, *J* = 4.8 Hz, II), 8.66 (4H, s, (CH)<sup>3</sup>, II), 8.72 (4H, s, (CH)<sup>3</sup>, I), 8.79 (4H, d, (CH)<sup>6</sup>, *J* = 5.2 Hz, I), 8.94 (4H, d, (CH)<sup>6</sup>, *J* = 5.2 Hz, III), 9.49 (4H, d, (CH)<sup>6</sup>, *J* = 4.8 Hz, II). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>): δ (ppm) -62.8 (CF<sub>3</sub>, BArF). MALDI-TOF: *m/z* calcd for C<sub>92</sub>H<sub>48</sub>B<sub>2</sub>F<sub>48</sub>N<sub>4</sub>O<sub>8</sub>Pd 650.0635 [M - 2·BArF]; found 650.2218. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1740 cm<sup>-1</sup> ν(COO), (KBr) 1742 cm<sup>-1</sup> ν(COO).

[*Pd*(*L4*)<sub>2</sub>][*BArF*]<sub>2</sub> (*L4d*). Mustard solid (yield 49%). <sup>1</sup>H NMR (400 MHz, 298 K, CDCl<sub>3</sub>): ratio I:II:III = 1.0:0.2:0.2; δ (ppm), integral ratio relative to each isomer: 3.94 (12H, s, CH<sub>3</sub>, I), 3.97 (12H, s, CH<sub>3</sub>, III), 4.02 (12H, s, CH<sub>3</sub>, II), 7.86 (4H, d, (CH)<sup>3</sup>, *J* = 6.4 Hz, III), 7.92 (4H, d, (CH)<sup>3</sup>, *J* = 8.0 Hz, I), 8.13 (4H, d, (CH)<sup>3</sup>, *J* = 8.4 Hz, II), 8.56 (4H, d, (CH)<sup>4</sup>, *J* = 8.0 Hz, I and III), 8.72 (4H, d, (CH)<sup>4</sup>, *J* = 8.4 Hz, II), 9.15 (4H, s, (CH)<sup>6</sup>, III), 9.20 (4H, d, (CH)<sup>6</sup>, I), 9.64 (4H, s, (CH)<sup>6</sup>, II), 7.47 (s, 24H<sup>para</sup> BArF), 7.71 (d, 48H<sup>ortho</sup> BArF). <sup>19</sup>F NMR (376.3 MHz, CDCl<sub>3</sub>): δ (ppm) -62.8 (BArF). MALDI-TOF: *m/z* calcd for C<sub>92</sub>H<sub>48</sub>B<sub>2</sub>F<sub>48</sub>N<sub>4</sub>O<sub>8</sub>Pd 650.0635 [M - 2BArF]; found 650.2895. IR (CH<sub>2</sub>Cl<sub>2</sub>): 1739 cm<sup>-1</sup> ν(COO<sup>-</sup>), (KBr) 1742 cm<sup>-1</sup> ν(COO<sup>-</sup>).

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Synthesis and characterization of [PdCl<sub>2</sub>(N–N)] complexes, NMR experiments, DFT calculations, MALDI-TOF analysis, and 2D-COSY and 2D-NOESY NMR spectra of complexes are available free of charge via the Internet at http://pubs.acs.org.

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