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# Synthesis of a Calix[6]arene-Derived Diphosphite, Its Palladium and Platinum Complexes, and the Remarkable Activity of (*syn*-Calix[6]arene diphosphite)Pd($CH_3$)($CH_3CN$)OTf in Carbon Monoxide and Ethene Copolymerization

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Two noninterconvertable conformations of calix[6]arene diphosphite (**1**) were synthesized starting from calix[6]arene and $PCl_3$. The conformations differ in the orientation of the phosphite moieties (syn and anti). In the syn conformation the phosphorus lone pairs of the phosphite have an exo orientation with respect to the cavity of the calixarene backbone. The fluxional behavior shown by *syn*-**1** in solution is described as a up−up−out ↔ out−up−up interconversion of the calix[6]arene backbone. The syn diphosphite behaves as an exclusively cis coordinating ligand toward palladium(II) and platinum(II). Two syn diphosphite ligands coordinate to palladium(0), and the geometry of the complex is probably a distorted tetrahedron. The X-ray structure of (*syn*-**1**)$PdCl_2$ demonstrated the cis coordination mode and the $C_2$ symmetry of the ligand. The cationic complex (*syn*-**1**)Pd($CH_3$)($CH_3CN$)OTf is the first reported complex based on a diphosphite ligand that shows catalytic activity in the copolymerization of carbon monoxide and ethene. Turnover frequencies were 850−5300 mol mol$^{-1}$ h$^{-1}$ (25 °C, 20 bar carbon monoxide/ethene). The $\langle M_n \rangle$ of all tested polymers was approximately 34 000 with a PDI of 2.3. From $^{13}$C NMR spectral data we conclude that hydrolysis of the acyl intermediate to a carboxylic acid is the most important chain-transfer mechanism. To a lesser extent (15% of all chain ends) $\beta$-H elimination of the alkyl intermediate gave rise to vinyl end groups. All elementary steps in chain propagation have been monitored by IR spectroscopy and low-temperature NMR experiments.

## Introduction

The palladium-catalyzed copolymerization of carbon monoxide and ethene using highly active palladium catalysts has attracted a lot of industrial and academic interest.[1−4] High molecular weight polymers with perfect alternation of the carbon monoxide and ethene monomers are produced.[5] In the last two decades many groups have devoted their research to the elucidation of the mechanism that leads to these perfectly alternating insertions.[6−14] The proposed mechanism involves the migratory insertion of carbon monoxide into a palladium−alkyl bond, which is kinetically favored over ethene insertion due to the preferential coordination of carbon monoxide, despite the thermodynamic more favorable homopolymerization of ethene (see Scheme 1). The subsequent step involves ethene insertion into the palladium−acyl bond which is thermodynamically favored over double insertion of carbon monoxide.[15,16]

Symmetric cis-coordinating ligands lead to the highest rates. The cis orientation of the growing polymer chain

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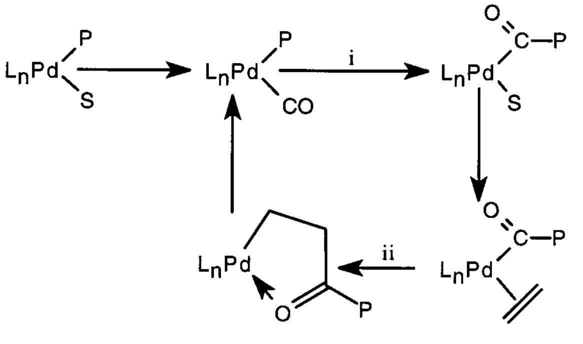
**Scheme 1. Elementary Steps in Palladium-Catalyzed Carbon Monoxide and Ethene Copolymerization**



P = growing polymer chain
i) CO insertion
ii) ethene insertion

and incoming monomer is needed to facilitate insertion.[15−17] Symmetric ligands prevent the necessity of extensive reorganizations during the catalytic cycle.[17] A flexible backbone and a relatively large bite angle (90−94°) enhance the reaction rate by facilitating the pseudorotations that may be involved in carbonylation of the palladium−carbon bond. Moreover, theoretical calculations have shown that large bite angles promote migratory insertion reactions on steric and electronic grounds.[18] Furthermore $\beta$-H elimination seems to be retarded by large bite angles.[6,7] Diphosphines, bipyridines, and diimines, as well as phosphine−phosphite, diphosphinites, P∧O, P∧S, N∧O, and P∧N∧O ligand systems have been used with various degrees of success (see Figure 1).[11,19−25]

Recently Nozaki et al. have used a bisnaphthol-based diphosphite in carbon monoxide/propene copolymerization, but no polymer was obtained.[11] Two reasons for the limited application of (di)phosphites up to now are as follows: (1) phosphites promote side reactions to palladium(0) complexes and thus decrease the concentration of active catalyst in the reaction mixture, (2) phosphites are sensitive to alcoholysis, and the use of methanol, the solvent in industrial carbon monoxide/ethene copolymerization, leads to decomposition. These problems can be circumvented by using rigid, symmetric diphosphites with small bite angles ($\phi$ < 109°) which preferably coordinate in a cis-fashion. To avoid the decomposition of ligands by alcoholysis, the catalysis can be performed in dichloromethane or other nonprotic solvents.[11,19,21,23]

Calixarenes are known for their rigid, well-defined three-dimensional structure, and their ability to act as selective complexating agents for many alkaline (earth) metals.[26] In the past decade the interest in the complexating properties of calixarenes has shifted toward transition metal complexation. This shift has resulted in the synthesis of an appreciable amount of phosphorus-containing calix[4]- and calix[6]arenes. These studies mainly deal with phosphines, phosphinites, and phosphites and their complexes, but hardly any catalysis has been reported so far.[27] The only phosphorus-containing calixarenes that have been used in catalysis are calix[4]arene diphosphites and diphosphines that were applied in the hydroformylation reaction (see Figure 2).[28,29]

Here we report on the results of our investigation into the complexating properties of the calix[6]arene diphosphite ligand,[30] the successful application of its complexes in the copolymerization of carbon monoxide and ethene including a study of the elementary insertion steps of this process.

## Results and Discussion

**Synthesis.** Calix[6]arene diphosphite (**1**) was synthesized in 20−40% yield from *p*-*tert*-butylcalix[6]arene and $PCl_3$ in the presence of a base such as NaH, $NEt_3$, or pyridine. A complete conversion to products was observed in the $^{31}P$ NMR spectrum, but an appreciable amount of product was lost during purification. Using a combination of NaH and DMF resulted in the highest yield of purified compound, but DMF is hard to separate from the products. Amine bases on the other hand have the disadvantage of forming ammonium salts that can be complexed in the calix[6]arene cavity.[31−33] The reported method of calix[4]arene phosphite synthesis using HMPT was not successful in the synthesis of **1**.[34−37]

**Structural Analysis.** In the $^{31}P$ NMR spectrum of the reaction mixture, obtained after the synthesis of **1**, two singlets are visible in the phosphite region at $\delta$ = 102.9 and 103.4 ppm with relative intensities of 10:1. Aleksiuk et al. found similar results in the synthesis of calix[6]arene diphosphate.[38,39] They proposed two con-

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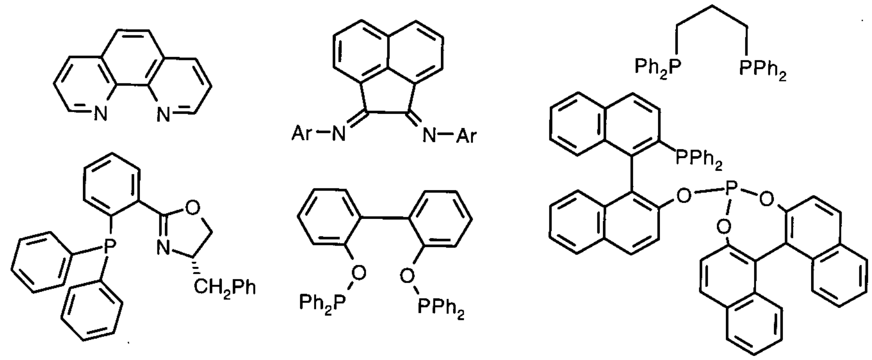

**Figure 1.** Several examples of ligands used in carbon monoxide and ethene copolymerization.

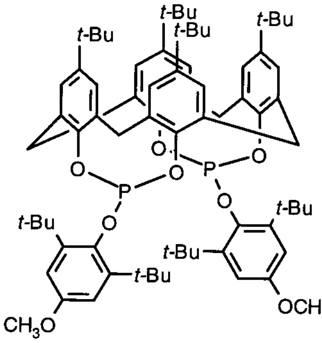

**Figure 2.** Calix[4]arene-based diphosphite.[28,29]

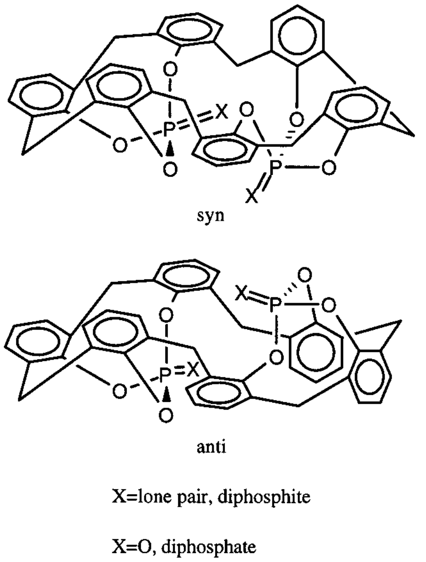

**Figure 3.** Schematic drawing of the syn and anti conformations of **1** and calix[6]arene diphosphate.

formations for the calix[6]arene backbone: syn and anti as depicted in Figure 3.

The $^1$H NMR spectrum of the reaction mixture of **1** showed a major compound that gave rise to two AB patterns (ratio 1:2) in the methylene region, whereas the minor compound gave one singlet and one AB pattern (ratio 1:2). The *tert*-butyl groups of both compounds are visible in the $^1$H NMR spectrum as two peaks with a ratio of 1:2. These data are in agreement with an overall $C_{2v}$ symmetry for the major compound (syn conformation) and $C_{2h}$ for the minor compound (anti conformation) depicted in Figure 4.

Regardless of the conformation of the backbone, the phosphorus lone pair in the phosphite can adopt an endo or exo orientation with respect to the cavity of the arene rings in the calixarene. In the X-ray study of the calix[6]arene diphosphate it was found that the orientation of the P=O moiety was exclusively exo.[38] We have convincing proof for the exo orientation of the phosphorus lone pairs in the diphosphite from an X-ray structure of (*syn*-**1**)PdCl$_2$ (vide infra).

In the $^1$H NMR spectrum of the syn conformation two doublets of the methylene groups are somewhat broadened, indicating fluxional behavior. When a sample of *syn*-**1** in toluene-$d_8$ was cooled stepwise to 230 K, the *tert*-butyl peak at $\delta$ = 1.07 ppm, the two methylene doublets at $\delta$ = 3.23 and $\delta$ = 4.45, and the Ar−H signals at $\delta$ = 6.4−6.8 ppm broadened significantly and split into two signals (in each case) of equal intensities. This pattern (shown in Figure 5 for the 270−245 K region for the methylene groups) can be explained by an overall $C_2$ symmetry with the $C_2$ axis perpendicular to the main plane of the calix[6]arene backbone. The same fluxional behavior was observed for the calix[6]arene diphosphate.[39] It is noted that $C_2$ symmetry implicates that *syn*-**1** is chiral. The "observed" planes of symmetry in the molecule in solution at ambient temperatures caused by the up−up−out ↔ out−up−up interconversion show that atropisomerization occurs under these conditions (see Figure 6). A $\Delta G^{\ddagger}$ of 53−54 kJ mol$^{-1}$ (270 K) was calculated for the fluxional process in the free diphosphite. This is similar to the value found for the *syn*-calix[6]arene diphosphate (58 kJ mol$^{-1}$, 303 K[38]).

**Complexation Studies.** Molecular modeling (MM2) showed a natural bite angle for *syn*-**1** of almost 90° for a metal complex with the calixarene backbone attached to the phosphite groups in a so-called up−up−out conformation.[40] Previous studies on calixarene phosphates showed that this is a favorable conformation. Therefore *syn*-**1** seemed an ideal cis-coordinating ligand, and we decided to synthesize a series of complexes with palladium and platinum.

The $^{31}$P NMR spectrum of (*syn*-**1**)PtCl$_2$ (**2**) shows one signal at $\delta$ = 49.7 ppm (satellites $^{195}$Pt; $^1J_{\mathrm{PtP}}$ = 5800 Hz); the very large coupling constant is indicative of a cis complex.[41] We conclude that the complex possesses a mirror plane situated between the two phosphorus atoms and bisecting the ligand. The $^1$H NMR spectrum shows two *tert*-butyl signals in a ratio of 1:2 and two AB patterns in the same ratio resulting from the methylene bridges. This suggests that a second mirror

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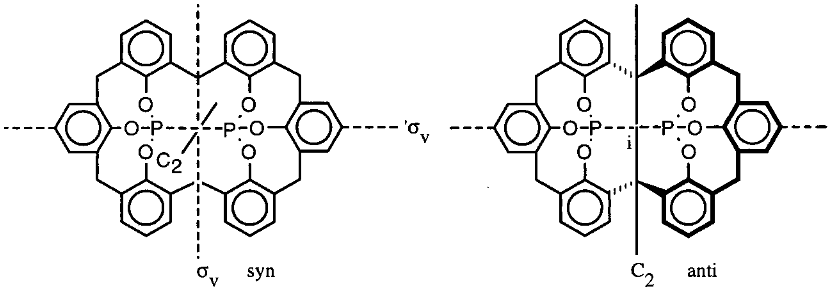

**Figure 4.** Symmetry elements in *syn*- and *anti*-**1**.

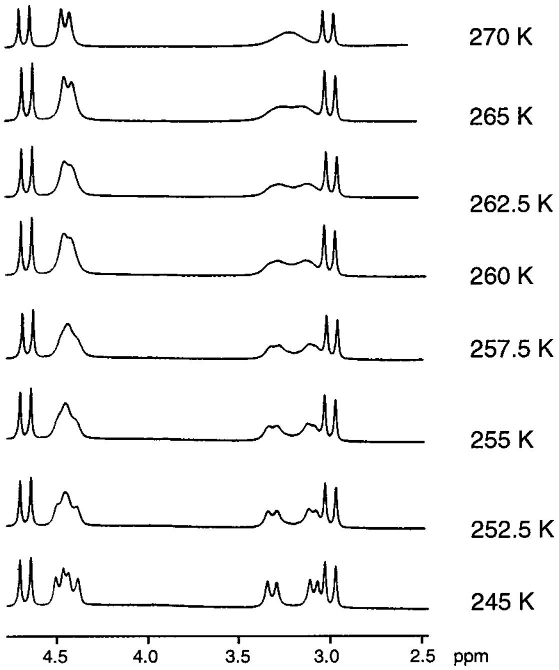

**Figure 5.** Variable-temperature $^1H$ NMR spectra of the methylene protons in *syn*-**1**.

plane is present, perpendicular to the first one and containing the two phosphorus atoms. The observed symmetry is a result of fluxional behavior of the ligand, leading to average signals. NMR data do not exclude a trans complex, but modeling shows that a bite angle of 180° is highly unlikely.

The $^{31}P$ and $^1H$ NMR data of (*syn*-**1**)$PdCl_2$ (**3**) are very similar to those of **2**. The $^{31}P$ NMR spectrum shows one singlet at 73.3 ppm, and the $^1H$ NMR data suggest two mutually perpendicular mirror planes in the ligand. Complex **3** afforded crystals suitable for X-ray analysis. An ORTEP drawing of the crystal structure of **3** is presented in Figure 7. The picture clearly shows the conformation of the calixarene backbone in both phosphite moieties to be up−up−out. Bond lengths around the phosphorus atom are within the usual range for coordinated phosphites, and the bite angle of the ligand is 94° (see Table 1). The actual structure is in good agreement with the molecular mechanics result. The ligand has noncrystallographic $C_2$ symmetry in the complex, and so it is chiral.

The $^{31}P$ NMR spectra of (*syn*-**1**)$Pd(CH_3)Cl$ (**4**) and (*syn*-**1**)$Pt(CH_3)Cl$ (**5**) show an AB pattern ($^2J_{PP}$ cis = 120 Hz for **4** and 52.3 Hz for **5**) as a consequence of the chemical inequivalency of the phosphorus atoms. The signal at low field is split further by a trans phosphorus to hydrogen coupling with the protons of the methyl group attached to the metal. In **5** additional $^{195}Pt$ satellites are seen on both phosphorus signals ($^1J_{PtP}$ = 7300 Hz, P trans to Cl; $^1J_{PtP}$ = 2700 Hz, P trans to $CH_3$). These data prove the cis geometry of the complex. The $^1H$ NMR data are in full agreement with these results, showing three AB patterns in the methylene region with intensities 1:1:1 for both complexes corresponding with the equivalent methylene bridges a−a′, b−b′, and c−c′ in Figure 8. Two-dimensional $^1H$ NMR data of **4** clearly showed that the pseudo triplet that appears at $\delta = 3.56$ ppm in the $^1H$ NMR spectrum consists of two superimposed doublets that are coupled with two other doublets at 4.52 and 4.71 ppm. The same phenomenon was observed in the $^1H$ NMR spectrum of **5**. Since **5** disproportionated to give **2** and (*syn*-**1**)$Pt(CH_3)_2$, we have not been able to obtain **5** in pure form. Therefore the assignment of the structure is based only on $^{31}P$ and $^1H$ NMR data.

When 2 equiv of *syn*-**1** were allowed to react with $Pd(dba)_2$, (*syn*-**1**)$_2$Pd(0) (**6**) was formed. At room temperature (chloroform-$d_1$ or toluene-$d_8$ solution) this compound shows one singlet in the $^{31}P$ NMR spectrum and a pattern in the $^1H$ NMR spectrum that is similar to the spectrum of the free ligand at low temperature (slow exchange), indicating that both ligands in the complex adopt a $C_2$ symmetry. Four conformers of **6** are compatible with these observations; rac and meso square planar and rac and meso tetrahedral, which are schematically depicted in Figure 9. As the temperature of a solution of **6** was raised to 363 K in toluene-$d_8$, the $^{31}P$ NMR spectrum did not change, but the $^1H$ NMR spectrum showed broadening of two *tert*-butyl signals, four methylene doublets, and some peaks in the aromatic region. This shows that the up−up−out ↔ out−up−up interconversion is taking place in the ligands. An additional possibility is the rotation of one ligand around its $C_2$ symmetry axis. This motion would convert a square-planar complex into a tetrahedral one. Steric factors, however, will favor the $S_4$-symmetric complex. With the spectroscopic evidence we obtained, we cannot draw any conclusion about the precise sequence of the intriguing up−up−out ↔ out−up−up interconversion of the coordinated ligands in **6**.

**Insertion Reactions in Neutral and Cationic *syn*-1 Palladium Complexes. Insertion Reactions Using Complex 4, NMR Studies.** The neutral (*syn*-**1**)$Pd(CH_3)Cl$ complex (**4** in Scheme 2) was dissolved in chloroform-$d_1$, and carbon monoxide gas was bubbled through the solution at room temperature for 10 min. This resulted in the formation of the palladium acetyl species (**7**) depicted in Scheme 2. In the $^{31}P$ NMR spectrum an AB pattern appeared at $\delta = 92.5$ and $\delta =$

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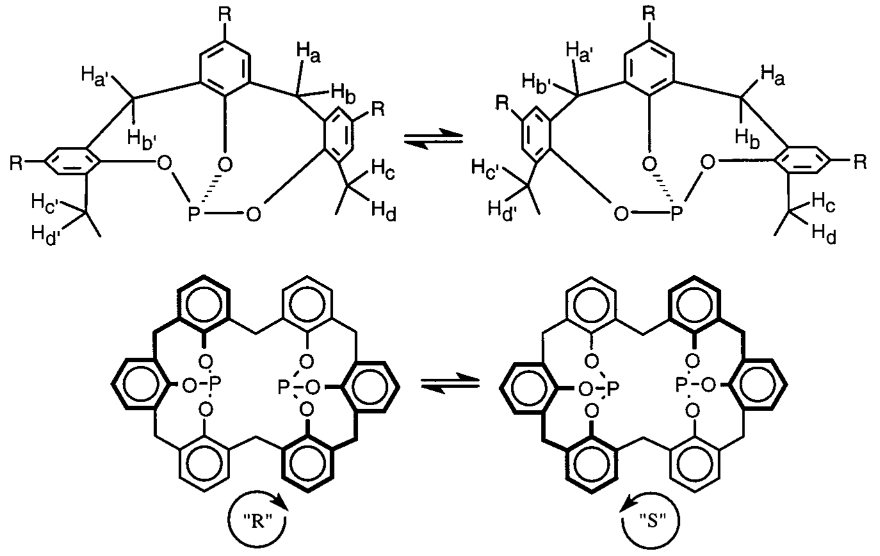

**Figure 6.** Schematic drawing of up−up−out ↔ out−up−up interconversion of the calix[6]arene backbone in *syn*-**1**.

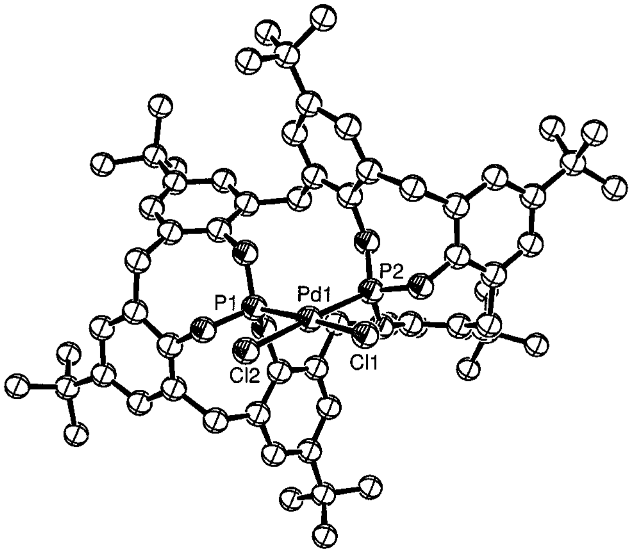

**Figure 7.** Anisotropic displacement plot[61] of **3**. Hydrogen atoms are omitted for clarity.

**Table 1. Selected Bond Lengths and Angles of 3**

| bond lengths (Å) | | bond angles (deg) | |
|---|---|---|---|
| Pd(1)−P(1) | 2.237(2) | P(1)−Pd(1)−P(2) | 94.09(7) |
| Pd(1)−P(2) | 2.236(2) | Cl(1)−Pd(1)−P(2) | 89.66(8) |
| Pd(1)−Cl(1) | 2.309(3) | Cl(2)−Pd(1)−P(1) | 89.51(8) |
| Pd(1)−Cl(2) | 2.317(2) | Cl(1)−Pd(1)−Cl(2) | 86.73(9) |
| P(1)−O(1) | 1.571(6) | Pd(1)−P(1)−O(1) | 112.0(2) |
| P(1)−O(2) | 1.578(5) | Pd(1)−P(1)−O(2) | 110.7(2) |
| P(1)−O(3) | 1.582(5) | Pd(1)−P(1)−-O(3) | 120.7(2) |
| P(2)−O(4) | 1.581(5) | Pd(1)−P(2)−O(4) | 110.7(2) |
| P(2)−O(5) | 1.583(6) | Pd(1)−P(2)−O(5) | 111.3(2) |
| P(2)−O(6) | 1.580(6) | Pd(1)−P(2)−O(6) | 121.6(2) |
| | | O(1)−P(1)−O(2) | 106.3(3) |
| | | O(1)−P(1)−(3) | 101.9(3) |
| | | O(2)−P(1)−O(3) | 103.8(3) |
| | | O(4)−P(2)−O(5) | 106.7(3) |
| | | O(4)−P(2)−O(6) | 101.3(3) |
| | | O(5)−P(2)−O(6) | 103.9(3) |

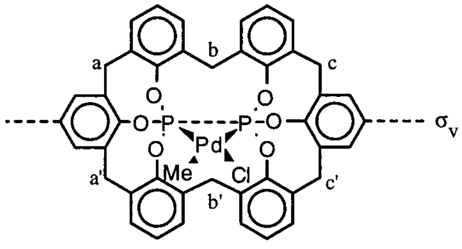

**Figure 8.** Symmetry relations in (*syn*-**1**)Pd($CH_3$)Cl (**4**).

106.3 ppm ($^2J_{PP}$ = 179 Hz). In the $^1$H NMR spectrum the doublet at $\delta$ = 1.60 ppm for the methyl group in the starting compound had disappeared, and instead a singlet at 2.77 ppm, indicative of an acetyl group coordinated to the palladium, was observed. This implies that carbon monoxide insertion is a very facile process in the neutral complex as was observed for other neutral $L_n$PdMeCl complexes where L denotes a phosphite ligand.[42] A subsequent insertion reaction using ethene as a substrate failed, which is ascribed to the absence of a vacant coordination site that inhibits ethene coordination. Therefore we decided to perform further insertion reactions using the cationic palladium complex **8**.

**Insertion Reactions Using Complex 8, NMR Studies.** The cationic (*syn*-**1**)Pd($CH_3$)($CH_3CN$)$^+$OTf$^-$ (**8**) was synthesized by treating **4** with 1 equiv of AgOTf in $CH_2Cl_2/CH_3CN$ (10:1 v/v). The $^1$H NMR spectrum (dichloromethane-$d_2$) shows a doublet for the methyl protons at 1.52 ppm ($^3J_{PH}$(trans) = 12 Hz), a singlet for the acetonitrile protons at 2.24 ppm, and signals characteristic of *syn*-**1**. The $^{31}$P NMR spectrum again showed an AB pattern ($\delta$ = 101.9 and $\delta$ = 91.0 ppm, $J_{PP}$ = 126 Hz). The signal at $\delta$ = 101.9 ppm appears as a double quartet as a consequence of coupling to the methyl group ($^3J_{PH}$ = 12 Hz). These data are in agreement with a cis-chelated complex with a coordinated acetonitrile molecule cis to the methyl group. When a solution of **8** in dichloromethane-$d_2$ was treated with carbon monoxide gas at −20 °C, again a reaction was observed leading to product **9**. In the $^{31}$P NMR spectrum of **9** a new AB type signal appeared at $\delta$ = 88.2 ppm and $\delta$ = 106.5 ppm ($J_{PP}$ = 198 Hz) without any coupling to protons. The $^1$H NMR spectrum shows a singlet at 2.77 ppm without coupling to phosphorus, indicating the formation of the acetyl group coordinated to the palladium atom. When subsequently ethene was bubbled through

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[42] Kayaki, Y.; Shimizu, I.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 917−927.

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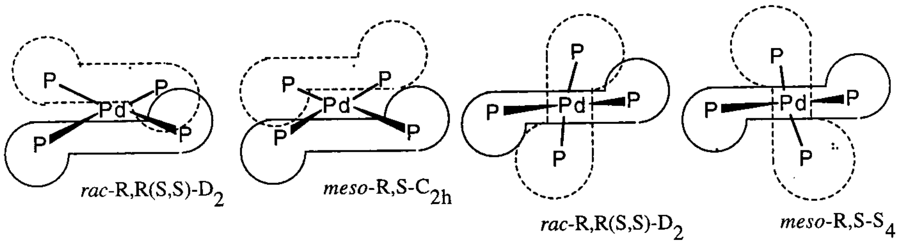
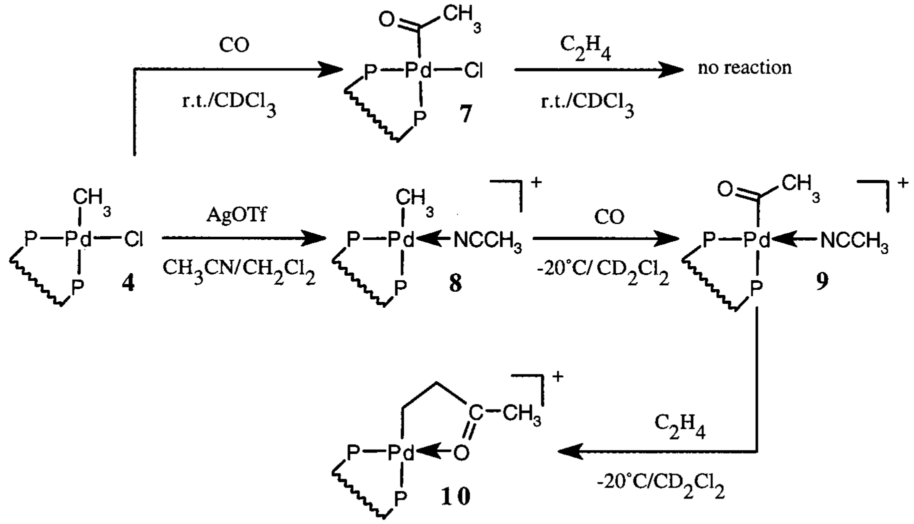


**Figure 9.** Both possible diastereomers of (*syn*-**1**)$_2$Pd(0) (**6**) in square-planar and tetrahedral arrangement.

**Scheme 2. Insertion Reactions into Neutral and Cationic *syn*-1 Palladium Complexes**



the reaction mixture for 30 min at −20 °C, the acetyl singlet at $\delta = 2.77$ ppm was replaced by a singlet at $\delta = 2.54$ ppm and two multiplets were observed at $\delta = 2.85$ ppm and $\delta = 3.44$ ppm. We assign the signal at $\delta = 2.85$ ppm to the methylene group bonded to the palladium atom and the signal at $\delta = 3.44$ ppm to the methylene group next to the ketone carbonyl group. A $^1$H{$^{31}$P} NMR spectrum, decoupled at the signal at 103.4 ppm, confirmed that hydrogens of both methylene groups are coupled to this phosphorus atom. Selective proton decoupling of the multiplet at $\delta = 2.85$ ppm in the $^1$H NMR spectrum caused the multiplet at $\delta = 3.44$ ppm to change to a double doublet ($J_{PH}$(trans) = 14 Hz and $J_{PH}$(cis) = 5 Hz). The signal of coordinated acetonitrile was replaced by a singlet at $\delta = 2.08$ ppm, originating from free acetonitrile, which indicates that the acetonitrile ligand on the palladium atom is displaced by the ketone oxygen atom of the growing "polymer" chain. The $^{31}$P NMR spectrum also showed that complete conversion to a new compound had occurred, giving rise to an AB pattern at $\delta = 90.4$ ppm and $\delta = 103.4$ ppm with $J_{PP} = 131$ Hz. The doublet at 103.4 ppm shows a coupling to both methylene groups in the palladium-bound alkyl species and appears as a double quintet as $^3J_{PH}$ and $^4J_{PH}$ are of comparable magnitude ($^3J_{PH} \approx {}^4J_{PH} \approx 14$ Hz). The $J_{PH}$(cis) coupling on the signal at $\delta = 103.4$ ppm with the hydrogen atoms of the methylene group next to the ketone moiety was not resolved in the $^{31}$P NMR spectrum. These data confirm the insertion of an ethene molecule into the palladium−carbon bond to form the stable five-membered ring species **10** (Scheme 2). In some of the experiments described above a singlet at 126 ppm was observed in the $^{31}$P NMR spectrum. This signal originates from (*syn*-**1**)$_2$palladium(0) (**6**), which was prepared independently from Pd(dba)$_2$ and 2 equiv of ligand (vide supra). Apparently, under the chosen conditions palladium(II) can be reduced to palladium(0), which results in the formation of **6** and palladium metal, which can sometimes be observed in the reaction mixture.

**Insertion Reactions Using Complexes 4 and 8, IR Studies.** An IR study on the insertion reactions mentioned above was executed as well. Carbon monoxide gas was bubbled through a sample of the neutral complex **4**, and the resulting solution was studied by means of IR spectroscopy. A C=O stretch frequency at 1717 cm$^{-1}$ was observed, which is indicative of the formation of **7**. A solution of the cationic complex **8** in dichloromethane was also brought into contact with carbon monoxide gas at room temperature under an argon atmosphere, and the sample was then studied by IR spectroscopy. A new absorption was observed at 1718 cm$^{-1}$, which was assigned to the acetyl complex **9**. This value is higher than that found for other, related palladium acyl species with phosphine ligands, but it is similar to the value obtained for the neutral acetyl complex **7**.[6,7,21] This reflects the higher electron-withdrawing capacity of the phosphite ligand compared to phosphines.When subsequently ethene was bubbled through the solution of the cationic acetyl complex **9**, we observed a strong diminution of the absorption at 1718 cm$^{-1}$ together with the appearance of a new absorption at 1624 cm$^{-1}$. The new absorption was assigned to complex **10**. This value is very similar to values found for comparable systems.[6] The carbonyl vibration of **10** is found at a low frequency, again reflecting the electron deficiency on the palladium atom

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**Table 2. Results of Carbon Monoxide/Ethene Copolymerization with Palladium Catalysts[h]**

| entry | catalyst | reaction time (h) | amount of polymer (mg) | turnover number (mol/ mol Pd) | additive |
|---|---|---|---|---|---|
| 1 | (*syn*-**1**)PdMe$^{+}$ [a] | 19 | | | |
| 2 | (*syn*-**1**)PdMe$^{+}$ | 18 | 620 | 1107 | |
| 3 | (*syn*-**1**)PdMe$^{+}$ | 22.5 | 630 | 1125 | TsOH |
| 4 | (*syn*-**1**)PdMe$^{+}$ | 18 | 3000 | 5357 | TsOH |
| 5 | (*syn*-**1**)PdMe$^{+}$ | 1.25 | jelly[b] | | |
| 6 | (*syn*-**1**)PdMe$^{+}$ [c] | 20.5 | 600 | 1071 | TsOH |
| 7 | (*syn*-**1**)PdMe$^{+}$ [d] | 19.5 | 700 | 1250 | |
| 8 | (*syn*-**1**)PdMe$^{+}$ [d] | 19 | 1306 | 2332 | TsOH |
| 9 | (*syn*-**1**)PdMe$^{+}$ [e] | 19 | 480 | 857 | |
| 10 | (**11**)$_n$PdMe$^{+}$ | 19 | | | TsOH |
| 11 | (**13**)PdMe$^{+}$ | 17 | | | TsOH |
| 12 | AgOTf-*syn* -**1** [f] | 18.5 | | | |
| 13 | $Pd_2(dba)_3$ [g] | 19.5 | | | TsOH |
| 14 | (*syn*-**1**)$_2$Pd(0) [e] | 17 | | | TsOH |

[a] $CH_2Cl_2$/MeOH (1:3 v/v total of 20 mL). [b] The sample still contains large amounts of $CH_2Cl_2$. [c] 30 mL of $CH_2Cl_2$. [d] 30 bar carbon monoxide/ethene (1:1). [e] 0.005 mmol cat. [f] 0.01 mmol *syn*-**1**. [g] 0.006 mmol cat./17.5 mg TsOH. [h] conditions: 20 mL of $CH_2Cl_2$, 20 bar of $CO/C_2H_4$ (1:1), 295 K, 0.01 mmol cat.

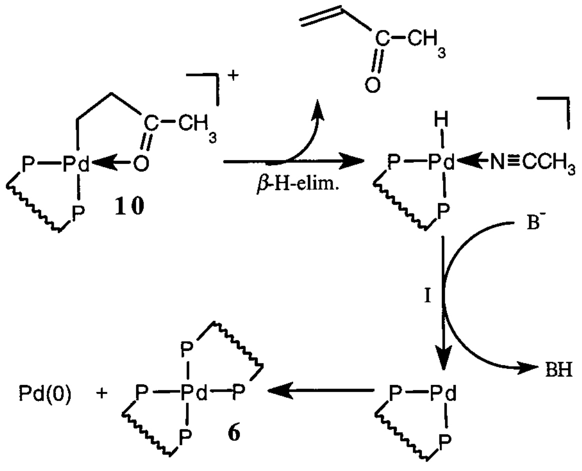
which is caused by the electron-withdrawing capacity of the phosphite ligand.

### Copolymerization of Carbon Monoxide/Ethene with Cationic (*syn*-1) $Pd(CH_3)(CH_3CN)^{+}OTf^{-}$ (8).

Several copolymerization experiments were performed with (*syn*-**1**)-$Pd(CH_3)(CH_3CN)^{+}OTf^{-}$ (**8**) and carbon monoxide/ethene. The effect of solvent, added acid, and carbon monoxide/ethene pressure have been studied. The results are summarized in Table 2. The initial pressure dropped 2−3 bar in the first 5 min during most experiments due to ethene and carbon monoxide dissolution, and it dropped slowly in the following period as a result of carbon monoxide and ethene consumption during the copolymerization reaction. When methanol was used as solvent (entry 1 in Table 2), no pressure drop due to carbon monoxide/ethene consumption was observed. In these runs the mixture contained palladium metal, and no polymer was observed. This is not surprising in view of the sensitivity of phosphites toward alcohols and water. As the concentration of catalyst is low, no attempt was undertaken to analyze possible decomposition products. The addition of *p*-toluenesulfonic acid had a positive effect on the yield of the produced polymer. Moreover no palladium metal was formed in runs with added *p*-toluenesulfonic acid. When catalysis is performed in $CH_2Cl_2$ the only chain termination mechanism that is operative is $\beta$-H elimination, whereas in protic solvents such as MeOH both protonolysis and esterification can take place.[16] In our system $\beta$-H elimination will lead to (*syn*-**1**)Pd−H$^{+}$, which can easily decompose to (*syn*-**1**)Pd(0) and H$^{+}$ in view of the electron-withdrawing character of diphosphite (*syn*-**1**) (see Scheme 3).

In the catalysis experiments using (*syn*-**1**)$Pd(CH_3)^{+}$ (**8**) we assume that the effect of addition of *p*-toluenesulfonic acid is to prevent reduction of palladium(II) by shifting the equilibrium of reaction I (Scheme 3) to the left. Experiments with Pd(0)(dba)$_2$ or (*syn*-**1**)$_2$Pd(0) (**6**) as catalysts in the presence of *p*-toluenesulfonic acid (entries 13 and 14 in Table 2) produced no polymer, and no pressure drop was observed. In experiment 13 *p*-toluenesulfonic acid probably reacts with palladium(0) to give Pd$^{II}$(OTs)$_2$ instead of forming the catalytically active hydride species.

**Scheme 3. Decomposition Pathway of Palladium(II) Catalyst to Palladium(0) in Copolymerization**



Complex **6** is not reactive toward *p*-toluenesulfonic acid under these conditions. To exclude the possibility of catalysis by transition metal complexes other than the desired compound **8**, a control catalytic run was performed with AgOTf and *syn*-**1** in a ratio of 1:1 (entry 12). The mixture of metal and ligand was stirred under an argon atmosphere for 20 min to allow the formation of the complex before it was pressurized with carbon monoxide/ethene. No polymer was formed in the catalysis experiment with *syn*-**1** and silver(I). Complexation of silver(I) by *syn*-**1** was observed in an independent complexation study. The formed complex was not isolated but only studied by $^{31}$P NMR, showing two doublets at $\delta = 105.5$ ppm with $^{1}J_{AgP} = 366$ and 423 Hz for $^{107}$Ag and $^{109}$Ag, respectively. These values indicate that two ligands are coordinated to the silver(I) atom.[43]

From the data presented in Table 2 no conclusion can be drawn as to the influence of pressure and catalyst concentration on the yield of polymer, although higher pressures (30 bar) seem to give rise to higher yields. The highest yield, however, was obtained at 20 bar of carbon monoxide/ethene pressure (entry 4). In general after a successful experiment the autoclave was filled with a thick white paste. High yields seemed to correlate with the occurrence of relatively fluid suspensions, and low yields correlated with the formation of thick slurries. The reason for the lack of control on the morphology of the polymer suspensions is unknown to us. In this exploratory study no attempts were made to control the morphology of the polymer, and therefore the yields show scattering.

In all cases the polymeric material showed the expected resonances at $\delta = 35.1$ ppm and $\delta = 212.0$ ppm for the methylene and carbonyl group, respectively, in the $^{13}$C NMR spectrum (hexafluoro-2-propanol/chloroform-$d_1$ or hexafluoro-2-propanol/benzene-$d_6$).[23] The IR spectra showed the low $\nu$(CO) at ca. 1695 cm$^{-1}$ that has been reported for carbon monoxide/alkene copolymers before.[11,44,45] A $M_w$ determination based on GPC tech-

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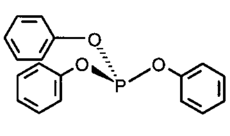
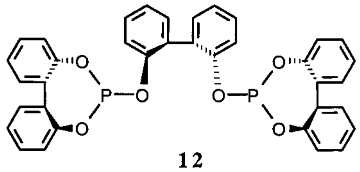
niques was performed on samples of polymer produced in the reactions of entries 4, 7, and 8. The $\langle M_n \rangle$ of these samples were determined at 36 000, 32 000, and 34 000, respectively. The PDI ($\langle M_w \rangle / \langle M_n \rangle$) values were determined at 2.23, 2.26, and 2.43 for the respective samples. The $\langle M_n \rangle$ values are not uncommon for carbon monoxide/ethene copolymers, although both shorter and longer chain lengths have been reported.[11,25] The measured $M_n$ values indicate that at least some catalyst centers produced more than one polymer chain, which means that a chain-transfer mechanism must be operative. This is also reflected in the PDI values. To examine the chain-transfer mechanism, we performed an end group analysis by means of $^{13}$C NMR spectroscopy. For the polymers produced in experiments 2 and 7 this resulted in the detection of mainly ethyl and carboxylic acid end groups next to small quantities (15%) of vinyl end groups in experiment 2. The presence of carboxylic acid end groups indicates that hydrolysis probably plays a major role in the chain-transfer mechanism. The water needed for this process is probably provided by very small quantities of water present in the autoclave, since dry glassware and solvents were used in the preparation of the catalyst. We performed no experiments in which water was added on purpose to examine the effects on average chain length and distribution of the produced copolymer. The low number of vinyl end groups shows that $\beta$-H elimination is of minor importance in this system. This is in accordance with the observation that ligands having bite angles larger than 90° suppress the $\beta$-H elimination.[6,46,47] Furthermore we assume that the C=O moiety in the five-membered chelate ring is more strongly bound using *syn*-**1** than in phosphine-ligated palladium complexes (vide supra). A necessary step in $\beta$-H elimination in this stage of polymerization is dissociation of the ketone group and rotation of the $\beta$-hydrogen toward the palladium center. By bonding the ketone group more strongly to the palladium center, *syn*-**1** suppresses the $\beta$-H elimination. This also suggests that displacement of the ketone oxygen on the palladium atom by carbon monoxide must be a concerted process. This explains why copolymerization is much slower using *syn*-**1** in catalysis compared with phosphine-based catalysis.

The other signals in the $^{13}$C NMR spectrum were consistent with an alternating structure of the copolymer. Only very small quantities of incorporation of $C_n$ fragments ($n$ > 7, 8) were observed as well as small amounts of furan type fragments. The frequency of incorporation was less than 1 for each polymer chain on average. These fragments are usually encountered in polyketone samples in small numbers.[48]

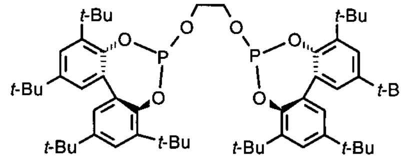
**Palladium Complexes with other (Di)phosphites and Their Use in Carbon Monoxide/Ethene Copolymerization.** The facile formation of carbon monoxide/ethene copolymer with *syn*-**1** as ligand and absence of data on the use of phosphites in carbon monoxide/alkene copolymerization prompted us to study other phosphites. Therefore attempts were made to use $L_nPd(CH_3)Cl$ complexes containing phosphite ligands **11**−**13**.



**11**



**12**



**13**

Synthesis of a $L_nPd(CH_3)Cl$ complex was successful for the monodentate triphenyl phosphite (**11**) ($n$ = 2) and 1,2-bis(2,4,8,10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)ethane (**13**) ($n$ = 1). 2,2′-Bis(5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)biphenyl (**12**) gave no single well-defined $L_nPd(CH_3)Cl$ complex but gave rise to a mixture of complexes together with several decomposition products. Presumably this was due to the bite angle of 100−130°, which may lead to the formation of both cis and trans complexes. It has been reported that **12** forms a very stable Pt(0) complex with P−Pt−P angles ranging from 102° to 115°.[49]

For the monodentate triphenyl phosphite (**11**) a 1:3 mixture of *cis*- and *trans*-$(\mathbf{11})_2Pd(CH_3)Cl$ (**14**) was found, as was reported earlier by Kayaki and co-workers.[50] Treatment of this complex with AgOTf resulted in the precipitation of AgCl and a colorless solution. The dissolved complex was tested in carbon monoxide/ethene copolymerization in the presence of *p*-toluenesulfonic acid under otherwise standard conditions. The solution showed very low to no activity. Hardly any pressure drop (0.4 bar) was observed in the course of 19 h of reaction time (see entry 10). Kayaki et al. reported that halide anion abstraction from a mixture of *cis*- and *trans*-**14** resulted in the formation of $(\mathbf{11})_3Pd(CH_3)^+$ and an uncharacterized palladium compound when $AgBF_4$ was used.[50] $(\mathbf{11})_3PdMe^+$ is not likely to lose a phosphite ligand in favor of carbon monoxide or ethene coordination, and it will therefore not be catalytically active. Apparently the uncharacterized palladium compound is inactive as well.

Ligand **13** gave rise to pure *cis*-$(\mathbf{13})Pd(CH_3)Cl$ (**15**), as could be judged from the AB pattern in the $^{31}$P NMR spectrum ($J_{PP}$ = 85 Hz) and a coupling on the lower field signal at $\delta$ = 140 ppm to the methyl group ($J_{PH}$(trans) = 12 Hz) and the double doublet in the $^1$H NMR spectrum for the methyl group ($J_{PH}$(trans) = 12 Hz and $J_{PH}$(cis) = 2 Hz). In the presence of acetonitrile, **15** was treated with AgOTf to yield a colorless solution. The white solid that was obtained upon evaporation of the solvent was stable under an argon atmosphere at room temperature, but when redissolved in dry chlorinated

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solvents (dichloromethane or chloroform), the solution rapidly turned brown with accompanying formation of palladium metal. Even in benzene-$d_6$ decomposition occurred. When a freshly prepared dichloromethane/acetonitrile solution of *cis*-(**13**)Pd($CH_3$)$^+$ was used in a catalysis experiment, no formation of metallic palladium was observed when the solution was transferred to the autoclave. Complex *cis*-(**13**)Pd($CH_3$)$^+$ showed no activity in copolymerization, as could be judged from the absence of any significant pressure drop in 17 h and the absence of solid polymer in the reaction mixture (entry 11). The solution was slightly gray, indicating the presence of metallic palladium. Thus the few common phosphite complexes tested gave no catalytic activity in polyketone synthesis.

## Concluding Remarks

We were able to synthesize *syn*-**1** in 20−40% yield. The ligand shows a tendency to form cis-coordinated complexes with palladium(II) in which it has an almost ideal bite angle of 94°. Furthermore it can stabilize palladium(0) as (*syn*-**1**)$_2$Pd(0). The geometry of this complex is presumably a (distorted) tetrahedron.

Even more remarkable about *syn*-**1** is its successful application in palladium-catalyzed copolymerization of carbon monoxide and ethene. No (di)phosphites with the same capability have been reported up to now. Tests with other (bidentate) phosphites have not resulted in the formation of active catalysts. Therefore *syn*-**1** is a unique ligand with respect to its behavior in carbon monoxide/ethene copolymerization. The successful application in copolymerization is attributed to the unique combination of the following features: (1) its bidentate coordination fashion with effective $C_{2v}$ symmetry, (2) its bite angle being slightly larger than 90°, (3) its rigid backbone that is chemically stable in the presence of a coordinatively unsaturated cationic transition metal center. Feature 2 facilitates a fast insertion of carbon monoxide, and it retards the rate of $\beta$-H elimination, thus increasing the overall reaction rate. Feature 3 in combination with the bite angle of 94° prohibits the formation of oligomeric structures with a trans configuration. None of the phosphites tested in copolymerization that have been discussed in the literature combine these characteristics.

## Experimental Section

**Chemicals.** All preparations were carried out under an inert atmosphere of dinitrogen or argon using standard Schlenk techniques unless stated otherwise. Toluene, benzene, THF, diethyl ether, pentane, and hexane were distilled from sodium/benzophenone. Chlorinated solvents, DMF, acetonitrile, triethylamine, and pyridine were distilled from $CaH_2$. Carbon monoxide (Air Liquide) and ethene (Praxair) were used without purification. *p-tert*-butylphenol, $PCl_3$, cod, 2,2′-bisphenol, and AgOTf were purchased from Aldrich. Formaldehyde was used as a 37% solution in water purchased from Janssen Chimica. NaH, ethylene glycol, and triphenyl phosphite were also purchased from Janssen Chimica. NaOH was purchased from Riedel de Haën and used without further purification. $PdCl_2$ was purchased from ABCR. 4,4′,6,6′-Tetra-*tert*-butyl-2,2′-bisphenol, (cod)$PdCl_2$, (cod)PdMeCl, and Pd(dba)$_2$ were synthesized following literature procedures.[51−54] The silica gel used for column chromatography (kieselgel 60, 70−230 mesh ASTM) was purchased from Merck.

**Apparatus.** Melting points (uncorrected) were determined on a Gallenkamp MFB 595 melting point apparatus. NMR measurements ($^1$H NMR (300.1 MHz), $^{13}$C{$^1$H} NMR (75.5 MHz), $^{31}$P{$^1$H} NMR (121.5 MHz)) were performed on a Bruker AMX 300 spectrometer. Chemical shifts are given in ppm using TMS or $H_3PO_4$ as a standard reference. NMR spectra were measured in chloroform-$d_1$ at 25 °C unless stated otherwise. IR spectra were taken on a Nicolet 510 FT-IR spectrophotometer. Mass spectrometric measurements were performed at the Institute for Mass Spectrometry of the University of Amsterdam. Elemental analyses were performed in our own laboratory on an Elementar Vario EL Apparatus (Foss Electric) or at the Micro Analytical Department of the University of Groningen. The copolymerization was performed in a stainless steel (SS 316) 180 mL autoclave, equipped with a glass liner, a gas inlet, a thermocouple, an external heating mantle, an internal cooling spiral, and a magnetic stirrer.

**Copolymerization of Carbon Monoxide and Ethene.** In a typical experiment the autoclave was evacuated and filled with argon. Then it was charged with 5 mL of a solution of (*syn*-**1**)Pd($CH_3$)$^+$OTf$^-$($CH_3CN$) (2 mM in $CH_2Cl_2$), and 15 mL of a suitable solvent was added. The autoclave was then flushed three times with carbon monoxide and pressurized with 10 bar of carbon monoxide. Subsequently 10 bar of ethene was added following the same procedure. The mixture was then allowed to react overnight. At that point the autoclave was depressurized and opened, and the content was analyzed. The produced polymer suspension was filtered and washed with $CH_2Cl_2$ and diethyl ether and subsequently dried in vacuo. The same procedure was followed for experiments with other phosphites; that is, the same concentration of palladium complex, amount of solvent, and pressures were applied.

**Synthesis of Calix[6]arene Diphosphite (1).** A suspension of 4.86 g (5 mmol) of calix[6]arene[55] was dissolved in 100 mL of anhydrous THF/DMF (4:1, v/v) and added dropwise to a suspension of 0.90 g (30 mmol) of NaH (80%) in 50 mL of anhydrous THF under an inert atmosphere. After stirring for 1.5 h at 40−45 °C, the red suspension was added dropwise simultaneously and at the same rate with a solution of 0.89 mL (10 mmol) of $PCl_3$ in 100 mL of anhydrous THF, to 50 mL of refluxing THF. After refluxing for 2 h the reaction mixture was allowed to cool to room temperature, and most of the solvent was evaporated. The resulting suspension was taken up in 100 mL of $CH_2Cl_2$ and washed quickly with 100 mL of water. The water layer was washed four times with 100 mL of $CH_2Cl_2$, the combined $CH_2Cl_2$ layers were dried over $MgSO_4$ and filtered, and the solvent was evaporated. The resulting solid was purified by column chromatography over silica gel with $CH_2Cl_2$ as eluent followed by recrystallization from hexane, yielding 1−2 g (20−40%) pure *syn*-**1** as a white powder. The *anti*-**1** could not be obtained in pure form, and therefore assignment of the structure was only done on the basis of NMR studies in the presence of *syn*-**1**. (*syn*-**1**): Decomp > 270 °C; $^1$H NMR $\delta = 1.20$ (s, 36H; *t*-Bu), 1.28 (s, 18H; *t*-Bu), 3.58 (d, $^2J_{HH} = 13.9$ Hz, 4H; $CH_2$ *eq*), 3.68 (d, $^2J_{HH} = 17.5$ Hz, 2H; $CH_2$ *eq*), 4.58 (d, $^2J_{HH} = 13.9$ Hz, 4H; $CH_2$ *ax*), 4.67 (d, $^2J_{HH} = 17.5$ Hz, 2H; $CH_2$ *ax*), 6.88 (d, $^4J_{HH} = 2.0$ Hz, 4H; ArH), 7.14 (d, $^4J_{HH} = 2.3$ Hz, 4H; ArH), 7.18 (s, 4H; ArH); $^{13}$C NMR $\delta = 31.8$ (s; $CH_3$), 34.5, 34.7 (s; $CH_2$), 36.2 (s, $C(CH_3)_3$), 125.0,

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125.7 (s; Ar*C*H), 140.3, 145.3, 146.7, 147.0, 148.2 (s; Ar*C*); $^{31}$P NMR $\delta$ = 102.9 (s, 2P; P(OR)$_3$); IR(KBr) $\nu$(cm$^{-1}$) 2963, 2869 (C−H alif.); 1481, 1469 (C═C); 1197, 1174 (C−O); 1107, 932, 890, 869, 854 (C−O−P); MS−FAB *m/z* (%): 57(100) [C(CH$_3$)$_3$$^+$], 1029(23) [M$^+$ − H]. Anal. Calcd for $C_{66}H_{78}O_6P_2$: C 77.01, H 7.64. Found: C 76.57, H 7.72.

*(anti* -**1**): $^{1}$H NMR $\delta$ = 1.16 (s, 36H; *t*-Bu), 1.26 (s, 18H; *t*-Bu), 3.57 (d, $^{2}J_{HH}$ = 13.5 Hz, 4H; CH$_2$ *eq*), 4.18 (s, 4H; CH$_2$), 4.56 (d, $^{2}J_{HH}$ = 13.5 Hz, 4H; CH$_2$ *ax*), 6.88, 7.11, 7.17 (m, 12H; ArH); $^{31}$P NMR $\delta$ = 103.4 (s, 2P; P(OR)$_3$).

**Alternative Synthesis.** A 7.94 g sample of calix[6]arene was azeotropically dried with dry toluene and suspended in 200 mL of toluene. A 10 mL sample of triethylamine was added to this suspension while stirring. After this addition the suspension turned into a clear yellow solution. This solution was then warmed to 70 °C, and a solution of 2.2 mL of PCl$_3$ in 20 mL of dry toluene was added. Salt precipitation was observed immediately. After 2 h of reflux the mixture was allowed to cool to room temperature, the salts were filtered off, and the clear toluene solution was evaporated to yield 4 g of a white solid. This solid was purified by column chromatography over silica with CH$_2$Cl$_2$ as an eluent. Recrystallization from hexane yielded 2 g of pure product. Alternatively pyridine can be used instead of triethylamine. Residual salts and calix[6]arene can often be observed when this method is used.

**Variable-Temperature $^{1}$H NMR Experiments.** Variable-temperature NMR spectra of *syn*-**1** were the result of 128 scans with a relaxation delay of 3 s. Spectra were taken at 270 K, 265−250 K with an interval of 2.5 deg, and at 245 and 240 K. The sample was allowed to stabilize at the desired temperature for 15 min before the measurement was started.

**(*syn*-1)PtCl$_2$ (2).** A 41.12 mg (0.04 mmol) sample of *syn*-**1** and 14.96 mg (0.04 mmol) of [PtCl$_2$(cod)] were dissolved in 5−10 mL of anhydrous CH$_2$Cl$_2$ or THF and stirred for several hours. After evaporation of the solvent, the complex was washed several times with anhydrous diethyl ether or pentane, and the residual solvent again removed by evaporation, yielding **2** as a white powder: decomp > 300 °C; $^{1}$H NMR $\delta$ = 1.25 (s, 18H; *t*-Bu), 1.26 (s, 36H; *t*-Bu), 3.18 (d, $^{2}J_{HH}$ = 14.6 Hz, 2H; CH$_2$ *eq*), 3.57 (d, $^{2}J_{HH}$ = 14.1 Hz, 4H; CH$_2$ *eq*), 4.71 (d, $^{2}J_{HH}$ = 14.6 Hz, 2H; CH$_2$ *ax*), 4.76 (d, $^{2}J_{HH}$ = 14.1 Hz, 4H; CH$_2$ *ax*), 6.96 (d, $^{4}J_{HH}$ = 2.2 Hz, 4H; ArH), 7.17 (s, 4H; ArH), 7.17 (d, $^{4}J_{HH}$ = 2.2 Hz, 4H; ArH); $^{13}$C NMR $\delta$ = 31.5, 31.7 (s; *C*H$_3$), 34.5, 34.9 (s; *C*H$_2$), 35.9 (s; *C*(CH$_3$)$_3$), 125.1, 126.5, 127.5 (s; Ar*C*H), 130.5, 131.8, 132.6, 149.2 (s; Ar*C*); $^{31}$P NMR $\delta$ = 49.7 (s, P), 49.7 (d, $^{1}J_{PtP}$ = 5800 Hz; P); IR(KBr) $\nu$(cm$^{-1}$) 2963 (C−H alif.); 1482, 1465 (C═C); 1191, 1166 (C−O); 1104, 960, 951 (C−O−P). Anal. Calcd for $C_{66}H_{78}O_6P_2PtCl_2$: C 61.20, H 6.07. Found: C 60.93, H 6.18.

**(*syn*-1)PdCl$_2$ (3).** A 41.12 mg (0.04 mmol) sample of *syn*-**1** and 11.40 mg (0.04 mmol) of [PdCl$_2$(cod)] were dissolved in 5−10 mL of anhydrous CH$_2$Cl$_2$ or THF and stirred for several hours. After evaporation of the solvent, the complex was washed several times with anhydrous diethyl ether or pentane, and the residual solvent again removed by evaporation, yielding **3** as a yellow powder. A few milligrams of **3** was dissolved in dry CH$_2$Cl$_2$, and the solution was brought into contact with dry diethyl ether. After slow evaporation of the solvent through a septum crystals were formed in a period of weeks: decomp > 240 °C; $^{1}$H NMR $\delta$ = 1.25 (s, 18H; *t*-Bu), 1.27 (s, 36H; *t*-Bu), 3.19 (d, $^{2}J_{HH}$= 14.3 Hz, 2H; CH$_2$ *eq*), 3.58 (d, $^{2}J_{HH}$ = 14.2 Hz, 4H; CH$_2$ *eq*), 4.72 (d, $^{2}J_{HH}$ = 14.3 Hz, 2H; CH$_2$ *ax*), 4.77 (d, $^{2}J_{HH}$= 14.2 Hz, 4H; CH$_2$ *ax*), 6.97 (d, $^{4}J_{HH}$ = 2.2 Hz, 4H; ArH), 7.16 (s, 4H; ArH), 7.19 (d, $^{4}J_{HH}$ = 2.2 Hz, 4H; ArH); $^{13}$C NMR $\delta$ = 31.5, 31.7 (s; *C*H$_3$), 34.6, 34.9 (s; *C*H$_2$), 36.8 (s; *C*(CH$_3$)$_3$), 125.1, 126.6, 127.6 (s; Ar*C*H), 130.5, 131.9, 149.4 (s; Ar*C*); $^{31}$P NMR $\delta$ = 73.3 (s, P); IR(KBr) $\nu$(cm$^{-1}$) 2958 (C−H alif.); 1482, 1465 (C═C); 1167 (C−O); 1112, 1102, 963, 885 (C−O−P). Anal. Calcd for $C_{66}H_{78}O_6P_2PdCl_2 \cdot C_4H_{10}O$: C 65.65, H 6.93. Found: C 64.47, H 6.85.

**(*syn*-1)Pd(CH$_3$)Cl (4).** A 41.12 mg (0.04 mmol) sample of *syn*-**1** and 10.58 mg (0.04 mmol) of (cod)Pd(CH$_3$)Cl were dissolved in 5−10 mL of anhydrous CH$_2$Cl$_2$ or THF and stirred for 3 h. After evaporation of the solvent, the complex was washed several times with anhydrous diethyl ether or pentane, and the residual solvent again removed by evaporation, yielding 39 mg (3.3 × 10$^{-2}$ mmol, 80%) of **4** as a yellow/white powder: decomp > 208 °C; $^{1}$H NMR $\delta$ = 1.25 (s, 18H; *t*-Bu), 1.27 (s, 36H; *t*-Bu), 1.60 (d, $^{3}J_{PH}$ = 12.0 Hz, 3H; Pd−CH$_3$), 3.13 (d, $^{2}J_{HH}$ = 14.8 Hz, 2H; CH$_2$ *eq*), 3.56 (pseudo-t, $^{2}J_{HH}$ = 13.9 Hz, 2H; CH$_2$ *eq*, $^{2}J_{HH}$ = 13.6 Hz, 2H; CH$_2$ *eq*), 4.52 (d, $^{2}J_{HH}$ = 13.9 Hz, 2H; CH$_2$ *ax*), 4.71 (d, $^{2}J_{HH}$ = 13.6 Hz, 2H; CH$_2$ *ax*), 4.86 (d, $^{2}J_{HH}$ = 14.8 Hz, 2H; CH$_2$ *ax*), 6.79−7.18 (m, 12H; ArH); $^{13}$C NMR $\delta$ = 31.5, 31.7 (s; *C*H$_3$), 32.8 (s; Pd−*C*H$_3$), 34.5, 34.8, 34.9 (s; *C*H$_2$), 36.0 (s; *C*(CH$_3$)$_3$), 124.9, 125.1, 126.1, 126.9 (s; Ar*C*H), 130.5, 130.9, 132.3, 133.0, 145.9, 148.2, 148.6 (s; Ar*C*); $^{31}$P NMR $\delta$ = 95.6 (d, $^{2}J_{PP}$ = 120 Hz, 1P; P trans to Cl), 102.8 (dq, $^{2}J_{PP}$ = 120 Hz, $^{3}J_{PH}$ = 12 Hz, 1P; P trans to CH$_3$); IR-(KBr) $\nu$(cm$^{-1}$) 2963 (C−H alif.); 1481, 1465 (C═C); 1194, 1170 (C−O); 1106, 946, 932, 899, 879 (C−O−P). Anal. Calcd for $C_{66}H_{78}O_6P_2PdCH_3Cl$: C 67.84, H 6.89. Found: C 67.30, H 6.98.

**(*syn*-1)Pt(CH$_3$)Cl (5).** A 41.12 mg (0.04 mmol) sample of *syn*-**1** and 14.14 mg (0.04 mmol) of [Pt(CH$_3$)Cl(cod)] were dissolved in 5−10 mL of anhydrous CH$_2$Cl$_2$ or THF and stirred for several hours. After evaporation of the solvent, the complex was washed several times with anhydrous diethyl ether or pentane, and the residual solvent again removed by evaporation, yielding **5** as a white powder: decomp > 280 °C; $^{1}$H NMR $\delta$ = 1.25 (s, 18H; *t*-Bu), 1.26 (s, 36H; *t*-Bu), 1.38 (dd, $^{3}J_{PH}$ = 11 Hz, $^{2}J$(Pt,H) = 2.4 Hz; 3H; CH$_3$), 3.14 (d, $^{2}J_{HH}$ = 14.8 Hz, 2H; CH$_2$ *eq*), 3.56 (pseudo-t, $^{2}J_{HH}$ = 13.8 Hz, 2H; CH$_2$ *eq*, $^{2}J_{HH}$ = 14.2 Hz, 2H; CH$_2$ *eq*), 4.57 (d, $^{2}J_{HH}$ = 13.8 Hz, 2H; CH$_2$ *ax*), 4.72 (d, $^{2}J_{HH}$ = 14.2 Hz, 2H; CH$_2$ *ax*), 4.85 (d, $^{2}J_{HH}$= 14.8 Hz, 2H; CH$_2$ *ax*), 6.91−7.19 (m, 12H; ArH); $^{13}$C NMR $\delta$ = 32.7, 32.9 (s; *C*H$_3$), 35.6 (s; *C*H$_2$), 37.0 (s; *C*(CH$_3$)$_3$), 126.2, 127.9, 128.2 (s; Ar*C*H), 131.7, 132.8, 133.0, 134.0, 147.3, 149.4, 149.7, 150.4 (s; Ar*C*); $^{31}$P NMR $\delta$ = 63.8 (d, $^{2}J_{PP}$ = 52, 1P; P trans to Cl), 63.8 (dd, $^{2}J_{PP}$ = 52 Hz, $^{1}J_{PtP}$ = 7300, 1P; Ptrans to Cl), 111.0 (dq, $^{2}J_{PP}$ = 52 Hz, $^{3}J_{PH}$ = 11 Hz, 1P; P trans to CH$_3$), 111.0 (ddq, $^{2}J_{PP}$ = 52 Hz, $^{1}J_{PtP}$ = 2700 Hz, $^{3}J_{PH}$ = 11 Hz, 1P; P trans to CH$_3$); IR(KBr) $\nu$(cm$^{-1}$) 2961, 2905, 2869 (C−H alif.); 1482, 1465 (C═C); 1193, 1169 (C−O); 1106, 948, 935, 899, 880 (C−O−P).

**(*syn*-1)$_2$Pd(0) (6).** A 45.8 mg (44.5 × 10$^{-3}$ mmol) sample of *syn*-**1** and 10 mg (1.8 × 10$^{-2}$ mmol) of Pd(dba)$_2$ were dissolved in 5−10 mL of anhydrous toluene and stirred until the original purple color turned into pale yellow. The solvent was then evaporated and the yellow residue washed with dry acetonitrile. An off-white solid was obtained by evaporating the residual solvents: yield 25.7 mg (11.9 × 10$^{-3}$ mmol, 68%); mp > 325 °C; $^{1}$H NMR $\delta$ = 0.71 (s, 36H; *t*-Bu), 1.23 (s, 36H; *t*-Bu), 1.31 (s, 36H; *t*-Bu), 3.01 (d, $^{2}J_{HH}$ = 15.4 Hz, 4H; CH$_2$ *eq*), 3.41 (d, $^{2}J_{HH}$ = 14.9 Hz, 4H; CH$_2$ *eq*), 3.52 (d, $^{2}J_{HH}$ = 12 Hz, 4H; CH$_2$ *eq*), 4.58 (d, $^{2}J_{HH}$ = 14.9 Hz, 4H; CH$_2$ *ax*), 4.61 (d, $^{2}J_{HH}$ = 12 Hz, 4H; CH$_2$ *ax*), 4.91 (d, $^{2}J_{HH}$ = 15.4 Hz, 4H; CH$_2$ *ax*), 6.41 (s, 4H; ArH), 6.93 (s, 4H; ArH), 6.97 (d, $^{4}J_{HH}$ = 1.8 Hz, 4H; ArH), 7.06 (d, $^{4}J_{HH}$ = 1.8 Hz, 4H; ArH), 7.17 (s, 8H; ArH); $^{13}$C NMR $\delta$ = 30.4, 31.3 (s; *C*H$_3$), 33.2, 34.0, 34.1 (s; *C*H$_2$), 33.0, 35.0, 37.3 (s; *C*(CH$_3$)$_3$), 123.6, 124.3, 124.9, 125.6, 127.3, 128.8 (s; Ar*C*H), 129.7, 131.2, 131.6, 132.8, 133.0, 133.7 (s; Ar*C*), 145.4, 145.9, 146.5, 146.6, 146.8, 147.6 (s; Ar*C*-O); $^{31}$P NMR $\delta$ = 126 (s, 4P); IR(KBr) $\nu$(cm$^{-1}$) 2962, 2900, 2850 (C−H alif.); 1480 (C═C); 1195, 1176 (C−O); 1109, 925, 856 (C−O−P); MS−FAB *m/z* (%) 57(100) [C(CH$_3$)$_3$$^+$], 2163(65) [M$^+$]. Anal. Calcd for $C_{132}H_{156}O_{12}P_4Pd$: C 73.23, H 7.27. Found: C 72.90, H 7.54.

**(*syn*-1)PdC(O)CH$_3$Cl (7).** A sample of **4** was dissolved in CH$_2$Cl$_2$, and carbon monoxide gas was bubbled through the solution at room temperature for several minutes. The complex was not isolated because it was found to be unstable in solution at ambient temperatures, resulting in formation of a red-colored compound: yield 100% based on $^{31}$P NMR; $^{1}$H NMR $\delta$

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$=$ 1.26 (br s, 54H; *t*-Bu), 2.77 (s, 3H; PdC(O)C$H_3$), 3.14 (d, $^2J_{HH}$ $=$ 14.6 Hz, 2H; CH$_2$ *eq*), 3.56 (pseudo-t, $^2J_{HH} \approx 14$ Hz, 4H; CH$_2$ *eq*), 4.53 (d, $^2J_{HH} = 13.7$ Hz, 2H; CH$_2$ *ax*), 4.65 (d, $^2J_{HH} = 14.6$ Hz, 2H; CH$_2$ *ax*), 4.81 (d, $^2J_{HH} = 14.8$ Hz, 2H; CH$_2$ *ax*), 6.92−7.18 (m, 12H; ArH); $^{31}$P NMR $\delta = 92.5$ (d, $^2J_{PP} = 179$ Hz, 1P; P trans to Cl), 106.3 (d, $^2J_{PP} = 179$ Hz, 1P; P trans to C(O)-CH$_3$); IR(KBr) $\nu$(cm$^{-1}$) 1717 (C=O).

**(*syn*-1)Pd(CH$_3$)(CH$_3$CN)$^+$OTf$^-$ (8).** A sample of 0.04 mmol (43.8 mg) of **4** was dissolved in a $CH_2Cl_2/CH_3CN$ mixture (10:1 v/v) and treated with 0.04 mmol (10.3 mg) of AgOTf. The precipitated AgCl was filtered off, and the filtrate was evaporated to dryness. The compound thus obtained was spectroscopically pure and used without further purification. $^1$H NMR (dichloromethane-$d_2$, −20 °C): $\delta = 1.25$ (s, 54H; *t*-Bu), 1.52 (d, $^3J_{PH} = 12$ Hz, 3H; Pd−CH$_3$), 2.24 (br s, 14H; C$H_3$CN), 3.28 (d, $^2J_{HH} = 14.8$ Hz, 2H; CH$_2$ *eq*), 3.69 (d, $^2J_{HH} = 14.1$ Hz, 2H; CH$_2$ *eq*), 3.72 (d, $^2J_{HH} = 14.1$ Hz, 2H; CH$_2$ *eq*), 4.44 (d, $^2J_{HH} =$ 14.1 Hz, 4H; CH$_2$ *ax*), 4.74 (d, $^2J_{HH} = 14.8$ Hz, 2H; CH$_2$ *ax*), 7.01−7.30 (m, 12H; ArH); $^{31}$P NMR (dichloromethane-$d_2$, −20 °C) $\delta = 91.0$ (d, $^2J_{PP} = 126$ Hz, 1P; P trans to CH$_3$CN), 101.9 (dq, $^2J_{PP} = 126$ Hz, $^3J_{PH} = 12$ Hz, 1P; P trans to CH$_3$).

**(*syn*-1)PdC(O)CH$_3$(CH$_3$CN)$^+$OTf$^-$ (9).** A sample of ca. 0.03 mmol of **8** was dissolved in an NMR tube directly after synthesis in 0.4 mL of dichloromethane-$d_2$ and cooled to −20 °C in an acetone/dry ice bath. Carbon monoxide gas was bubbled through the solution in the NMR tube at −20 °C using a septum and a second needle to vent the excess gas. After 10 min the sample was transferred to the NMR apparatus and measured at −20 °C. For IR measurements the same procedure was followed using Schlenk techniques. After synthesis of complex **9** the solution was transferred into an IR cell at room temperature and measured immediately: yield 90% based on NMR; $^1$H NMR (dichloromethane-$d_2$, −20 °C) $\delta =$ 1.24 (s, 54H; *t*-Bu), 2.22 (bs, 15H; C$H_3$CN), 2.77 (s, 3H; C(O)-C$H_3$), 3.28 (d, $^2J_{HH} = 14.7$ Hz, 2H; CH$_2$ *eq*), 3.71 (2 × d, 4H; CH$_2$ *eq*), 4.41 (2 × d, 4H; CH$_2$ *ax*), 4.69 (d, $^2J_{HH} = 14.7$ Hz, 2H; CH$_2$ *ax*), 6.74−7.29 (m, 12H; ArH); $^{31}$P NMR (dichloromethane-$d_2$, −20 °C) $\delta = 88.2$ (d, $^2J_{PP} = 198$ Hz, 1P; P trans to CH$_3$-CN), 106.5 (d, $^2J_{PP} = 198$ Hz, 1P; P trans to C(O)CH$_3$); IR(CH$_2$Cl$_2$) $\nu$(cm$^{-1}$) 1718 (CO).

**(*syn*-1)PdCH$_2$CH$_2$C(O)CH$_3$$^+$OTf$^-$ (10).** A sample of **9** prepared in the way described above was treated with ethene gas at −20 °C in the NMR tube for 20 min, following the same procedure as was used for carbon monoxide gas. The sample was then transferred to the NMR apparatus and measured immediately at −20 °C. A solution of **9** prepared in the way described above was treated with ethene gas at room temperature for 10 min before it was transferred into an IR cell with a syringe: yield 100% based on NMR; $^1$H NMR (dichloromethane-$d_2$, −20 °C) $\delta = 1.25$ (s, 54H; *t*-Bu), 2.08 (bs, 15H; C$H_3$CN), 2.54 (s, 3H; C(O)C$H_3$), 2.85 (m, $^3J_{HH} = 5.6$ Hz, $^3J_{PH}$ $= 14$ Hz, 2H; Pd−CH$_2$C$H_2$C(O)), 3.31 (d, $^2J_{HH} = 14.6$ Hz, 2H; CH$_2$ *eq*), 3.44 (m, $^3J_{HH} = 5.6$ Hz, $^3J_{PH}$(trans) $= 14$ Hz, $^3J_{PH}$(cis) $= 14$ Hz, 2H; Pd−C$H_2$CH$_2$C(O)), 3.69 (d, $^2J_{HH} = 14.1$ Hz, 2H; CH$_2$ *eq*), 3.71 (d, $^2J_{HH} = 14.3$ Hz, 2H; CH$_2$ *eq*), 4.49 (pseudot, 4H; CH$_2$ *ax*), 4.74 (d, $^2J_{HH} = 14.6$ Hz, 2H; CH$_2$ *ax*), 7.03−7.30 (m, 12H; ArH); $^{31}$P NMR (dichloromethane-$d_2$, −20 °C) $\delta =$ 90.4 (d, $^2J_{PP} = 131$ Hz, 1P; P trans to C=*O*), 103.4 (dq, $^2J_{PP} =$ 131 Hz, $^3J_{PH} = 14$ Hz, 1P; P trans to −C$H_2$CH$_2$C(O)); IR(CH$_2$-Cl$_2$) $\nu$(cm$^{-1}$) 1624 (CO).

**2,4,8,10-Tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo-[*a,c*]cyclohepten-6-chloride.** This compound was prepared according to a slightly modified literature procedure.[56] 4,4′,6,6′-Tetra-*tert*-butyl-2,2′-bisphenol (4.1 g, 10 mmol) was azeotropically dried with dry toluene and dissolved in ca. 30 mL of dry toluene, and 5 mL of triethylamine was added. This solution was added dropwise to a solution of 1 mL of PCl$_3$ (11 mmol) in 150 mL of toluene at 0 °C under an argon atmosphere. After 1.5 h stirring at 0 °C the reaction was complete according to the $^{31}$P NMR spectrum. The mixture thus obtained was used without purification in the synthesis of (1,2-bis(2,4,8,-10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)ethane): $^{31}$P NMR (unlocked reaction mixture) $\delta =$ 173.7 (s, P; P(OR)$_2$Cl).

**2,2′-Bis(5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)biphenyl (12).** This ligand was synthesized using a literature procedure.[49] $^1$H NMR: $\delta = 6.87{-}7.55$ (m, 24H; ArH). $^{31}$P NMR: $\delta = 145$ (s, P; P(OR)$_3$).

**1,2-Bis(2,4,8,10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)ethane (13).** This ligand was synthesized using a literature procedure.[56] To a solution of 2,4,8,10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-chloride in toluene was added a solution of 0.45 mL of 1,2-ethanediol and 2 mL of triethylamine in 20 mL toluene at room temperature. After stirring overnight the formed salt was filtered off, and the filtrate was concentrated by evaporation of the solvent. Acetonitrile was added to the white solid, and the suspension was filtered and dried in vacuo. The white solid thus obtained was spectroscopically pure and used without further purification: mp = 235 °C; $^1$H NMR (benzene-$d_6$) $\delta = 1.31$ (s, 36H; *t*-Bu), 1.61 (s, 36H; *t*-Bu), 3.95 (d, $J = 5.6$ Hz, 4H; CH$_2$), 7.40 (d, $^4J_{HH} = 2.3$ Hz, 4H; ArH), 7.64 (d, $^4J_{HH} = 2.2$ Hz, 4H; ArH); $^{13}$C NMR (benzene-$d_6$) $\delta =$ 31.00, 31.36 (s; *C*H$_3$), 34.43, 35.42 (s; *C*(CH$_3$)$_3$), 63.89 (s; *C*H$_2$O), 124.21, 126.80 (s; Ar*C*H), 133.28 (d, $^2J_{PC} = 3.0$ Hz; Ar*C*), 140.30, 146.51 (s; Ar*C*), 146.84 (d, $^3J_{PC} = 5.3$ Hz; Ar*C*); $^{31}$P NMR (benzene-$d_6$) $\delta = 134.5$ (s, 2P; P(OR)$_3$).

**Bis(triphenyl phosphite)Pd(CH$_3$)Cl (14).** This compound was synthesized via a literature procedure:[50] $^1$H NMR $\delta = 0.29$ (t, $^3J_{PH} = 5.4$ Hz, 3H; −CH$_3$ trans complex), 0.65 (dd, $^3J_{PH}$-(trans) $= 11.3$ Hz, $^3J_{PH}$(cis) $= 2.1$ Hz, 3H; −CH$_3$ cis complex), 6.90−7.33 (m; ArH of both cis and trans complex); $^{31}$P NMR $\delta$ $= 107.4$ (s, 2P; P of trans complex), 108.5 (d, 1P, $^2J_{PP} = 84$ Hz; P cis to −CH$_3$), 115.0 (dq, 1P, $^2J_{PP} = 84$ Hz, $^3J_{PH} = 11.3$ Hz; P trans to −CH$_3$).

**(1,2-Bis(2,4,8,10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)ethane)Pd(CH$_3$)Cl (15).** A 0.08 mmol (78 mg) sample of (1,2-bis(2,4,8,10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a,c*]cyclohepten-6-yloxy)-ethane) (**13**) was azeotropically dried with toluene and dissolved in toluene. Subsequently 0.08 mmol (20 mg) of (cod)Pd(CH$_3$)Cl was added, and the solution was allowed to stir for 3 h. The solution was concentrated, pentane was added, and the formed precipitate was washed several times with pentane. The solid was then dried in vacuo. Yield: 62 mg (0.057 mmol, 71%); mp = 227 °C; $^1$H NMR (benzene-$d_6$) $\delta =$ 1.27 (s, 18H; *t*-Bu), 1.32 (s, 18H; *t*-Bu), 1.44 (dd, $^3J_{PH}$(trans) $=$ 12 Hz, $^3J_{PH}$(cis) $= 2$ Hz, 3H; Pd−CH$_3$), 1.76 (s, 18H; *t*-Bu), 1.85 (s, 18H; *t*-Bu), 3.79 (d, $J = 13.3$ Hz, 4H; CH$_2$), 7.35 (d, $^4J_{HH} =$ 2.3 Hz, 2H; ArH), 7.41 (d, $^4J_{HH} = 2.3$ Hz, 4H; ArH), 7.67 (d, $^4J_{HH} = 2.3$ Hz, 2H; ArH), 7.72 (d, $^4J_{HH} = 2.3$ Hz, 2H; ArH); $^{13}$C NMR (benzene-$d_6$) $\delta = 31.3$, 31.4, 32.2, 32.3 (s; *C*H$_3$), 34.7, 36.0 (s; *C*(CH$_3$)$_3$), 66.3 (s; *C*H$_2$), 124.9, 125.5 (s; Ar*C*H), 145.0 (d, $J_{PC} = 12.1$ Hz; Ar*C*H), 146.5 (d, $J_{PC} = 12.1$ Hz; Ar*C*H), 132.0 (s; Ar*C*), 132.4 (d, $J_{PC} = 2.3$ Hz; Ar*C*), 140.0 (d, $J_{PC} = 3.0$ Hz; Ar*C*), 147.7, 148.4 (s; Ar*C*); $^{31}$P NMR (benzene-$d_6$) $\delta = 130.7$ (d, 1P, $^2J_{PP} = 85$ Hz; P cis to −CH$_3$), 140.0 (dq, 1P, $^2J_{PP} = 85$ Hz, $^3J_{PH} = 12$ Hz; P trans to −CH$_3$); IR(KBr) $\nu$(cm$^{-1}$) 2963, 2900, 2850 (C−H alif.); 1460, 1439, 1400, 1364 (C=C); 1223, 1170 (C−O); 1123, 1087, 929, 885 (C−O−P). Anal. Calcd for $C_{59}H_{87}O_6P_2PdCl$: C 64.64, H 8.01. Found: C 63.85, H 8.00.

**Crystal Structure Determination and Refinement of 3.** A yellow, block-shaped crystal, cut from a larger aggregate, was glued to the tip of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-Turbo diffractometer on rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of 25 well-centered reflections

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**Table 3. Crystallographic Data for 3**

| | |
|---|---|
| Crystal Data | |
| formula | $C_{66}H_{78}Cl_2O_6P_2Pd.2C_4H_{10}O.CH_2Cl_2$[a] |
| molecular weight | 1451.8[a] |
| crystal system | orthorhombic |
| space group | $P2_12_12_1$ (No. 19) |
| $a$, Å | 17.5161(15) |
| $b$, Å | 19.6126(13) |
| $c$, Å | 21.838(3) |
| $V$, Å$^3$ | 7502.1(13) |
| $D_{calc}$, g cm$^{-3}$ | 1.285[a] |
| $Z$ | 4 |
| $F$(000) | 3056[a] |
| $\mu$, cm$^{-1}$ | 4.8[a] |
| crystal size, mm | 0.2 × 0.2 × 0.2 |
| Data Collection | |
| $T$, K | 150 |
| $\theta_{min}$, $\theta_{max}$, deg | 0.93, 27.49 |
| wavelength (Mo Kα), Å | 0.71073 (graphite monochromator) |
| scan type | $\omega$ |
| $\Delta\omega$, deg | $0.95 + 0.35 \tan\theta$ |
| hor., ver. aperture, mm | $3.00 + 1.50 \tan\theta$, 4.00 |
| X-ray exposure time, h | 26 |
| linear decay, % | 2 |
| ref reflns | $\bar{2}\,\bar{3}\,4$, $\bar{3}\,\bar{2}\,4$, $4\,\bar{4}\,\bar{2}$ |
| data set ($hkl$) | −22:0, −25:13, −28:0 |
| total no. of data | 9721 |
| total no. of unique data | 9656 |
| Refinement | |
| no. of refined params | 713 |
| wR2[b] | 0.1250 |
| $R$[c] | 0.0626 [for $5134 F_o > 4\sigma(F_o)$] |
| $S$ | 0.836 |
| $w^{-1}$[d] | $\sigma^2(F^2) + (0.0438P)^2$ |
| $(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$ | 0.000, 0.002 |
| min. and max. residual density, e/Å$^{-3}$ | −0.64, 0.88 |

[a] Including disordered solvent contribution (see text). [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $R = \sum ||F_o| - |F_c||/\sum|F_o|$. [d] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

(set4)[57] in the range 11.6° < $\theta$ < 13.80°. The unit-cell parameters were checked for the presence of higher lattice symmetry.[58] Crystal data and details on data collection and refinement are given in Table 3. Data were corrected for $Lp$ effects and the observed linear decay, but not for absorption. The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86).[59] Refinement on $F^2$ was carried out by full-matrix least-squares techniques (SHELXL-93);[60] no observance criterium was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. Connected channels, with a total volume of 2203 Å$^3$-per unit cell, were found to be filled with disordered solvent molecules, probably diethyl ether and methylene chloride in a ratio of 2:1. No satisfactory model could be refined. This disordered density was taken into account with the SQUEEZE procedure, as implemented in PLATON.[61] A total electron count of 461 per unit cell was found and corrected for. The highly anisotropic displacement parameters of the methyl carbon atoms of the *tert*-butyl moieties are indicative of slight rotational disorder. Refinement of a racemic twin model resulted in better $R$-values; the component ratio refined to 0.22(5):0.78. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms, respectively. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.[62] Geometrical calculations and illustrations were performed with PLATON.[61] All calculations were performed on a DECstation 5000/125.

Full information on the crystal structure determination can be found as Supporting Information of ref 30.

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**Supporting Information Available:** Further details of the structure determinations, including atomic coordinates, bond lengths and angles, and thermal parameters for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990209P

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