Nonsymmetric Palladium Complexes of Partly Fluorinated Bisphosphine Ligands: Efficient Catalysts for Flexible Propene/CO Copolymer Materials of Ultrahigh Molecular Weight

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Five new nonsymmetric 1-diphenylphosphino-3-{bis[aryl]phosphino}propane ligands **1b**−**f** [aryl: **b** = 3,5-bis(trifluoromethyl)phenyl, **c** = 3,5-dimethylphenyl, **d** = 3,5-difluorophenyl, **e** = 2-(trifluoromethyl)phenyl, **f** = 2,4,6-trifluorophenyl] and their corresponding neutral dichloro palladium(II) **2b**−**f**, diiodo palladium(II) **3d**,**e**, and dicationic diacetonitrile palladium(II) ditetrafluoroborate complexes **4b**−**f** were synthesized. The symmetric ligand 1,3-bis{bis[3,5-bis(trifluoromethyl)phenyl]phosphino}propane (**1a**) and the related palladium(II) complexes **2a** and **4a** were prepared for comparison. Solid state structures of new ligands were determined by X-ray structure analysis in the form of the dichloro (**2a**−**c**,**f**) and diiodo (**3d**,**e**) compounds. The properties of the symmetric (**4a**) and nonsymmetric catalysts (**4b**−**f**) were tested in propene/CO copolymerization experiments. A clear correlation between primarily steric effects of these ligands and the catalyst activity as well as the molecular weight of the resulting polyketone materials was observed. The nonsymmetric structure **4b**, bearing CF_3 groups in the 3,5-position of two aryl units on one phosphorus side, proved to be the most effective catalyst, which reached an activity maximum (12.7 kg[mol(Pd) × h]$^{-1}$) and led at the same time to propene/CO copolymers of high molecular weight ($\bar{M}_w \approx 5 \times 10^5$ g mol^{-1}). The same catalyst species **4b** affords even ultrahigh molecular weight ethene/propene/CO terpolymers with $\bar{M}_w \approx 8 \times 10^5$ g mol^{-1}. These novel polyketones possess a predominantly regio*ir*regular microstructure, leading to interesting flexible material properties in contrast to already known regioregular and thereby brittle propene/CO copolymers.

Introduction

The metal-catalyzed copolymerization of olefins with polar monomers is still an attractive field to create new materials from simple technical monomers. In particular, the highly crystalline ethene/CO copolymers represent an established and well-investigated class of such polar structures.[1,2] We recently opened a route to regio- and stereo*ir*regular and hence elastic propene/CO co- and propene/ethene/CO terpolymers of increased molecular weight that—besides new material properties—offer a chance for improved processability, due to reduced melting transitions.[3,4] Nevertheless, the insufficient activity of the applied (dppp)Pd(II) catalysts[5] prompted us to look for other catalyst lead structures. We report here on a series of new nonsymmetric bisphosphine ligands bearing partially fluorinated aromatic substituents at one of the phosphorus moieties, on the corresponding palladium(II) complexes, and on their polymerization performance (Chart 1).[6,7] This structural motif of partly fluoro-substituted, nonsymmetric complexes allows the combination of a superior

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(1) (a) *Eur. Plast. News* **1995**, *Oct*, 57. (b) Shell, Carilon Thermoplastic Polymers, Information Sheet, 1994.

(2) For recent reviews see: (a) Bianchini, C.; Meli, A. *Coord. Chem. Rev.* **2002**, *225* (1−2), 35. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. *Angew. Chem., Int. Ed.* **2000**, *38*, 428. (d) Drent, E.; Budzelaar, P. H. M. *Chem. Rev.* **1996**, *96*, 663. (e) Cavell, K. *J. Coord. Chem. Rev.* **1996**, *155*, 209.

(3) (a) Mücke, A.; Rieger, B. *Macromolecules* **2002**, *35*, 2865. (b) Huhn, W.; Hollmann, F.; Hild, S.; Kriewall, T.; Rieger, B. *Macromol. Mater. Eng.* **2000**, *283*, 115.

(4) This approach was taken up by other groups that used Consiglio's concept of alkyl-substituted bisphosphine ligands to produce propene/CO copolymers of relatively high molecular weight by comprising a regioregular microstructure that leads to brittle polymers. (a) Lindner, E.; Schmid, M.; Wald, J.; Queisser, J. A.; Geprägs, M.; Wegner, P.; Nachtigal, C. *J. Organomet. Chem.* **2000**, *602*, 173. (b) Batistini, A.; Consiglio, G.; Suter, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 303. (c) Barsacchi, M.; Batistini, A.; Consiglio, G.; Suter, U. W. *Macromolecules* **1992**, *25*, 3604.

(5) dppp: 1,3-bis(diphenylphosphino)propane.

(6) For reports on nonsymmetric catalysts in 1-olefin/CO copolymerization reactions see: (a) Gambs, C.; Chaloupka, S.; Consiglio, G.; Togni, A. *Angew. Chem.* **2000**, *112*, 2602; *Angew. Chem., Int. Ed.* **2000**, *39*, 2486. (b) Nozaki, K.; Hiyama, T. *Organometallics* **2000**, *19*, 2031. (c) Nozaki, K.; Sato, N.; Tonomura, Y.; Yasutomi, M.; Takaya, H.; Hiyama, T.; Matsubara, T.; Koga, N. *J. Am. Chem. Soc.* **1997**, *119*, 12779. (d) Keim, W.; Mass, H. *J. Organomet. Chem.* **1996**, *514*, 271. (e) Van Leeuwen, P. W. N. M.; Roobeek, C. F.; van der Heijden, H. *J. Am. Chem. Soc.* **1994**, *116*, 12117.

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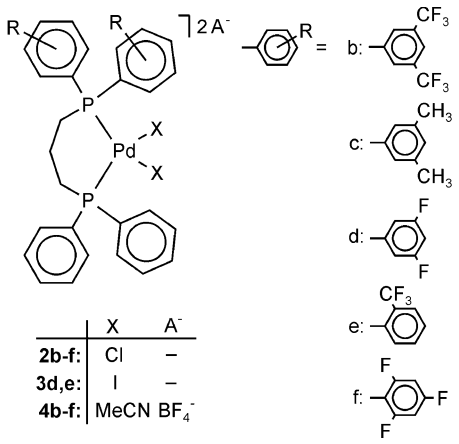
Chart 1. Novel Nonsymmetric Bisphosphine Pd(II) Complexes



catalyst activity with unexpectedly high product molecular weights and interesting properties of the flexible polyketone materials, due to a variable regioregularity of their microstructure.

Results and Discussion

Ligand and Complex Synthesis. The symmetric bisphosphine **1a** is accessible by treatment of the deprotonated secondary phosphine **5** with 0.5 equiv of 1,3-dibromopropane (Scheme 1A). Nonsymmetric propyl-bridged bisphosphines are accessible by the reaction of secondary phosphides with 3-chloropropyl diarylphosphines.[8] In a modified procedure ligand **1b** was obtained in high yield and purity by deprotonation of the CF_3-substituted compound **5** with KOH in DMSO,[9] followed by addition of the alkyl chloride **6**.[10]

This strategy is not suitable for the preparation of nonsymmetric bisphosphines containing ring-fluorinated phenyl groups (e.g., Scheme 1B, **1d**,**f**), as the phosphide anion attacks the aryl−fluorine bond. Therefore, phenyl(3-phosphinopropyl)phosphine (**8**) (from **7** by reduction with $LiAlH_4$[11]) was treated with 2 equiv of Br_2,[12] resulting in the hydrobromide **9**, which affords after deprotonation and substitution with the fluorinated Grignard reagents the desired ligands **1c**−**f**.

The dichloro palladium(II) complexes **2a**−**f** were prepared by reaction of the corresponding bisphosphines (**1a**−**f**) with $(COD)PdCl_2$ in CH_2Cl_2 (Scheme 2). Complexes **2d**,**e** were converted into the diiodo palladium(II) compounds (**3d**,**e**) by treatment with NaI in DMSO to achieve better solubility and crystallization properties. The dicationic complexes **4a**−**f** were obtained from **2a**−**d**,**f** and **3e** by halide abstraction using $AgBF_4$ in acetonitrile.

Solid State Structures. Single crystals of the dichloro (**2a**−**c**,**f**) and diiodo complexes (**3d**,**e**), grown from solvent mixtures (cf. Experimental Section), were characterized by X-ray structure analysis. The crystallographic results of **2a**,**b**,**f** and **3e** are depicted in Figures 1−4 and Table 1, and the data of **2c** and **3d** are summarized in the Supporting Information.

The gross coordination geometry around the Pd(II) centers in all investigated solid state structures is nearly ideal square-planar, independent of the particular substitution of the chelating bisphosphine ligand and of the halide atoms (Cl: **2a**−**c**,**f**; I: **3d**,**e**). The structures of the symmetric complex **2a** and the nonsymmetric complex **2b** indicate the bulkiness of the CF_3-substituted phenyl groups, which afford a parallel orientation of axial phenyl rings. This leads in the case of **2a** to a shielding of the Pd(II) center (cf. polymerization experiments). The bond angles P−Pd−Hal range from 86.03 (8)° to 90.31(3)° at the PPh_2 side and from 86.60(4)° to 92.39(11)° at the PAr_2 moiety (Table 2).[13−15] However, no clear correlation of angles, bond lengths, and the particular aryl substitution of the complexes can be found. There is no indication that number or position of CF_3, CH_3, and F substituents in the complexes **2a**−**c**,**f** and **3d** influence bond lengths and bond angles in a predictable manner. Only in the case of **3e** are the P−Pd−I angle (92.39(11)°) and the Pd−P bond length (2.310(4) Å) at the ortho-CF_3-substituted part increased compared to the corresponding values at the phenyl side (87.93(11)°; 2.276(4) Å), resulting from repulsive effects of these bulky ortho-substituents. The same argument can be used to explain the splitting of ^1H and ^{19}F NMR signals in the Pd(II) complexes of ligand **1e**, as free rotation of the aryl fragments is restricted.

Complexes **2a**−**c** and **3d** were found in the solid state to exist in a chair conformation formed by the six-membered metallacycles. This implies that the two aromatic substituents on one side of the P1−Pd−P2 plane are both oriented either in an axial or in an equatorial direction. Complexes **2f** and **3e** show a twist conformation of the metallacycles, affording an axial/equatorial orientation of the phenyl groups attached to the phosphorus atoms. However, we have no evidence that the different bridge arrangements are present in solution as well. The ^{31}P NMR spectra give just one signal for **2a** and two resonances for the nonsymmetric complexes, as expected for systems with highly flexible bridge conformations.

Propene/CO Co- and Terpolymerization Experiments. All copolymerization experiments were per-

(7) For reports on nonsymmetric complexes in catalysis see: (a) Casey, P. C.; Paulsen, E. L.; Beuttenmueller, E. W.; Proft, B. R.; Matter, B. A.; Powell, D. R. *J. Am. Chem. Soc.* **1999**, *121*, 63. (b) RajanBabu, T. V.; Casalnuovo, A. L. *J. Am. Chem. Soc.* **1996**, *118*, 6325. (c) Nozaki, K.; Li, W.; Horiuchi, T.; Takaya, H.; Saito, T.; Yoshida, A.; Matsumara, K.; Kato, Y.; Imai, T.; Miura, T.; Kumobayashi, H. *J. Org. Chem.* **1996**, *61*, 7658. (d) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033.

(8) (a) Renaud, E.; Russell, R. B.; Fortier, S.; Brown, S. J.; Baird, M. C. *J. Organomet. Chem.* **1991**, *419*, 403. (b) Arpac, E.; Dahlenburg, L. *Z. Naturforsch.* **1980**, *35b*, 146. (c) Grim, S. O.; Barth, R. C. *J. Organomet. Chem.* **1975**, *94*, 327.

(9) For deprotonation of sec. phosphines in DMSO with KOH see: (a) Tsvetkov, E. N.; Bondarenko, N. A.; Malakhova, I. G.; Kabachnik, M. I. *Synthesis* **1986**, *3*, 198. (b) Tsvetkov, E. N.; Bondarenko, N. A.; Malakhova, I. G.; Kabachnik, M. I. *J. Gen. Chem. USSR* (Engl. Transl.) **1985**, *55* (1), 8.

(10) For the synthesis of **1b** via radical-induced addition of secondary phosphines and allylphosphines see Supporting Information.

(11) For similar reactions see: Baacke, M.; Hietkamp, S.; Morton, S.; Stelzer, O. *Chem. Ber.* **1981**, *114*, 2568.

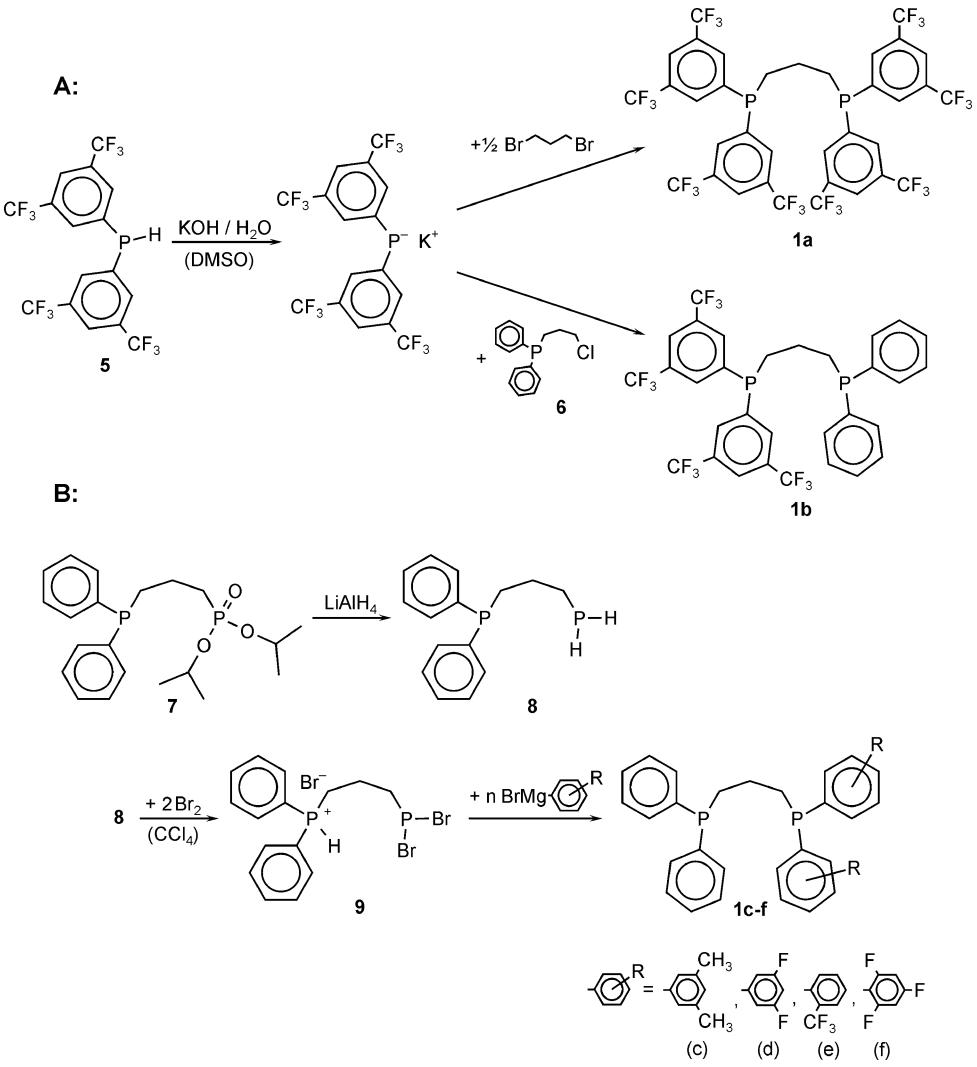
(12) For similar reactions see: Goerlich, J. R.; Weiss, J.-V.; Jones, P. G.; Schmutzler, R. *Phosphorus, Sulfur Silicon* **1992**, *66*, 223.

(13) The bond lengths and angles around the Pd(II) ion of all investigated complexes (Table 2) are similar to corresponding literature-known values in related phenyl-substituted bisphosphine dihalide Pd(II) compounds. $(dppp)PdCl_2$ (cf. ref 14): Pd−P (2.244(1)/2.249(2) Å); Pd−Cl (2.351(1)/2.358(2) Å). The bond angles P−Pd−P (90.58(5)°) and Cl−Pd−Cl (90.78(5)°) resemble those found in our study. The values of the diiodo complexes **3d**,**e** resemble those of [1,2-bis(diphenylphosphino)ethane]PdI_2 (cf. ref 15): Pd−P (2.2608(14)/2.2756(12) Å); Pd−I bond lengths (2.6649(8)/2.6446(10) Å).

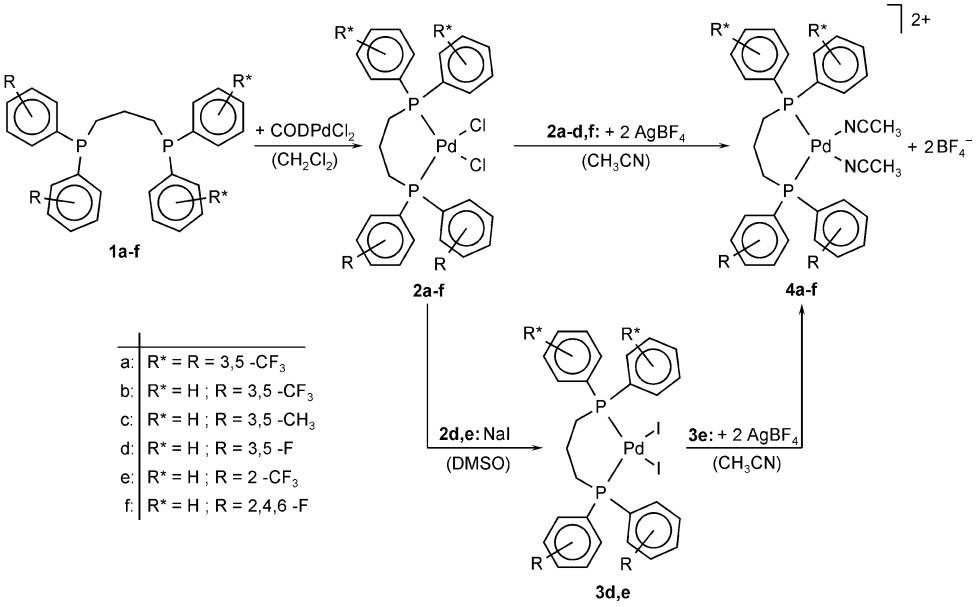
(14) Steffen, W. L.; Palenik G. J. *Inorg. Chem.* **1976**, *15*, 2432.

(15) Oberhauser, W.; Bachmann, C.; Stampfl, T.; Haid, R.; Brügeller, P. *Polyhedron* **1997**, *16*, 2827.

Scheme 1. Synthesis of the Symmetric (1a) and Nonsymmetric Bisphosphine Ligands (1b−f)



Scheme 2. Preparation of the Neutral (2a−f, 3d,e) and Dicationic Pd(II) Complexes (4a−f)



formed in a 250 mL steel autoclave. The catalyst precursor complexes **4a**−**g** (**4g**: $[(CH_3CN)_2dpppPd](BF_4)_2$) were dissolved in dichloromethane and activated by adding an optimized amount of methanol.[16,17] The polydispersities of all copolymer products are in the range $\bar{M}_w/\bar{M}_n = 1.4-1.8$, indicating the homogeneity of the copolymerization reactions (Table 3). All experiments have been performed at least twice to ensure

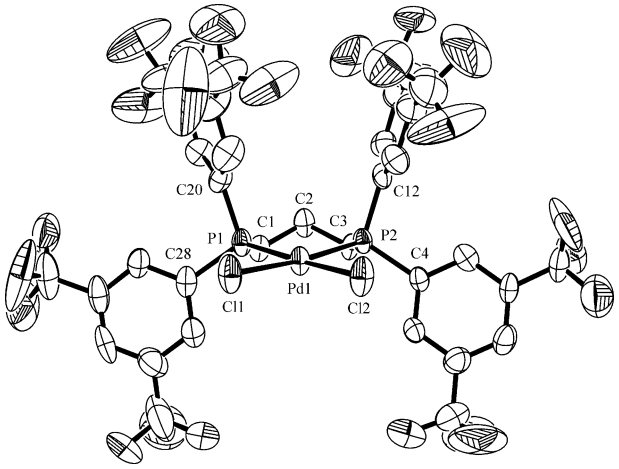


Figure 1. ORTEP plot and atom-labeling scheme of complex **2a**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms, THF molecules, and second independent complex molecule are omitted.

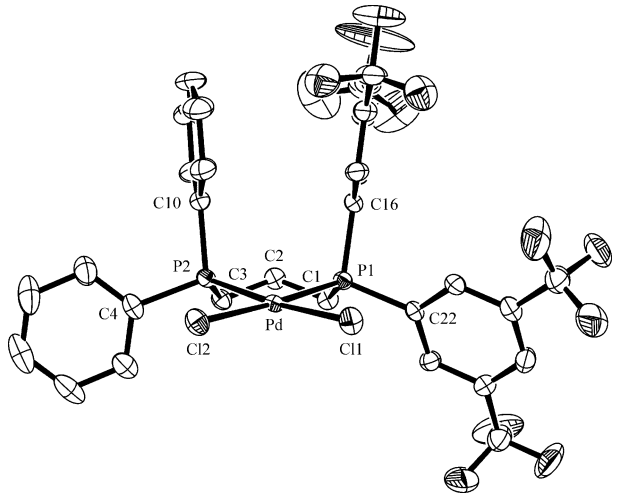


Figure 2. ORTEP plot and atom-labeling scheme of complex **2b**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms are omitted.

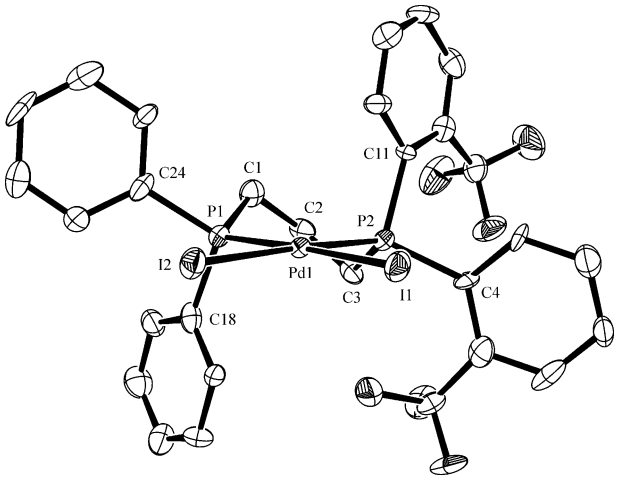


Figure 3. ORTEP plot and atom-labeling scheme of complex **3e**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms and $CHCl_3$ molecules are omitted.

reproducibility. We used the dppp complex **4g** as reference catalyst, which gave regio*ir*regular propene/CO copolymers with medium to high molecular weights of about $\bar{M}_w = 1.6 \times 10^5$ g mol^{-1} (Table 3, entry 7).[18] To screen the influence of bulky, electron-withdrawing substituents on the aromatic fragments of the basic dppp ligand system, all four phenyl groups were exchanged in a first approach by 3,5-bis(trifluoromethyl)-phenyl units, leading to the symmetric complex **4a**, bearing eight CF_3 groups in all meta-positions of the phenyl rings. Polymerization experiments, however, revealed that this catalyst is obviously sterically overcrowded, so that the activity ($\approx$ 0.5 of the dppp catalyst **4g**) and—as a consequence—also the molecular weight of the polymer product are considerably reduced ($\bar{M}_w = 1.0 \times 10^5$ g mol^{-1}).

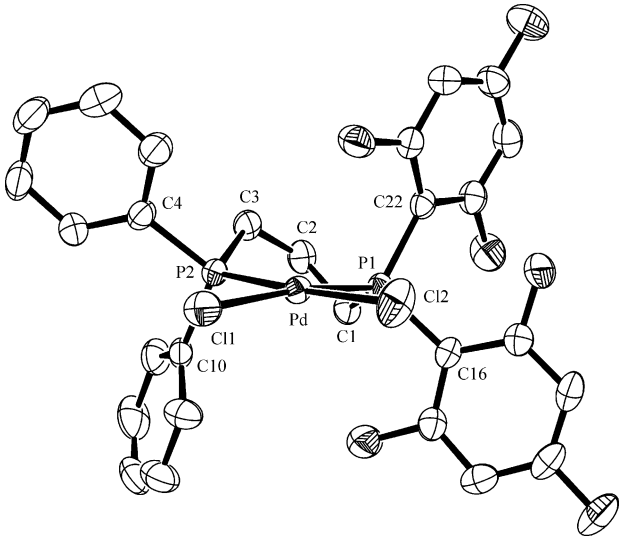


Figure 4. ORTEP plot and atom-labeling scheme of complex **2f**. Thermal ellipsoids are depicted at the 50% probability level. Hydrogen atoms and DMSO molecules are omitted.

This situation changed completely when the nonsymmetric complex **4b**, bearing four *m*-CF_3 substituents on only one ligand side, was applied (Figure 5). Most interestingly, **4b** leads to significantly increased activity (Table 3, entry 2), reaching values up to about 13 kg [mol(Pd) $\times$ h]$^{-1}$. In addition, **4b** gives the highest molecular weight propene/CO copolymers ($\bar{M}_w \approx 5 \times 10^5$ g mol^{-1}) that still shows flexible material properties,[19] due to the just slightly enriched regioregularity relative to the dppp catalyst **4g** (H−T; **4g**: 56%, **4b**: 71%; Table 3). This success prompted us to look into ethene/propene/CO terpolymerization experiments using our recently developed "pulse feed polymerization technique" (PFP)[3b] comprising the pulsewise addition of the faster ethene monomer to a running propene/CO copolymerization experiment. This protocol simulates a low, nonconstant C_2 concentration during the entire polymerization period affording new, soluble C_2/C_3/CO-terpolymers with high C_2 content. The molecular weight

(16) Abu-Surrah, A. S.; Wursche, R.; Eckert, G.; Pechold, W.; Rieger, B. *Macromolecules* **1996**, *29*, 4806.
(17) The actual concentration of catalytically active bisphosphine Pd(II) units was determined by adding a defined amount of inert standard (diphenylmethylphosphineoxide) to ^{31}P NMR samples of the catalyst precursors **4a**−**g**. The ratio of the ^{31}P signals from phosphineoxide to P resonances of the complex delivers the desired concentration values (error ± 5%).
(18) Abu-Surrah, A. S.; Rieger, B. *Top. Catal.* **1999**, *7*, 165.
(19) Detailed analysis of material properties will be published elsewhere.

Table 1. Summary of Crystal Data and Structure Refinement Parameters for 2a, 2b, 3e, and 2f

	2a·1.5THF	**2b**	**3e**·2$CHCl_3$	**2f**·DMSO
empirical formula	$C_{41}H_{30}Cl_2F_{24}O_{1.5}P_2Pd$	$C_{31}H_{22}Cl_2F_{12}P_2Pd$	$C_{31}H_{26}Cl_6F_6I_2P_2Pd$	$C_{29}H_{26}Cl_2F_6OP_2PdS$
fw	1241.89	861.73	1147.36	775.80
cryst color and shape	colorless prism	colorless prism	red needle fragment	yellow prism
cryst size, mm	0.50 × 0.25 × 0.07	0.37 × 0.34 × 0.15	0.40 × 0.26 × 0.15	0.24 × 0.22 × 0.15
cryst syst	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1$	$P2_1/n$	$P2_1/n$
a, Å	15.591(4)	13.626(2)	11.509(2)	12.377(3)
b, Å	27.100(8)	8.655(1)	15.023(2)	17.507(3)
c, Å	12.828(3)	13.946(2)	23.074(5)	14.526(3)
α, deg	101.92(2)	90	90	90
β, deg	90.37(2)	90.56(1)	102.92(2)	95.72(3)
γ, deg	77.52(2)	90	90	90
V, Å^3	5174(2)	1644.7(3)	3888.5(13)	3132.1(11)
Z	4	2	4	4
$D_{calcd.}$, g/cm^3	1.594	1.740	1.960	1.645
T, K	193	173	173	223
abs coeff, mm^{-1}	0.643	0.915	2.612	0.991
F(000)	2456	852	2200	1552
θ range, deg	2.57−24.00	2.77−25.98	2.20−24.00	2.02−25.92
index range	$0 \le h \le 17$	$-16 \le h \le 16$	$-13 \le h \le 13$	$-15 \le h \le 15$
	$-30 \le k \le 31$	$-10 \le k \le 10$	$-17 \le k \le 16$	$-19 \le k \le 19$
	$-14 \le l \le 14$	$-17 \le l \le 17$	$-26 \le l \le 26$	$-17 \le l \le 17$
no. of reflns collected	14 728	19 316	24 182	24 200
no. of unique reflns	14 178 [*R*(int) = 0.0363]	6184 [*R*(int) = 0.0365]	6030 [*R*(int) = 0.0526]	5749 [*R*(int) = 0.0442]
goodness-of-fit on F^2	1.036	1.008	1.255	0.999
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0759	R1 = 0.0247	R1 = 0.0854	R1 = 0.0296
	wR2 = 0.1745	wR2 = 0.0649	wR2 = 0.2018	wR2 = 0.0638
R indices (all data)	R1 = 0.1022	R1 = 0.0259	R1 = 0.0961	R1 = 0.0446
	wR2 = 0.1908	wR2 = 0.0654	wR2 = 0.2058	wR2 = 0.0667
largest diff peak and hole, e/Å^3	0.888 and −0.738	0.665 and −0.404	2.586 and −1.754	1.002 and −0.511

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2a, 2b, 3e, and 2f

2a		**2b**		**3e**		**2f**	
			Bond Lengths				
Pd(1)−P(1)	2.235(2)	Pd−P(1)	2.253(1)	Pd(1)−I(1)	2.641(2)	Pd−P(1)	2.233(1)
Pd(1)−P(2)	2.243(2)	Pd−P(2)	2.263(1)	Pd(1)−I(2)	2.631(2)	Pd−P(2)	2.247(1)
Pd(1)−Cl(1)	2.338(2)	Pd−Cl(1)	2.359(1)	Pd(1)−P(1)	2.276(4)	Pd−Cl(1)	2.357(1)
Pd(1)−Cl(2)	2.321(2)	Pd−Cl(2)	2.347(1)	Pd(1)−P(2)	2.310(4)	Pd−Cl(2)	2.355(1)
P(1)−C(1)	1.822(7)	P(1)−C(1)	1.817(3)	P(1)−C(1)	1.844(16)	P(1)−C(1)	1.831(3)
P(2)−C(3)	1.802(8)	P(2)−C(3)	1.825(3)	P(2)−C(3)	1.842(15)	P(2)−C(3)	1.834(3)
			Bond Angles				
P(1)−Pd(1)−P(2)	93.52(8)	P(1)−Pd−P(2)	89.49(3)	P(1)−Pd(1)−P(2)	90.71(14)	P(1)−Pd−P(2)	90.19(3)
Cl(1)−Pd(1)−Cl(2)	91.57(8)	Cl(1)−Pd−Cl(2)	90.27(3)	I(1)−Pd(1)−I(2)	88.91(5)	Cl(1)−Pd−Cl(2)	92.49(3)
P(1)−Pd(1)−Cl(1)	86.03(8)	P(1)−Pd−Cl(1)	89.55(3)	P(1)−Pd(1)−I(1)	176.55(11)	P(1)−Pd−Cl(2)	87.48(3)
P(1)−Pd(1)−Cl(2)	175.85(9)	P(1)−Pd−Cl(2)	176.20(4)	P(1)−Pd(1)−I(2)	87.93(11)	P(1)−Pd−Cl(1)	173.20(3)
P(2)−Pd(1)−Cl(2)	88.52(8)	P(2)−Pd−Cl(2)	90.31(3)	P(2)−Pd(1)−I(2)	177.04(12)	P(2)−Pd−Cl(1)	90.17(3)
P(2)−Pd(1)−Cl(1)	174.27(10)	P(2)−Pd−Cl(1)	174.23(4)	P(2)−Pd(1)−I(1)	92.39(11)	P(2)−Pd−Cl(2)	176.28(3)

of these terpolymer products rises to values up to $\bar{M}_w \approx 8 \times 10^5$ g mol^{-1} (activity: 14 kg [mol(Pd) × h]$^{-1}$, Table 3, entry 8), which belong to the highest ever reported values for this versatile class of materials.

To optimize the effect of a nonsymmetric catalyst architecture, the four *m*-CF_3 groups in **4b** were exchanged by sterically less demanding *m*-CH_3 and *m*-F substituents, affording the nonsymmetric complex species **4c** and **4d**, respectively. This, however, did not lead to substantial improvements relative to **4g**, with respect to both catalyst activity and product molecular weight. Introduction of CF_3 groups in 2- (**4e**) or fluorine substituents in the 2,4,6-position (**4f**) on two of the four aromatic units resulted in a significant reduction of catalyst performance, so that in the case of **4e** only low molecular weight propene/CO copolymers in low yield could be obtained.

The present study used six symmetric and nonsymmetric CH_3-, CF_3-, and F-substituted complexes for the copolymerization of propene and CO. Only the nonsymmetric catalyst **4b**, bearing four *m*-CF_3 groups, shows properties (activity, product molecular weight) that are superior to our reference **4g**. We have right now no genuine and consistent explanation for the outstanding

Table 3. Propene/Carbon Monoxide Copolymerization Experiments with Catalysts 4a−g and Ethene/Propene/CO Terpolymerization (PFP) Using 4b

entry	catalyst	yield[c]	activity[d]	$\bar{M}_w$[e]	$\bar{M}_w/\bar{M}_n$	regioreg.[f]	flexible
1[a]	**4a**	1.3	1.5	1.0	1.8	80	no
2[a]	**4b**	10.7	12.7	4.7	1.7	71	yes
3[a]	**4c**	3.4	4.1	1.7	1.5	64	yes
4[a]	**4d**	4.0	4.8	2.0	1.5	58	yes
5[a]	**4e**	0.4	0.5	0.3	1.4	68	yes
6[a]	**4f**	1.9	2.3	1.1	1.4	66	yes
7[a]	**4g**	2.9	3.5	1.6	1.5	56	yes
8[b]	**4b**	4.4	13.7	7.7	1.6	*g*	yes

[a] P/CO copolymerization: 250 mL steel autoclave, catalyst (40 μmol), CH_2Cl_2 (150 mL), MeOH (0.25 mL), propene (60 g), constant pressure CO (60 bar), 25 °C, 21 h. [b] E/P/CO terpolymerization: 250 mL steel autoclave, catalyst (15 μmol), CH_2Cl_2 (150 mL), MeOH (0.25 mL), propene (60 g), ethene (6 s pulse, 2 h interval), constant pressure CO (60 bar), 25 °C, 21 h. [c] [g]. [d] [kg(mol(Pd) h)$^{-1}$]. [e] [× 10^5 g mol^{-1}], determined by GPC in THF. [f] [%], ratio of head−tail units (H−T), determined by ^{13}C NMR. [g] Not determined.

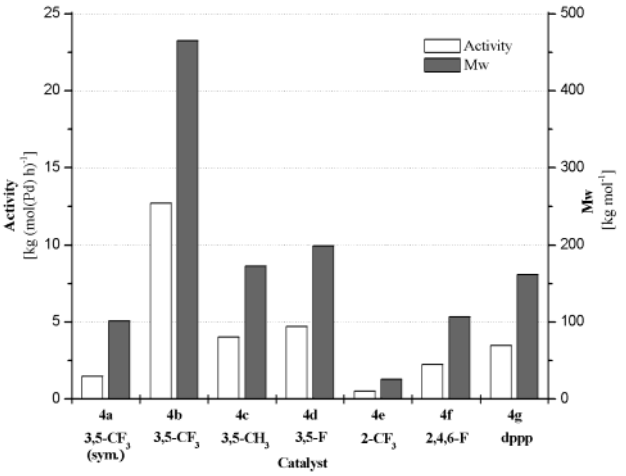


Figure 5. Comparison of catalyst activities and molecular weights.

Table 4. ^{31}P NMR Shifts of the P(Ar)$_2$ Part of Ligands 1a−f and Complexes 4a−f

	a	b	c	d	e	f
ligand **1**[a]	−14.9	−13.8	−17.0	−12.4	−26.7	−53.1
complex **4**[b]	21.1	14.3	12.0	14.4	31.4	−19.6

[a] [ppm], measured in $CDCl_3$, ^{31}P NMR shifts of P(Ph)$_2$ parts ranging between −16.5 and −17.3 ppm. [b] [ppm], measured in CD_3CN, ^{31}P NMR shifts of P(Ph)$_2$ parts ranging between 14.4 and 12.0 ppm.

performance of **4b**. A comparison of the ^{31}P NMR spectra of the ligands **1a**−**f** and of the corresponding dicationic palladium complexes **4a**−**f** (Table 4) does not point toward electron-donating or -withdrawing ligand effects as a satisfying reason for the observed catalytic potentials. The chemical shifts of the P atoms bearing substituted phenyl groups (**1a**−**d**) are nearly identical; only **1f** shows a significant chemical shift deviation. However, catalyst **4f** gives polymerization properties that are mediocre, with values for activity and molecular weight similar to **4a**,**g**.[20] Coordination of the ortho CF_3-substituted ligand on palladium in complex **4e** leads to a ^{31}P NMR shift of the aryl-substituted phosphorus, situated downfield of the PPh_2 signal, quite in contrast to the ^{31}P spectrum of ligand **1e**.[21] From steric considerations (see structure discussion) it is obvious that **4a** is sterically overcrowded, so that activity and molecular weight are low, due to hindrance of monomer coordination and orientation. The same effect can be used to explain the high regioregularity (H−T: 80%, Table 3) of products resulting from **4a**, leading to a preference of 1,2- over 2,1-propene insertions.[22] It is also conceivable that catalysts bearing CF_3 or F substituents in ortho-position (**4e**,**f**) show reduced activities and product molecular weights, due to steric hindrance again or to metal−F interactions, which compete with olefin coordination. The regioregularity of propene ketones resulting from **4b**−**d**,**g** seems also to follow the steric demand of the substituents decreasing in the order CF_3 (**4b**; H−T: 71%) > CH_3 (**4c**; 64%) > F (**4d**; 58%) > H (**4g**; 56%). This indicates that the 1,2-insertion of propene is controlled by the size of the phenyl groups. However, these arguments cannot be used to understand the high activity of **4b** relative to **4c**,**d**.[23] All three nonsymmetric catalysts contain four substituents in *m*-position. If the size of these groups controls the rates, **4d** would be expected to be the fastest catalyst. However, **4c** and **4d** show activities and molecular weights that are very similar to the dppp catalyst **4g**, and only **4b** has optimal properties. One contribution to this effect could be found in the slightly raised regioregularity of **4b** products, because the reduced rate for 2,1-insertions should decrease the concentration of species with a secondary carbon atom attached to the Pd(II) center and should therefore add to the overall chain growth rate. However, we do not think that this is a major contribution.

Conclusion

In our search for propene/CO copolymerization catalysts with improved performance, the present investigations lead to nonsymmetric Pd(II)-phosphine complexes as a new and successful structural motif. In particular, the substitution pattern of the nonsymmetric catalyst **4b**, bearing 3,5-bis(trifluoromethyl)phenyl substituents on one phosphorus moiety, proved to be surprisingly efficient, leading to high activities (13−14 kg [mol(Pd) × h]$^{-1}$) and enabled us to produce flexible propene/CO copolymers with high ($\bar{M}_w = 4.7 \times 10^5$ g mol^{-1}) and C_2/C_3/CO terpolymer of ultrahigh molecular weight ($\bar{M}_w = 8 \times 10^5$ g mol^{-1}). The solid state structures of all applied catalyst precursors were determined in order to find a structural explanation of this effect. The results, however, give right now no genuine explanation for the outstanding performance of only **4b**. Further investigations will be directed to gain a deeper insight into the basic mechanisms to understand this effect and to apply it to the production of new materials, using different monomer combinations.

Experimental Section

General Procedures. All reactions were performed under argon atmosphere using standard Schlenk techniques. Solvents were dried by distillation from drying agents (CaH_2 for dichloromethane, P_2O_5 for CCl_4, $LiAlH_4$ for diethyl ether, THF, and *n*-pentane) and deoxygenated. Dry acetonitrile was received from Roth, deoxygenated in vacuo, and stored over 3 Å molecular sieves. DMSO and H_2O were deoxygenated in vacuo. Chemicals were used as received from Merck (Br_2), Aldrich (1,3-dibromopropane, $AgBF_4$), Lancester (5-bromo-*m*-xylene), and ABCR (1-bromo-3,5-bis(trifluoromethyl)benzene, 1-bromo-3,5-difluorobenzene, 1-bromo-2,4,6-trifluorobenzene, 1-bromo-2-(trifluoromethyl)benzene). Bis[3,5-bis(trifluoromethyl)phenyl]-phosphine,[24] 3-chloropropyldiphenylphosphine,[25] diisopropyl-3-(diphenylphosphino)propylphosphonate,[26] (COD)$PdCl_2$,[27] and **4g**[28] were prepared according to literature procedures. ^{1}H, ^{13}C,

(20) This is in slight contrast to previous work of Consiglio et al. (cf. ref 6a). These authors found a relation between an activity increase and electron-withdrawing effects of CF_3-substituted, chiral bisphosphine Pd(II) catalysts.

(21) For similar shift behavior see ref 7a.

(22) This gives in the case of catalyst **4a** a regioregular and thus brittle material.

(23) In the present study the increase of activity is always connected with higher product molecular weights. This indicates that the enhanced activity results from a faster olefin insertion rate, which was shown to be the rate-limiting step in this polymerization reaction.

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^{19}F, and ^{31}P NMR spectra were recorded on a Bruker DRX 400. In ^{1}H and ^{13}C spectra TMS was used as internal standard. ^{31}P shifts have been referenced to the external standard H_3PO_4 (85%). ^{19}F NMR spectra are calibrated to CCl_3F as internal standard. IR spectra were measured on a Bruker IFS 113v spectrometer. Mass spectra were acquired with Finnigan SSQ 7000 and TSQ 7000 instruments. X-ray structure analyses were performed as described. In the polymerization experiments propene (2.6), ethene (2.7), and carbon monoxide (2.0) were used without further purification as received from BASF.

Caution. Grignard reagents of fluorinated aromatics can be explosive in the solid state and therefore should be handled carefully in diluted solution.

1,3-Bis{bis[3,5-bis(trifluoromethyl)phenyl]phosphino}-propane (1a). Bis(3,5-bis(trifluoromethyl)phenyl)phosphine (**5**) (7.06 g, 15.41 mmol) was suspended in DMSO (60 mL). Addition of an aqueous solution of KOH (1.12 g, 20.03 mmol, 1.5 mL of H_2O) gave a dark red solution. After stirring for 30 min 1,3-dibromopropane (1.55 g, 7.71 mmol) was added and stirred for a further 48 h at room temperature. The reaction mixture was poured into H_2O. The precipitate was separated, dissolved in ether, washed three times with water, dried (Na_2SO_4), and evaporated. The residue was washed with *n*-pentane and evaporated in vacuo.

Yield: 5 g (68%). ^{1}H NMR ($CDCl_3$): δ 7.88 (s, 4H, para Ar), 7.77 (d, 8H, ortho Ar), 2.35 (t, 4H, $-CH_2P$), 1.61 (m, 2H, $-CH_2-$). ^{13}C NMR ($CDCl_3$): δ 139.93 (d, ipso Ar), 132.7−132.1 (m, ortho Ar, meta Ar), 123.65 (sept, para Ar), 122.89 (q, CF_3), 28.86 (vt, $-CH_2P$), 21.92 (t, $-CH_2-$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −14.88 (s). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −63.62 (s). MS (EI, *m*/*z* (%)): 743 (100) $[M - Ar]^+$, 956 (15) $[M]^+$, 937 (8) $[M - F]^+$.[29]

1-Diphenylphosphino-3-{bis[3,5-bis(trifluoromethyl)-phenyl]phosphino}propane (1b). Bis(3,5-bis(trifluoromethyl)phenyl)phosphine (**5**) (6.34 g, 13.84 mmol) was suspended in DMSO (50 mL) and deprotonated by addition of aqueous KOH solution (1.01 g, 17.99 mmol, 2 mL of H_2O). The dark red solution was stirred for 30 min. A solution of 3-chloropropyldiphenylphosphine (**6**) (3.40 g, 12.94 mmol) in DMSO (15 mL) was added, and the mixture was stirred for 24 h at room temperature and an additional 2 h at 50 °C. The reaction mixture was poured into water (300 mL) after cooling to ambient temperature. NaCl was added to the resulting emulsion. The separated oily phase was dissolved in ether, washed three times with water, dried over Na_2SO_4, and evaporated. Excess bis(3,5-bis(trifluoromethyl)phenyl)phosphine was removed by distillation at 130 °C in vacuo.

Yield: 6.6 g (70%). ^{1}H NMR ($CDCl_3$): δ 7.86 (s, 2H, para Ar), 7.75 (d, 4H, ortho Ar), 7.39−7.32 (m, 4H, Ph), 7.31−7.27 (m, 6H, Ph), 2.27 (t, 2H, $-CH_2PAr_2$), 2.22 (t, 2H, $-CH_2PPh_2$), 1.59 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 140.65 (d, ipso Ar), 138.00 (d, ipso Ph), 132.8−132.3 (m, ortho Ph, meta Ar, ortho Ar), 123.34 (sept, para Ar), 122.99 (q, CF_3), 29.37 (vt, $-CH_2P$), 28.97 (vt, $-CH_2P'$), 22.15 (vt, $-CH_2-$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −13.84 (s, PAr_2), −17.16 (s, PPh_2). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −63.45 (s). MS (CI, *m*/*z* (%)): 665 (100) $[M - F]^+$, 685 (89) $[MH]^+$, 607 (6) $[M - Ph]^+$, 471 (5) $[M - Ar]^+$.

General Procedure for the Preparation of Ligands 1c−f. [3-(Dibromo)phosphino)propyl](diphenyl)phosphonium bromide (**9**) was prepared in CCl_4 from 1 equiv of **8** and 2 equiv of Br_2 according to the procedure described below. The obtained product was cooled to −78 °C after complete evaporation of CCl_4. Precooled solvent (THF in the case of **1e** and ether in the case of **1c**,**d**,**f**) was added to suspend the solid foam. A solution of arylmagnesium bromide was prepared by slow addition of the corresponding aryl bromide in THF to an excess of magnesium turnings in THF and heating to slight reflux for 30 min. The filtered Grignard solution was added slowly to the suspension of **9** at −78 °C. After 15 min the reaction mixture was allowed to warm to room temperature and stirred overnight. It was hydrolyzed with water and adjusted to pH 7.

After special workup, described in detail for each of the ligands, the bisphosphines **1c**−**f** are yielded in a purity of 100% in ^{31}P NMR but containing some impurities in ^{1}H NMR. By conversion to the corresponding dichloro palladium(II) derivatives a complete purification is easily possible. The pure uncoordinated ligands are accessible by treating the complexes with aqueous sodium cyanide solution in CH_2Cl_2 overnight and subsequent workup.

1-Diphenylphosphino-3-[bis(3,5-dimethylphenyl)phosphino]propane (1c). Following the general procedure, **8** (2.19 g, 8.41 mmol, 80 mL of CCl_4) was bromated with Br_2 (2.69 g, 16.83 mmol, 10 mL of CCl_4) and suspended in ether (100 mL). 3,5-Dimethylphenylmagnesium bromide was prepared from 5-bromo-*m*-xylene (4.68 g, 25.24 mmol, 20 mL of THF) and Mg (0.77 g, 31.56 mmol, 20 mL of THF). After hydrolyses some CH_2Cl_2 was added and the organic layer was separated. The aqueous phase was extracted twice with CH_2Cl_2. The combined organic extracts were washed with water, dried (Na_2SO_4), and evaporated. Purification of the crude product by chromatography over silica with CH_2Cl_2 gave **1c** as an oily product.

Yield: 1.5 g (38%). ^{1}H NMR ($CDCl_3$): δ 7.38−7.33 (m, 4H, Ph), 7.30−7.26 (m, 6H, Ph), 6.98 (br d, 4H, ortho Ar), 6.91 (br s, 2H, para Ar), 2.25 (s, 12H, CH_3), 2.21−2.12 (m, 4H, $-CH_2P$), 1.60 (m, 2H, $-CH_2-$). ^{13}C NMR ($CDCl_3$): δ 138.69 (d, ipso), 138.31 (d, ipso′), 137.66 (d, meta Ar), 132.65 (d, ortho Ph), 130.35 (d, ortho Ar), 129.04 (s, para Ar), 128.42 (s, para Ph), 128.32 (d, meta Ph), 29.87−29.40 (m, $-CH_2P$, $-CH_2P'$), 22.55 (vt, $-CH_2-$), 21.27 (s $-CH_3$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −16.74 (s), −16.96 (s). MS (CI, *m*/*z* (%)): 469 (100) $[MH]^+$, 391 (15) $[M - Ph]^+$, 363 (8) $[M - Ar]^+$. Anal. Calcd for $C_{31}H_{34}P_2$: C, 79.46; H, 7.31. Found: C, 79.21; H, 7.17.

1-Diphenylphosphino-3-[bis(3,5-difluorophenyl)phosphino]propane (1d). Following the general procedure described above, **9** was prepared from **8** (4.40 g, 16.91 mmol, 180 mL of CCl_4) and Br_2 (5.40 g, 33.81 mmol, 20 mL of CCl_4) and suspended in ether (200 mL). The required 3,5-difluorophenylmagnesium bromide was obtained from 1-bromo-3,5-difluorobenzene (9.80 g, 50.72 mmol, 20 mL of THF) and Mg (1.55 g, 63.39 mmol, 20 mL of THF). For further workup the organic layer was separated, and the aqueous phase was extracted three times with ether. The combined organic phases were dried (Na_2SO_4), and the solvent was removed in vacuo. The residue was extracted several times with *n*-pentane. Evaporation of the combined organic solutions gave an oily product, which was purified by chromatography over silica with CH_2Cl_2.

Yield: 3.4 g (42%). ^{1}H NMR ($CDCl_3$): δ 7.40−7.34 (m, 4H, Ph), 7.32−7.28 (m, 6H, Ph), 6.83 (m, 4H, ortho Ar), 6.75 (tt, 2H, para Ar), 2.19 (t, 2H, $-CH_2P$), 2.13 (t, 2H, $-CH_2P'$), 1.56 (m, 2H, $-CH_2-$). ^{13}C NMR ($CDCl_3$): δ 162.89 (ddd, meta Ar), 142.05 (dt, ipso Ar), 138.21 (d, ipso Ph), 132.63 (d, ortho Ph), 128.67 (s, para Ph), 128.44 (d, meta Ph), 115.03 (vsex, ortho Ar), 104.63 (t, para Ar), 29.44 (vt, $-CH_2P$), 29.07 (vt, $-CH_2P'$), 22.01 (vt, $-CH_2-$). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ −12.42 (s, PAr_2), −17.17 (s, PPh_2). $^{19}F\{^{1}H\}$ NMR ($CDCl_3$): δ −109.01 (s). MS (CI, *m*/*z* (%)): 485(100) $[MH]^+$, 371(49) $[M - Ar]^+$, 407 (9) $[M - Ph]^+$.

1-Diphenylphosphino-3-{bis[(2-(trifluoromethyl)phenyl]-phosphino}propane (1e). As described in the general procedure, Br_2 (3.47 g, 21.75 mmol, 15 mL of CCl_4) was added to **8** (2.83 g, 18.87 mmol, 140 mL of CCl_4), and the resulting product was suspended in THF (120 mL). In this synthesis 1 equiv **9** was treated with 5 equiv of the 2-(trifluoromethyl)-phenylmagnesium bromide, which was obtained from 1-bromo-

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(29) Due to technical problems in elemental analysis of fluorinated compounds only selected complexes of fluorinated ligands were characterized by elemental analysis. However, NMR, MS, IR, and X-ray structure analysis were applied to confirm composition of all reported compounds.

2-(trifluoromethyl)benzene (12.23 g, 54.35 mmol, 40 mL of THF) and Mg (1.65 g, 67.94 mmol, 30 mL of THF). After the reaction was hydrolyzed, the THF was evaporated in vacuo. The precipitated solid was separated and washed two times with water. The residue was extracted three times with degassed acetone, and the combined extracts were evaporated. The remaining solid was dissolved in CH_2Cl_2, washed twice with water, and dried (Na_2SO_4). After removing the solvent in vacuo, the residue was washed once with a small amount of *n*-pentane. The remaining residue was extracted twice with ether. The filtered extracts were combined and evaporated. Further purification of the crude product, performed by chromatography over silica with CH_2Cl_2, gave the bisphosphine as an oily compound.

Yield: 2.2 g (38%). ^{1}H NMR ($CDCl_3$): δ 7.71−7.65 (m, 2H, arom.), 7.45−7.32 (m, 10H, arom.), 7.30−7.25 (m, 6H, arom.), 2.24−2.12 (m, 4H, $-CH_2P$), 1.62 (m, 2H, $-CH_2-$). ^{13}C NMR ($CDCl_3$): δ 138.26 (d, ipso Ph), 136.84 (d, ipso Ar), 134.12 (qd, CCF_3), 133.19 (s, Ar), 132.64 (d, ortho Ph), 131.46 (s, Ar), 128.74 (s, Ar), 128.57 (s, para Ph), 128.40 (d, meta Ph), 126.67 (br, m, Ar), 124.15 (q, CF_3), 30.19 (vt, $-CH_2P$), 29.57 (vt, $-CH_2P'$), 22.40 (dd, $-CH_2-$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −17.28 (s, PPh_2), −26.70 (sept, PAr_2). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −57.66 (d). MS (CI, *m*/*z* (%)): 594 (100) $[MH]^+$, 529 (57) $[M - F]^+$, 403 (37) $[M - Ar]^+$.

1-Diphenylphosphino-3-[bis(2,4,6-trifluorophenyl)phosphino]propane (1f). According to the general procedure, **9** was prepared from **8** (4.18 g, 16.05 mmol, 180 mL of CCl_4) and Br_2 (5.13 g, 32.1 mmol, 20 mL of CCl_4) and suspended in ether (200 mL). A solution of 2,4,6-trifluorophenylmagnesium bromide was obtained from 1-bromo-2,4,6-trifluorobenzene (10.16 g, 48.15 mmol, 30 mL of THF) and Mg (1.47 g, 60.18 mmol, 20 mL of THF). After adjusting to pH 7 the organic layer was separated and the aqueous phase was extracted three times with ether. The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo. The yielded brownish oil was purified by chromatography over silica with CH_2Cl_2. The oily product was extracted several times with *n*-pentane. The extracts were combined and evaporated to give **1f** as an oil.

Yield: 4.2 g (51%). ^{1}H NMR ($CDCl_3$): δ 7.39−7.33 (m, 4H, Ph), 7.31−7.27 (m, 6H, Ph), 6.58 (m, 4H, meta Ar), 2.57 (m, 2H, $-CH_2PAr_2$), 2.19 (t, 2H, $-CH_2PPh_2$), 1.54 (m, 2H, $-CH_2-$). ^{13}C NMR ($CDCl_3$): δ 164.73 (dm, ortho Ar), 163.91 (dm, para Ar), 138.30 (d, ipso Ar), 132.62 (d, ortho Ph), 128.53 (s, para Ph), 128.36 (d, meta Ph), 108.7−107.3 (m, ipso Ar), 101.0−100.2 (m, meta Ar), 29.26 (dd, $-CH_2PPh_2$), 25.31 (m, $-CH_2PAr_2$), 22.82 (dd, $-CH_2-$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −16.54 (s, PPh_2), −53.12 (quint, PAr_2). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −98.39 (dd, ortho F), −106.30 (t, para F). MS (CI, *m*/*z* (%)): 521 (100) $[MH]^+$, 389 (26) $[M - Ar]^+$, 501 (14) $[M - F]^+$, 443 (8) $[M - Ph]^+$.

Dichloro{1,3-bis[bis[3,5-bis(trifluoromethyl)phenyl]-phosphino]propane}palladium(II) (2a). A solution of (COD)-$PdCl_2$ (0.76 g, 2.65 mmol) in CH_2Cl_2 (40 mL) was treated with a solution of **1a** (2.53 g, 2.65 mmol) in CH_2Cl_2 (25 mL). After stirring for 1 h, the main CH_2Cl_2 amount was removed by an argon stream due to foaming in vacuo. For precipitation *n*-pentane was added, and the product was washed with ether and *n*-pentane. Drying in vacuo gave product **2a** as a pale yellow solid.

Yield: 2.9 g (95%). ^{1}H NMR (acetone-d_6): δ 8.53 (br d, 8H, ortho Ar), 8.28 (br s, 4H, para Ar), 3.29 (m, 4H, $-CH_2P$), 2.38 (m, 2H, $-CH_2-$). ^{31}P{^{1}H} NMR (acetone-d_6): δ 16.11 (s). ^{19}F{^{1}H} NMR (acetone-d_6): δ −62.45 (s). MS (FAB, *m*/*z* (%)): 1097 (100) $[M - Cl]^+$, 1062 (23) $[M - 2Cl]^+$, 849 (23) $[M - 2Cl,Ar]^+$. Anal. Calcd for $C_{35}H_{18}Cl_2F_{24}P_2Pd$: C, 37.08; H, 1.60. Found: C, 36.89; H, 1.66.

Single crystals of **2a** suitable for X-ray analysis were grown from THF solution layered with cyclohexane. The unit cell contains two independent complex molecules with a slightly different orientation of the aromatic rings. Some of the CF_3 groups show disordering. An additional 1.5 disordered THF molecules per complex molecule (side occupation factor 0.75) are incorporated in the crystal, which results in a relatively high final *R*-value.

Dichloro{1-diphenylphosphino-3-[bis[3,5-bis(trifluoromethyl)phenyl]phosphino]propane}palladium(II) (2b). A solution of ligand **1b** (2.16 g, 3.16 mmol) in CH_2Cl_2 (20 mL) was added to a solution of $(COD)PdCl_2$ (0.9 g, 3.16 mmol) in CH_2Cl_2 (60 mL). After stirring the mixture for 1 h, it was concentrated and the complex was precipitated with *n*-pentane. Washing with ether and *n*-pentane and drying in vacuo gave the complex **2b** as a yellow solid.

Yield: 2.6 g (96%). ^{1}H NMR ($CDCl_3$): δ 8.13 (br d, 4H, ortho Ar), 7.96 (br s, 2H, para Ar), 7.71 (m, 4H, Ph), 7.47 (m, 2H, Ph), 7.37 (m, 4H, Ph), 2.64−2.48 (m, 4H, $-CH_2P$), 2.09 (m, 2H, $-CH_2-$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 13.33 (d), 13.02 (d). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −63.38 (s). MS (FAB, *m*/*z* (%)): 827 (100) $[M - Cl]^+$, 790 (18) $[M - 2Cl]^+$, 749 (12) $[M - Cl,Ph]^+$, 577 (9) $[M - 2Cl,Ar]^+$. Anal. Calcd for $C_{31}H_{22}Cl_2F_{12}P_2Pd$: C, 43.21; H, 2.57. Found: C, 43.01; H, 2.57.

Single-crystals of **2b** suitable for X-ray analysis were obtained by crystallization from acetonitrile solution layered with ether.

Dichloro{1-diphenylphosphino-3-[bis(3,5-dimethylphenyl)phosphino]propane}palladium(II) (2c). A solution of $(COD)PdCl_2$ (0.46 g, 1.60 mmol) in CH_2Cl_2 (40 mL) was treated with a solution of **1c** (0.75 g, 1.60 mmol) in CH_2Cl_2 (20 mL) and stirred for 1 h. The mixture was concentrated in vacuo, and the complex was precipitated by adding *n*-pentane. Washing with ether and *n*-pentane and drying in vacuo gave complex **2c** as a yellow-orange solid.

Yield: 1.0 g (94%). ^{1}H NMR ($CDCl_3$): δ 7.81−7.74 (m, 4H, Ph), 7.47−7.33 (m, 10H, arom), 7.04 (br s, 2H, para Ar), 2.39−2.28 (m, 4H, $-CH_2P$), 2.26 (s, 12H, $-CH_3$), 1.99 (m, 2H, $-CH_2-$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.7 (d), 11.4 (d). MS (FAB, *m*/*z* (%)): 609 (100) $[M - Cl]^+$, 574 (20) $[M - 2Cl]^+$, 533 (6) $[M - Cl,Ph]^+$. Anal. Calcd for $C_{31}H_{34}Cl_2P_2Pd$: C, 57.65; H, 5.31. Found: C, 57.48; H, 5.24.

Single-crystals of **2c** suitable for X-ray analysis were obtained by crystallization from CH_2Cl_2 solution layered with *n*-pentane. The crystals include two independent complex molecules and four CH_2Cl_2 molecules per unit cell.

Dichloro{1-diphenylphosphino-3-[bis(3,5-difluorophenyl)phosphino]propane}palladium(II) (2d). A solution of **1d** (1.96 g, 4.06 mmol) in CH_2Cl_2 (20 mL) was added to $(COD)PdCl_2$ (1.16 g, 4.06 mmol) in CH_2Cl_2 (80 mL). After stirring at room temperature for 1 h the solution was concentrated in vacuo. The complex was precipitated by addition of *n*-pentane and washed with ether and *n*-pentane. Drying in vacuo gave **2d** as a microcrystalline solid.

Yield: 2.6 g (95%). ^{1}H NMR (DMSO-d_6): δ 7.76 (m, 4H, arom), 7.57−7.44 (m, 12H, arom), 2.83 (m, 2H, $-CH_2P$), 2.72 (m, 2H, $-CH_2P'$), 1.78 (m, 2H, $-CH_2-$). ^{31}P{^{1}H} NMR (DMSO-d_6): δ 16.5 (br), 13.3 (br). ^{19}F{^{1}H} NMR (DMSO-d_6): δ −107.50 (s). MS (FAB, *m*/*z* (%)): 625 (100) $[M - Cl]^+$, 589 (37) $[M - 2Cl]^+$, 547 (26) $[M - Cl,Ph]^+$. Anal. Calcd for $C_{27}H_{22}Cl_2F_4P_2Pd$: C, 49.01; H, 3.35. Found: C, 48.79; H, 3.48.

Dichloro{1-diphenylphosphino-3-[bis[2-(trifluoromethyl)phenyl]phosphino]propane}palladium(II) (2e). A solution of $(COD)PdCl_2$ (1.96 g, 6.87 mmol) in CH_2Cl_2 (120 mL) was treated with a solution of bisphosphine **1e** (3.77 g, 6.87 mmol) in CH_2Cl_2 (40 mL) and stirred for 1 h. After concentrating the solution *n*-pentane was added for precipitation. The solid was washed with ether and *n*-pentane and dried in vacuo.

Yield: 4.8 g (96%). ^{1}H NMR ($C_2D_2Cl_4$): δ 9.41 (m, 1H, Ar) 7.82−7.32 (m, 16H, arom), 7.02 (m, 1H, Ar), 2.80−2.62 (m, 2H), 2.30−2.04 (m, 3H), 1.71−1.50 (m, 1H). ^{31}P{^{1}H} NMR ($C_2D_2Cl_4$): δ 37.14 (m, PAr_2), 12.47 (d, PPh_2). ^{19}F{^{1}H} NMR

($C_2D_2Cl_4$): δ −54,27 (s), −54.37 (d). MS (FAB, *m*/*z* (%)): 689 (100) $[M - Cl]^+$, 653 (48) $[M - 2Cl]^+$, 611 (7) $[M - Cl,Ph]^+$.

Dichloro{1-diphenylphosphino-3-[bis(2,4,6-trifluorophenyl)phosphino]propane}palladium(II) (2f). Ligand **1f** (3.58 g, 6.88 mmol) was dissolved in CH_2Cl_2 (30 mL) and added to a solution of $(COD)PdCl_2$ (1.96 g, 6.88 mmol) in CH_2Cl_2 (120 mL). After 1 h the product was precipitated by concentrating the solution in vacuo. The precipitation was completed by adding *n*-pentane. The complex was washed with ether and *n*-pentane and dried in vacuo.

Yield: 4.6 g (97%). ^1H NMR (DMSO-d_6): δ 7.84 (m, 4H, Ph), 7.63−7.51 (m, 6H, Ph), 7.40 (m, 4H, Ar), 2.62 (m, 2H, $-CH_2P$), 2.54 (m, 2H, $-CH_2P'$), 1.88 (m, 2H, $-CH_2-$). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 16.37 (d), −16.23 (m). $^{19}F\{^1H\}$ NMR (DMSO-d_6): δ −93.18 (vt, ortho F), −100.99 (t, para F). MS (FAB, *m*/*z* (%)): 661 (100) $[M - Cl]^+$, 625 (37) $[M - 2Cl]^+$. Anal. Calcd for $C_{27}H_{20}Cl_2F_6P_2Pd$: C, 46.48; H, 2.89. Found: C, 46.17; H, 2.99.

Single crystals of **2f** suitable for X-ray analysis were grown from DMSO solution layered with ether. Four molecules of DMSO were found to be included within the unit cell.

Diiodo{1-diphenylphosphino-3-[bis(3,5-difluorophenyl)-phosphino]propane}palladium(II) (3d). Compound **3d** was prepared according to the procedure described for **3e** from the dichloro complex **2d** (0.45 g, 0.68 mmol), DMSO (10 mL), and NaI (0.41 g, 2.72 mmol) and isolated as a red-orange solid.

Yield: 0.31 g (54%). ^1H NMR (acetone-d_6): δ 7.83−7.76 (m, 4H, arom), 7.54−7.43 (m, 10H, arom), 7.20 (tt, 2H, para Ar), 2.92 (m, 2H, $-CH_2P$), 2.82 (m, 2H, $-CH_2P'$), 2.12 (m, 2H, $-CH_2-$). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 3.37 (dquint, PAr_2), 1.42 (d, PPh_2). $^{19}F\{^1H\}$ NMR (acetone-d_6): δ −108.12 (d). MS (FAB, *m*/*z* (%)): 844 (6) $[M]^+$, 717 (100) $[M - I]^+$, 589 (29) $[M - I,HI]^+$.

Single crystals of **3d** suitable for X-ray analysis were grown from a chloroform solution layered with *n*-hexane. The crystals enclose strongly disordered solvent molecules, which could not be identified and located, even though satisfying final *R*-indices have been achieved in structure refinement.

Diiodo{1-diphenylphosphino-3-[bis[2-(trifluoromethyl)-phenyl]phosphino]propane}palladium(II) (3e). A solution of the dichloro complex **2e** (3.68 g, 5.07 mmol) in DMSO (80 mL) was treated with NaI (3.04 g, 20.3 mmol) and stirred for 48 h at room temperature. After addition of water (500 mL), the resulting mixture was extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed three times with water, dried (Na_2SO_4), and evaporated. The crude product was purified by chromatography over silica with CH_2Cl_2 and precipitated with *n*-pentane to give **3e** as a red-orange microcrystalline solid.

Yield: 3.27 g (71%). ^1H NMR ($CDCl_3$): δ 9.58 (m, 1H, Ar), 7.91−7.34 (m, 16H, arom), 7.09 (m, 1H, Ar), 2.90−2.71 (m, 2H), 2.34−2.17 (m, 2H), 2.17−2.04 (m, 1H), 1.91−1.70 (m, 1H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 23.06 (m, PAr_2), −0.40 (d, PPh_2). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −54.70 (s), −55.55 (d). MS (FAB, *m*/*z* (%)): 781 (100) $[M - I]^+$, 653 (44) $[M - I,HI]^+$. Anal. Calcd for $C_{29}H_{24}F_6I_2P_2Pd$: C, 38.33; H, 2.66. Found: C, 38.21; H, 2.54.

Crystallization from a chloroform solution layered with *n*-pentane gave single crystals of **3e**, which were suitable for X-ray analysis. The crystals contain two molecules of $CHCl_3$ per complex molecule. The carbon atom of one $CHCl_3$ could not be located due to disordering.

Diacetonitrile{1,3-bis[bis[3,5-bis(trifluoromethyl)-phenyl]phosphino]propane}palladium(II) Ditetrafluoroborate (4a). $AgBF_4$ (0.61 g, 3.12 mmol) was added to a solution of **2a** (1.77 g, 1.56 mmol) in acetonitrile (80 mL). After stirring for 2 h the solution was filtered and concentrated in vacuo. The solution was filtered again and the complex precipitated with ether. The solid was washed with ether and *n*-pentane and dried in vacuo to give **4a**.

Yield: 1.4 g (68%). ^1H NMR (acetone-d_6): δ 8.55 (d, 8H, ortho Ar), 8.44 (s, 4H, para Ar), 3.58 (m, 4H, $-CH_2P$), 2.71 (m, 2H, $-CH_2-$), 2.09 (s, 6H, CH_3CN). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 18.57 (s). $^{19}F\{^1H\}$ NMR (acetone-d_6): δ −62.32 (s, CF_3), −148.16 (s, BF_4). IR (KI, ν (cm^{-1})): 2329, 2300 (w, C≡N); 1130 (sbr, BF_4). MS (FAB, *m*/*z* (%)): 1061 (25) $[M - 2CH_3CN,2BF_4]^+$, 605 (100) $[M - 2CH_3CN,2BF_4,PAr_2]^+$.

Diacetonitrile{1-diphenylphosphino-3-[bis[3,5-bis-(trifluoromethyl)phenyl]phosphino]propane}palladium-(II) Ditetrafluoroborate (4b). Complex **2b** (1.12 g, 1.30 mmol) was dissolved in acetonitrile (70 mL), and $AgBF_4$ (0.51 g, 2.60 mmol) was added. After stirring for 2 h the solution was separated from the precipitated silver salt and evaporated in vacuo. The residue was extracted with CH_2Cl_2. After the extract was concentrated in vacuo and filtered, the complex was precipitated by adding *n*-pentane. Washing the product with *n*-pentane and drying in vacuo gave complex **4b**.

Yield: 1.1 g (81%). ^1H NMR (CD_3CN): δ 8.28 (s, 2H, para Ar), 8.11 (d, 4H, ortho Ar), 7.68−7.59 (m, 6H, Ph), 7.56−7.49 (m, 4H, Ph), 2.98−2.85 (m, 4H, $-CH_2P$), 2.30 (m, 2H, $-CH_2-$), 1.95 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.3 (d), 14.1 (d). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −62.1 (s, CF_3), −150.1 (s, BF_4). IR (KI, ν (cm^{-1})): 2328, 2300 (w, C≡N); 1130 (sbr, BF_4). MS (FAB, *m*/*z* (%)): 790 (100) $[M - 2CH_3CN,2BF_4]^+$.

Diacetonitrile{1-diphenylphosphino-3-[bis(3,5-dimethylphenyl)phosphino]propane}palladium(II) ditetrafluoroborate (4c). $AgBF_4$ (0.24 g, 1.26 mmol) was added to a solution of **2c** (0.41 g, 0.63 mmol) in acetonitrile (80 mL). Stirring for 2 h was followed by workup described in the procedure of compound **4b** to give **4c**.

Yield: 0.4 g (78%). ^1H NMR (CD_3CN): δ 7.66−7.58 (m, 6H, Ph), 7.55−7.49 (m, 4H, Ph), 7.23 (br s, 4H, ortho Ar), 7.20 (br s, 2H, para Ar), 2.77 (m, 4H, $-CH_2P$), 2.29 (s, 12H, $-CH_3$), 2.22 (m, 2H, $-CH_2-$), 1.95 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 13.0 (br), 12.0 (br). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −150.2 (s, BF_4). IR (KI, ν (cm^{-1})): 2325, 2297 (w, C≡N); 1061 (sbr, BF_4). MS (FAB, *m*/*z* (%)): 593 (56) $[M - 2CH_3CN, BF_4,BF_3]^+$, 574 (100) $[M - 2CH_3CN,2BF_4]^+$.

Diacetonitrile{1-diphenylphosphino-3-[bis(3,5-difluorophenyl)phosphino]propane}palladium(II) Ditetrafluoroborate (4d). A solution of **2d** (1.56 g, 2.36 mmol) in acetonitrile (50 mL) was treated with $AgBF_4$ (0.92 g, 4.72 mmol) and stirred for 12 h. After workup according to the procedure of **4b**, complex **4d** was isolated as a pale yellow solid.

Yield: 1.6 g (80%). ^1H NMR (CD_3CN, 343 K): δ 7.72−7.63 (m, 6H, Ph), 7.58−7.53 (m, 4H, Ph), 7.32−7.25 (m, 4H, ortho Ar), 7.20 (tt, 2H, para Ar), 2.86−2.77 (m, 4H, $-CH_2P$), 2.29 (m, 2H, $-CH_2-$), 1.95 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.4 (m), 12.7 (m). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −105.5 (s, meta F), −150.0 (s, BF_4). IR (KI, ν (cm^{-1})): 2326, 2299 (w, C≡N); 1065 (sbr, BF_4). MS (FAB, *m*/*z* (%)): 609 (39) $[M - 2CH_3CN, BF_4,BF_3]^+$, 590 (100) $[M - 2CH_3CN,2BF_4]^+$.

Diacetonitrile{1-diphenylphosphino-3-[bis[2-(trifluoromethyl)phenyl]phosphino]propane}palladium-(II) Ditetrafluoroborate (4e). $AgBF_4$ (0.43 g, 2.22 mmol) was added to a suspension of **3e** (1.01 g, 1.11 mmol) in acetonitrile (80 mL). After stirring the reaction mixture for 2 h workup according to procedure **4b** gave **4e**.

Yield: 0.9 g (89%). ^1H NMR (CD_3CN): δ 8.61−8.47 (br, 1H, arom), 8.07−7.37 (m, 17H, arom), 3.12−2.94 (br, 2H), 2.71 (br, 2H), 2.53−2.29 (br, 1H), 2.10−1.96 (br, 1H), 1.95 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 31.4 (m, PAr_2), 13.2 (d, PPh_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −54.1 (s, br, CF_3), −54.4 (s, br, CF_3), −150.4 (s, BF_4). IR (KI, ν (cm^{-1})): 2327, 2299 (w, C≡N); 1074 (sbr, BF_4). MS (FAB, *m*/*z* (%)): 673 (22) $[M - 2CH_3CN, BF_4,BF_3]^+$, 654 (100) $[M - 2CH_3CN,2BF_4]^+$.

Diacetonitrile{1-diphenylphosphino-3-[bis(2,4,6-trifluorophenyl)phosphino]propane}palladium(II) Ditetrafluoroborate (4f). Complex **2f** (1.93 g, 2.76 mmol) was suspended in acetonitrile (100 mL). After $AgBF_4$ (1.07 g, 5.52 mmol) was added, the suspension was stirred for 12 h. Following the procedure described for **4b** the suspension was worked up to give **4f**.

Yield: 1.9 g (76%). ^{1}H NMR (CD_3CN): δ 7.75−7.65 (m, 6H, Ph), 7.64−7.54 (m, 4H, Ph), 7.03 (m, 4H, Ar), 2.99 (m, 2H, $-CH_2P$), 2.77 (m, 2H, $-CH_2P'$), 2.32 (m, 2H, $-CH_2-$), 1.95 (s, CH_3CN). $^{31}P\{^1H\}$ NMR (CD_3CN): δ 14.4 (d, PPh_2), −19.6 (m, PAr_2). $^{19}F\{^1H\}$ NMR (CD_3CN): δ −93.4 (vt, ortho F), −96.0 (t, para F), −150.5 (s, BF_4). IR (KI, ν (cm^{-1})): 2327, 2299 (w, C≡N); 1099 (sbr, BF_4). MS (FAB, *m*/*z* (%)): 645 (20) $[M - 2CH_3CN,BF_4,BF_3]^+$, 626 (100) $[M - 2CH_3CN,2BF_4]^+$.

Diphenyl(3-phosphinopropyl)phosphine (8). A solution of diisopropyl 3-(diphenylphosphino)propylphosphonate (**7**) (23.12 g, 58.8 mmol) in ether (100 mL) was added slowly to a suspension of $LiAlH_4$ (4.5 g, 118 mmol) in ether (150 mL) at 0 °C. The reaction mixture was stirred for a further 30 min at 0 °C and overnight at room temperature. The suspension was hydrolyzed at 0 °C. Further water was added until the precipitated salt agglomerated. The organic phase was separated and the residue extracted with ether. The combined organic layers were washed with water, dried, and evaporated to give **8** as a colorless, air-sensitive oil.

Yield: 13.4 g (88%). ^{1}H NMR ($CDCl_3$): δ 7.43−7.38 (m, 4H, Ph), 7.34−7.27 (m, 6H, Ph), 2.64 (dt, 2H, $-PH_2$), 2.11 (t, 2H, $-CH_2P_{(Ph)}$), 1.70−1.57 (m, 4H, $-CH_2-CH_2-P_{(prim)}$). ^{13}C NMR ($CDCl_3$): δ 138.57 (d, ipso Ph), 132.65 (d, ortho Ph), 128.52 (s, para Ph), 128.38 (d, meta Ph), 29.27 (dd, $-CH_2-P$), 29.02 (dd, $-CH_2-P'$), 15.39 (dd, $-CH_2-$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −16.29 (s, PPh_2), −137.97 (s, $P_{(prim)}$). MS (CI, *m*/*z* (%)): 261 (100) $[MH]^+$.

[3-(Dibromo)phosphino)propyl](diphenyl)phosphonium Bromide (9). Diphenyl(3-phosphinopropyl)phosphine (**8**) (4.18 g, 16.05 mmol) was dissolved in CCl_4 (180 mL) and cooled to 10 °C. Bromine (5.13 g, 32.10 mmol) in CCl_4 (20 mL) was added rapidly through a dropping funnel. After stirring for 10 min the solvent and HBr were removed in vacuo at about 10 °C. The resulting product was converted directly to the desired ligands.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 182.91 (s, $-PBr_2$), 59.10 (s, $-P_{phosphonium}$).

Propene/CO Co- and Terpolymerization Experiments. The corresponding dicationic palladium(II) complex (**4a**−**g**) was dissolved in CH_2Cl_2 (150 mL) and activated by addition of dry methanol (0.25 mL). The resulting solution was placed in a 250 mL steel autoclave equipped with a mechanical gas entrainment stirrer, which was charged subsequently with propene (60 g) and with carbon monoxide up to a constant pressure of 60 bar. After a reaction time of 21 h at 25 °C the remaining gases were vented off. The resulting copolymer solution was diluted with CH_2Cl_2 and stirred with water for 2 h. The organic phase was separated, filtered, and concentrated. The remaining solvent was evaporated and the copolymer dried in vacuo at 60 °C. PFP experiments were performed according to the method described above for propene/CO copolymerization reactions with additional ethene pulses according to the literature procedure.[3b]

Polymer Analysis. ^{13}C NMR of the copolymers for determination of regioregularity were recorded on a Bruker DRX 400 in $CDCl_3$. Molecular weights and molecular weight distributions were measured by GPC in THF relative to polystyrene standards.

Crystal Structure Determinations of 2a, 2b, 2c, 3d, 3e, and 2f. Crystal data of the compounds **2a** and **2c** were collected by M.K. (University of Helsinki) with a Rigaku AFC7S single-crystal diffractometer at 193(2) K using Mo Kα radiation (graphite monochromator), $\lambda = 0.71073$ Å (ω-scans). Intensities were corrected for Lorentz and polarization effects.[30] A ψ-scan absorption correction was performed.[31] In **2a** a decay correction of 5.5% was made. The structure **2a** was solved by Patterson technique and subsequent Fourier analyses, SHELX-97.[32] Non-hydrogen atoms were refined anisotropically, except fluorine atoms, with a site occupation factor 0.25, which were refined isotropically. Fluorine atoms with a site occupation factor of less than 1.0 were refined using DFIX and ISOR restraints and with fixed coordinates during the final cycles of calculations. All tetrahydrofuran molecules are partially occupied, having a site occupation factor of 0.75. Hydrogen atoms were refined on calculated positions. After removing it from mother liquid the specimen loses its crystalline appearance and diffraction ability very soon, within 1−2 min. A special cold temperature device technique with inert oil was needed to convey the crystals alive to the diffractometer. In **2c** direct methods were used. Non-H atoms were treated anisotropically and hydrogen atoms were refined on calculated positions. Refinement of both compounds was done by a least-squares method based on F^2 with all reflections, and the displacement factor of the H atoms was 1.2× (or 1.5× for methyl hydrogens) that of the host atom.[32]

X-ray structure determinations of **2b**, **3d**, **3e**, and **2f** were carried out by U.T. (University of Ulm). The crystals were mounted on glass fibers. X-ray data were collected on a STOE IPDS instrument using graphite-monochromatized Mo Kα radiation, $\lambda = 0.71073$ Å. Crystal data are listed in Table 1 and Supporting Information together with refinement details. Absorption corrections (analytical method) were applied for **3d** and **3e**. The structures were solved by the Patterson method.[33] The atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined using F^2 data.[32] Hydrogen atoms were included in the final refinement cycles in a riding mode. One of the $CHCl_3$ molecules of crystallization of **3e**·$2CHCl_3$ shows some disorder.

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center: CCDC 193834 (**2a**), CCDC 197101 (**2b**), CCDC 193835 (**2c**), CCDC 197102 (**2f**), CCDC 197100 (**3d**), CCDC 197099 (**3e**).

Supporting Information Available: Synthesis of **1b** via radical-induced addition of secondary phosphines and allylphosphines. Preparation and characterization of allyl{bis-[3,5-bis(trifluoromethyl)phenyl]}phosphine (**12**). ORTEP plot, crystallographic data, and selected bond lengths and angles of compounds **2c** and **3d**. Complete crystallographic data of complexes **2a**−**c**,**f** and **3d**,**e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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