

Copolymerization of ethylene and carbon monoxide by phosphinite-modified palladium catalysts

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Abstract

Novel palladium complexes with bidentate phosphinite and mixed phosphine–phosphinite ligands of the general formula $[(P^*P)Pd(Me)Cl]$ were prepared. After halide abstraction, these complexes are highly active catalysts for the copolymerization of ethylene and CO, yielding high molecular weight polyketones with activities of up to 30000 mol per mol Pd. The preference of *cis*- or *trans*-coordination, depending on the chelate ring size, was investigated. In complexes with up to 11-membered chelates, a *cis*-fixation of the ligands is observed, whereas bigger chelates afforded catalytically inactive *trans*-complexes.

Keywords: Copolymerization; Carbon monoxide; Polyketone; Palladium; Phosphinite; *Trans*-complexes

1. Introduction

In the last decade copolymers of olefins and carbon monoxide, so called polyketones (Fig. 1), have attracted great academic and industrial interest. Recently, Shell announced the technical production of Carilon, a terpolymer of ethylene, propylene and CO [1]. The most active catalyst systems reported consist of a palladium salt and a bidentate ligand. Phosphines, e.g. 1,3-bis(diphenylphosphino)propane (dppp) and its derivatives [2], and nitrogen-donor ligands such as 2,2'-bipyridyl and 1,10-phenanthroline [3] form very active catalysts.

The generally accepted mechanism for the copolymerization of ethylene and carbon monoxide is depicted in Scheme 1. It involves the alternate insertion of the monomers into a palladium–carbon bond. Since this insertion reaction is restricted to the adjacent coordina-

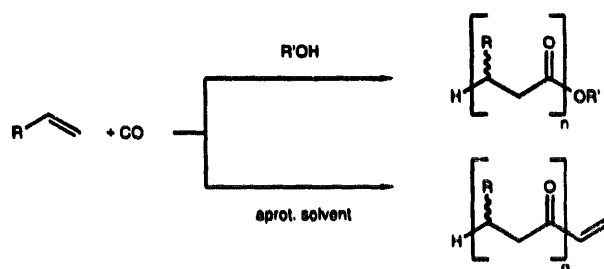
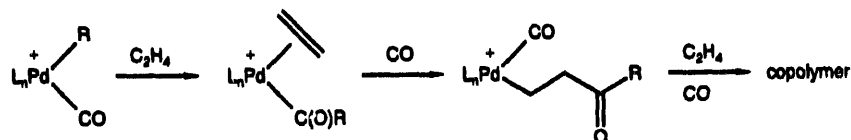


Fig. 1. Olefin/carbon monoxide copolymers.

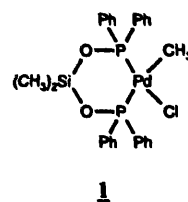
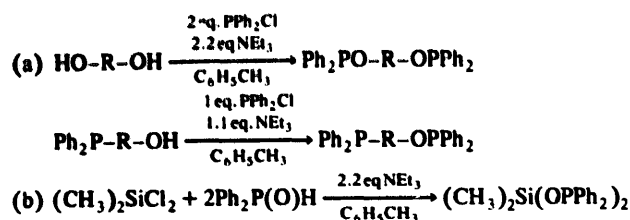
tion sites, chain propagation can only take place when the monomer and the growing polymer chain are *cis* to one another. Therefore, ligands chelating predominantly in a *cis*-configuration are essential for effective catalysts.

So far, bidentate phosphinites have not been disclosed as potential ligands in the polyketone synthesis. Since many divalent alcohols are commercially available, they are easily accessible, yet applications are

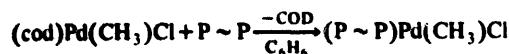
^{*} Corresponding author.



Scheme 1. Mechanism for the copolymerization of ethylene and CO.



Scheme 2. Ligand preparation.



Scheme 3. Complex preparation.

scarce and mainly to be found in asymmetric catalytic reactions [4–6].

2. Results and discussion

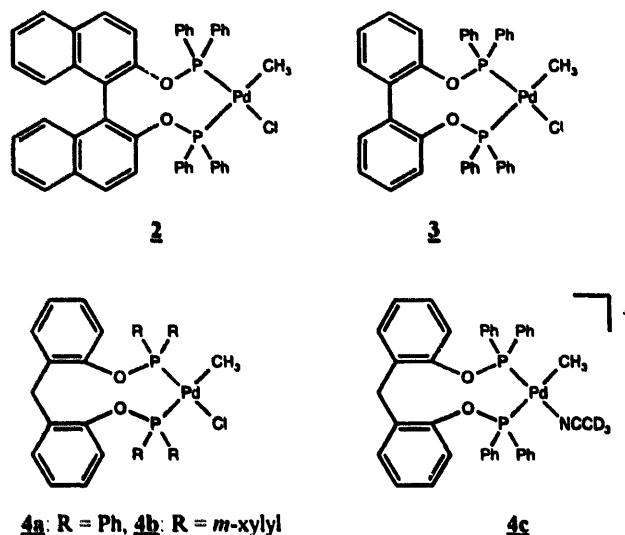
In this paper, we wish to present new phosphinite-modified palladium complexes. The ligands are prepared either from the corresponding alcohols or from the respective phosphinic acid and dimethylsilyldichloride in the presence of NEt_3 as a base (Scheme 2). From these ligands, neutral palladium–methyl complexes were prepared by a ligand substitution reaction (Scheme 3) according to a well-established route [7].

2.1. Bidentate phosphinite ligands

Phosphinites have a stronger *trans*-effect than phosphines. Therefore, phosphinite-modified palladium complexes should exhibit intrinsically higher rates in reactions which involve the migration of a group *trans* to the ligand, as is the case for the presently studied copolymerization reaction. However, the generally lower basicity of phosphinites compared with phosphines in the first place renders them less suitable for this reaction, since reduction of Pd(II) under CO -pressure as one of the possible deactivation pathways should be suppressed more effectively by the stronger coordinating phosphines. Thus, the preparation of sufficiently stable phosphinite complexes could be a promising compromise.

Palladium complexes with derivatives of dppp , which forms six-membered chelate-rings, have proven to be the most active polyketone-catalysts. Therefore **1** was prepared as a phosphinite analogue to the previously reported complex $[(\text{dppp})\text{Pd}(\text{Me})\text{Cl}]$ [7] with respect to the ring size.

Since phosphinites are moisture-sensitive and prone to the Arbuzov-rearrangement, our further work concentrated on the more stable phenol-derived phosphinites.

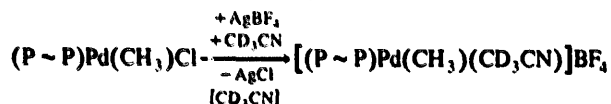
Fig. 2. *Cis*-complexes 1–4b.

Ligands derived from divalent aromatic alcohols yielded complexes **2–4b** with increasing flexibility in the ligand backbone (Fig. 2).

1–4b form *cis*-chelates, which can be concluded from their ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR data. The exclusive *cis*-coordination found for **4a** was maintained after a halide abstraction reaction with AgBF_4 in deuterated acetonitrile (Scheme 4), yielding the cationic species **4c**.

In **4b** electron-donating methyl groups are introduced in the ligand by *meta*-xylyl-substitution on the two phosphorus donor atoms. Thus, their basicity is enhanced and a more phosphine-like coordination strength can be expected.

On replacing the methylene group of the ligand backbone in **4a** by an ethylene group, an 11-membered ring is formed upon metal chelation. From the NMR data it can be deduced that **5** is on the verge of preferential *cis*- and *trans*-geometry. The product mixture obtained consists of *cis*-coordinated **5a** and at least two *trans*-coordinated species, of which **5b** is probably the major species. Upon redissolving and stirring for 24 h, no change in the *cis/trans* ratio of 1:1.5 is ob-



Scheme 4. In-situ formation of cationic complexes.

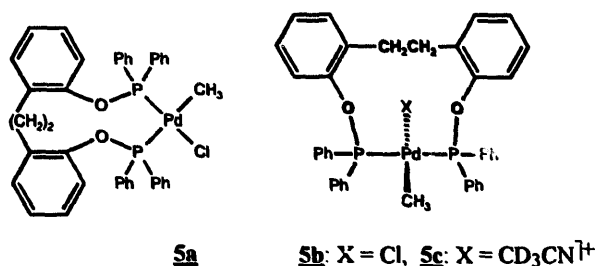


Fig. 3. Neutral and cationic species of 5.

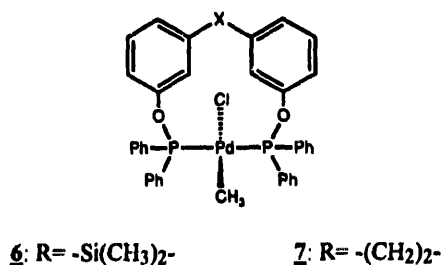
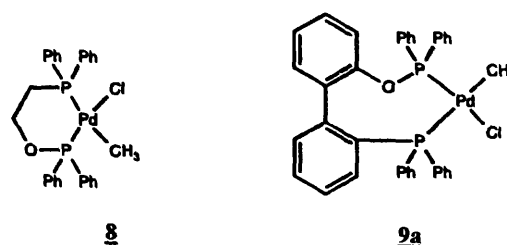
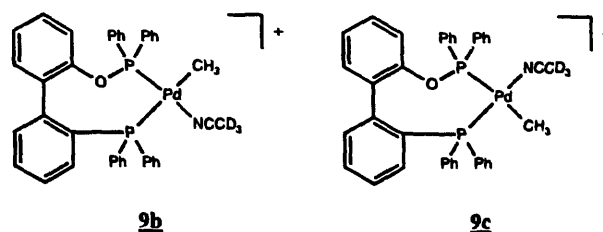
served. However, after the above-mentioned halide abstraction reaction creating a free coordination site, the complex immediately isomerizes to give exclusively the *trans*-coordinated **5c** (Fig. 3).

Enlarging the chelate by one more atom to a 12-membered ring by placing the bridge in the *meta*-position to the phosphinite function results in the exclusive formation of *trans*-complex **6**. In the 13-membered chelate of **7** the ligand is also *trans*-coordinating (Fig. 4).

2.2. Mixed phosphine–phosphinite ligands

Complexes with mixed phosphine–phosphinite ligands are well suited for monitoring insertion reactions of olefins and carbon monoxide into metal–carbon bonds, which are important steps in the copolymerization reaction of ethylene and carbon monoxide. By stoichiometric reactions of such phosphine–phosphinite-coordinated palladium complexes, the migration of a hydrocarbonyl group to the coordinated CO or olefin could be shown to be the preferred mechanism [8].

Preparation of **8** and **9a** afforded two species in each case. Fig. 5 depicts the major isomers, which are the thermodynamically favoured complexes with the methyl group *trans* to the phosphine donor. Smaller amounts of the species with the phosphine function and methyl group *cis* to one another were also obtained with *trans*/*cis* ratios of 4.5:1 (**8**) and 6:1 (**9a**). After halide abstraction as described for **5**, partial isomerization took place with **9a** to give a mixture of **9b** and **9c** with a ratio of 9.5:1 (Fig. 6g). This observation correlates with data reported for the cationic form of **8** [9].

Fig. 4. *Trans*-complexes **6** and **7**.Fig. 5. Mixed phosphine–phosphinite complexes **8** and **9** (major isomers).Fig. 6. Cationic complexes **9a** and **9b.2e**

2.3. Copolymerization of ethylene and carbon monoxide

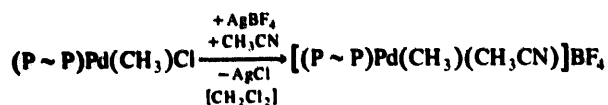
The neutral complexes described above were inactive towards ethylene–CO mixtures. After a halide abstraction reaction with AgBF₄ in the presence of acetonitrile (Scheme 5), they proved to be efficient polymerization catalysts. The catalytic reaction was carried out in dichloromethane as the solvent under a constant pressure of 60 bar of a 1:1 ethylene/CO mixture. A reaction temperature of 62°C was found to be optimal. The results of the copolymerization reactions are shown in Table 1.

Complex **1** exhibits an activity that is lower by orders of magnitude compared with values reported for dppp-modified systems [10]. The grey colour of the polymeric product obtained with **1**, which is caused by precipitated Pd(0), indicates that, under reaction conditions, rapid degradation of the catalyst takes place.

Table 1
Copolymerization of ethylene and carbon monoxide

| Precursor complex | TON [mol per mol Pd] |
|-------------------|----------------------|
| 1 | 2100 |
| 2 | 800 |
| 3 | 2700 |
| 4a | 20000 |
| 4b | 26000 |
| 5a/b | 10100 |
| 6 | 0 |
| 7 | 0 |
| 8 | 6500 |
| 9a | 11000 |

62°C, 5 h reaction time, 60 bar (ethylene: C 1:1).



Scheme 5. Preparation of catalyst solution.

The same seems to be true for complexes **2** and **3**, which also yield coloured products. In contrast, a white fluffy polymer is obtained with **4a**. Comparing the results obtained with **2**, **3** and **4a**, the ligand flexibility seems to be essential for the formation of a stable chelate, which leads to dramatic increases of activity (800 mol per mol Pd for **2**, 20000 mol per mol Pd for **4a**). Interestingly, the 10-membered ring system in **4a** shows the highest activity. For bidentate phosphines, the activity rapidly decreases with increasing ring size (dppp > dppb > dppf) [10]. For an explanation, the formation of oligomeric and *trans*-coordinated species promoted by ligands with longer backbones was discussed [7]. Thus, the rather unusual 10-membered chelate of **4a** meets two features required for high catalytic activities: exclusive *cis*-coordination and a rather stable chelate.

The generally lower basicity of phosphinites compared with phosphines is partly compensated for in **4b** by the introduction of electron-donating methyl groups. Indeed, the enhanced coordination strength leads to activities for **4b** that are increased by 30% compared with **4a**.

The activity observed for **5** is surprising since the migratory insertion mechanism of the copolymerization reaction requires a *cis*-geometry for the square-planar palladium complex. From the result of the catalytic reaction one can guess that under reaction conditions at least small amounts of a highly active *cis*-coordinated species are formed. Once a *cis*-complex is formed and the polymerization reaction has started, the growing polymer chain stabilizes the *cis*-configuration by chela-

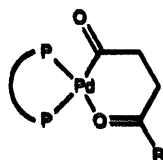


Fig. 7. Chelation by growing polymer chain.

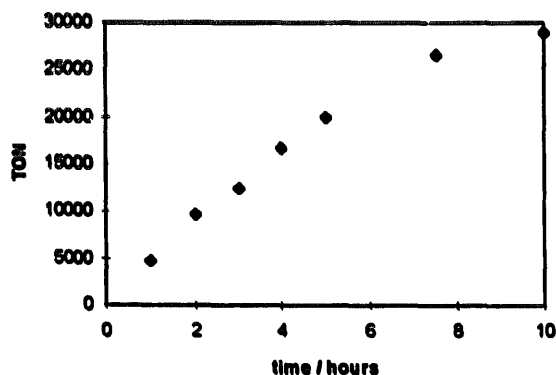
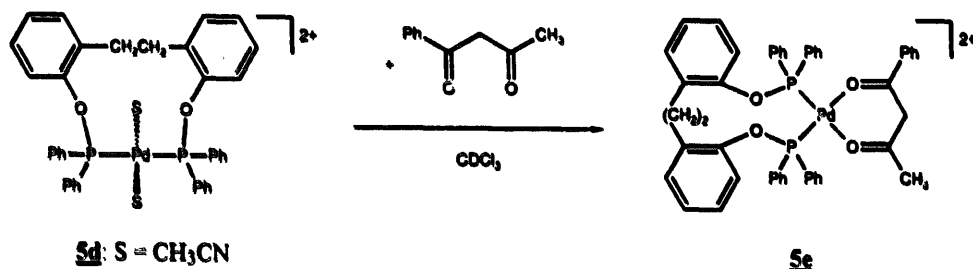
tion (Fig. 7). To confirm that this is possible for **5**, the following experiment was carried out. A solution of $[(\text{P} \wedge \text{P})\text{Pd}(\text{CH}_3\text{CN})_4]^{2+}$ (**5d**), with $\text{P} \wedge \text{P} = 1,2\text{-bis}(o\text{-diphenylphosphinoxyphenyl})\text{ethane}$, was prepared in situ from $[\text{Pd}(\text{CH}_3\text{CN})_4](\text{BF}_4)_2$ and one equivalent of the $\text{P} \wedge \text{P}$ -ligand in CDCl_3 . The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows one singlet for the *trans*-coordinated complex. One equivalent of benzoylacetone as a potentially chelating agent was added, and immediately one fourth of the precursor complex was transformed into a *cis*-coordinated bischelate (**5e**), which exhibits two doublets in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (Fig. 8).

The inactivity of the *trans*-coordinated complexes **6** and **7** indicates that in contrast to **5**, also under reaction conditions, exclusive *trans*-coordination is maintained.

In the mixed-donor complexes **8** and **9a**, ligands exhibit a coordination behaviour between phosphinites and phosphines. Comparing **3** and **9a**, where one phosphinite function is replaced by a stronger coordinating phosphine donor, the complex is stabilized and consequently the activity is significantly increased. A similar explanation can be given for **8**, which is three times more active than the equally 6-membered ring system **1**.

2.4. Catalyst stability

Insufficient catalyst stability towards CO-pressure, resulting in Pd(II)-reduction, and incorporation of the catalyst in the polymer are two common pathways for the deactivation of polyketone catalysts. For **4a**, the deactivation was monitored by running experiments with

Fig. 9. Catalyst stability of **4a**.Fig. 8. *Cis* / *trans*-isomerization of **5d**.

different reaction times under otherwise identical reaction conditions (Fig. 9).

No induction period was observed, and the activity was nearly constant throughout the first 5 h. After 10 h and a turnover number of approximately 30000 mol per mol Pd, the catalyst was still active. This behaviour is comparable with results achieved with phosphine-based systems.

2.5. Polymer properties

A sample of the white, fluffy polymer prepared with **4a** melted at 260°C. Intrinsic viscosity was measured at 60°C in *m*-cresol, yielding a limiting viscosity number of 3.75 dl g⁻¹. GPC analysis was carried out in 1,1,1,3,3,3-hexafluoroisopropanol at room temperature. The polymer had a molecular weight of $M_n = 145000$ and $M_w = 396000$ respectively.

3. Experimental

All reactions were carried out under argon using standard Schlenk techniques. Solvents were dried and distilled under argon before use. NMR spectra were recorded on Bruker AC 300 or Varian Unity 500 spectrometers. Chemical shifts are reported in ppm relative to TMS or external 85% H₃PO₄, positive shifts representing deshielding. Starting materials were obtained commercially or prepared by standard procedures.

3.1. Ligand preparation

All ligands except for bis(diphenylphosphineoxy)dimethylsilane, which was prepared according to a published method for an analogous compound [11], were synthesized following the same procedure. As an example, the preparation of bis(2,2'-diphenylphosphineoxyphenyl)methane is described.

Bis(2,2'-dihydroxyphenyl)methane (2.31 g, 11.5 mmol) was dried by dissolving several times in 10 ml of toluene followed by evaporation under high vacuum. The alcohol was dissolved in 40 ml of toluene, NEt₃ (2.56 g, 25.3 mmol) was added and the solution was cooled to -20°C. Diphenylphosphinechloride (5.07 g, 23.0 mmol) dissolved in 10 ml of toluene was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirred overnight. Precipitated [HNEt₃]Cl was filtered off and the solution was evaporated, yielding a slightly yellow-coloured oil (6.41 g, 98%). Small amounts of impurities, which were observed for other ligands, could be removed by washing with acetonitrile.

3.2. Preparation of palladium complexes

Complexes **1–4b**, **8** and **9a** were prepared according to the following procedure.

Equimolar amounts (ca. 1 mmol) of ligand and [(cod)Pd(Me)Cl] were dissolved separately in 3 ml of benzene. Combination of the solutions under stirring afforded practically quantitative precipitation of the product. Filtering, washing with benzene/pentane mixture and drying yielded the analytically pure complexes as white powders.

Since the *trans*-complexes **5b**, **6** and **7** remain in solution when the starting solutions are combined, quantitative precipitation was effected by adding 20 ml of pentane. After filtering, washing with pentane and drying, the complexes were obtained as yellow solids.

3.3. Preparation of catalyst solutions

A solution of the precursor complexes (0.03 mmol in 20 ml CH₂Cl₂) was added to 1.02 equivalents AgBF₄ dissolved in 0.5 ml of acetonitrile. The solution was weighed, and approximately half of the solution was removed via a syringe and charged into the prepared autoclave. The remaining solution was weighed, and thus the amount of catalyst solution used was calculated.

3.4. Copolymerization of ethylene and CO

The polymerization experiments were carried out in a 300 ml stainless-steel autoclave equipped with a mechanical stirrer. The autoclave was evaporated and filled with argon. After charging with the catalyst solution, 90 ml of CH₂Cl₂ were added via a syringe. The autoclave was immersed into a heated oil bath and allowed to come to reaction temperature. It was purged and pressurized with 60 bar of a prepared ethylene/CO mixture (1:1), which was fed in throughout the reaction time. The autoclave was cooled and vented. After filtering off, the polymer was vacuum-dried and weighed.

3.5. Analytical data

1. ¹H NMR (CDCl₃): δ 7.95–7.10 (m, 20H, ar), 0.56 (dd, $J_{\text{PH}} = 8.1$ Hz, 5.1 Hz, 3H, Pd-CH₃), 0.14 (s, 6H, Si-CH₃); ³¹P{¹H} NMR (CDCl₃): δ 114.5 (d, $J_{\text{PP}} = 34.2$ Hz), 99.8 (d, $J_{\text{PP}} = 34.2$ Hz).

2. ¹H NMR (CDCl₃): δ 8.05–6.70 (m, 32H, ar), 0.77 (dd, $J_{\text{PH}} = 8$ Hz, 5.6 Hz, 3H, Pd-CH₃), ³¹P{¹H} NMR (CDCl₃): δ 131.7 (d, $J_{\text{PP}} = 31.5$ Hz), 125.8 (d, $J_{\text{PP}} = 31.5$ Hz).

3. ¹H NMR (CDCl₃): δ 8.20 (m, 28H, ar), 0.58 (dd, $J_{\text{PH}} = 7.8$ Hz, 5.1 Hz, 3H, Pd-CH₃), ³¹P{¹H} NMR (CDCl₃): δ 128.0 (d, $J_{\text{PP}} = 34$ Hz), 115.0 (d, $J_{\text{PP}} = 34$ Hz).

4a. ^1H NMR (CDCl_3): δ 7.95–6.40 (m, 28H, ar), 4.03 (s, 2H, CH_2), 0.80 (dd, $J_{\text{PH}} = 8.9$ Hz, 4.8 Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 127.2 (d, $J_{\text{PP}} = 45$ Hz), 119.3 (d, $J_{\text{PP}} = 45$ Hz).

4b. ^1H NMR (CDCl_3): δ 7.25–6.45 (m, 20H, ar), 4.09 (s, 2H, CH_2), 2.14 (s, 12H, ar- CH_3), 2.13 (s, 12H, ar- CH_3), 0.74 (dd, $J_{\text{PH}} = 8.8$ Hz, 4.6 Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 126.4 (d, $J_{\text{PP}} = 46$ Hz), 119.7 (d, $J_{\text{PP}} = 46$ Hz).

4c. ^1H NMR (CD_3CN): δ 7.55–6.50 (m, 28H, ar), 4.09 (s, 2H, CH_2), 0.49 (dd, $J_{\text{PH}} = 7.7$ Hz, 3.7 Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 125.7 (d, $J_{\text{PP}} = 35.8$ Hz), 117.1 (d, $J_{\text{PP}} = 35.8$ Hz).

5a/b. ^1H NMR (CDCl_3): δ 7.85–6.25 (m, 28H, ar), 3.10–2.55 (m, 4H, CH_2CH_2), 0.83 (dd, $J_{\text{PH}} = 8.4$ Hz, 5.3 Hz, 3H, Pd- CH_3), -0.28 (t, $J_{\text{PH}} = 5.1$ Hz, 3H, Pd- CH_3), -0.65 (t, $J_{\text{PH}} = 5.4$ Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 124.5 (d, $J_{\text{PP}} = 35.1$ Hz), 116.9, 116.7, 112.2 (d, $J_{\text{PP}} = 35.1$ Hz).

5c. ^1H NMR (CD_3CN): δ 7.80–7.05 (m, 28H, ar), 2.67 (s, 4H, CH_2CH_2), -0.87 (t, $J_{\text{PH}} = 6.1$ Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 117.2.

6. ^1H NMR (CDCl_3): δ 7.95–6.95 (m, 28H, ar), 0.52 (s, 3H Si- CH_3), 0.46 (s, 3H, Si- CH_3), 0.13 (t, $J_{\text{PH}} = 5.9$ Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 116.1.

7. ^1H NMR (CDCl_3): δ 7.95–6.65 (m, 28H, ar), 3.01 (m, 4H, CH_2CH_2), -0.05 (t, $J_{\text{PH}} = 5.4$ Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 113.4.

8. ^1H NMR (CDCl_3): δ 7.80–7.20 (m, 20H, ar), 3.90 (m, 2H, CCH_2), 2.40 (m, 2H, PCH_2), 0.64 (dd, $J_{\text{PH}} = 7.4$ Hz, 4.5 Hz, dd, $J_{\text{PH}} = 8.6$ Hz, 3.8 Hz, 3H, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 129.7 (d, $J_{\text{PP}} = 43$ Hz), 108.7 (d, $J_{\text{PP}} = 52$ Hz), 27.2 (d, $J_{\text{PP}} = 52$ Hz), 5.5 (d, $J_{\text{PP}} = 43$ Hz).

9a. ^1H NMR (CD_2Cl_2): δ 7.80–6.40 (m, 28H, ar), 0.94 (dd, $J_{\text{PH}} = 7.6$ Hz, 4.3 Hz, Pd- CH_3), 0.46 (dd,

$J_{\text{PH}} = 8.2$ Hz, 4.0 Hz, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 134.0 (d, $J_{\text{PP}} = 34.4$ Hz), 127.2 (d, $J_{\text{PP}} = 37.8$ Hz), 35.6 (d, $J_{\text{PP}} = 37.8$ Hz), 13.0 (d, $J_{\text{PP}} = 34.4$ Hz).

9b/c. ^1H NMR (CD_3CN): δ 7.70–6.20 (m, 28H, ar), 0.85 (dd, $J_{\text{PH}} = 7.1$ Hz, 3.0 Hz, Pd- CH_3), 0.50 (dd, $J_{\text{PH}} = 7.6$ Hz, 2.6 Hz, Pd- CH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): δ 135.4 (d, $J_{\text{PP}} = 35.6$ Hz), 126.1 (d, $J_{\text{PP}} = 40.7$ Hz), 38.5 (d, $J_{\text{PP}} = 40.7$ Hz), 16.4 (d, $J_{\text{PP}} = 35.6$ Hz).

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