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o-Diarylphosphinoferrocene Sulfonate Palladium Systems for Nonalternating Ethene−Carbon Monoxide Copolymerization

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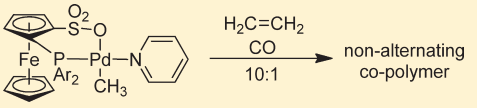
Supporting Information

ABSTRACT: A series of ferrocene-derived *o*-diarylphosphino/sulfonate ligands were prepared. Treatment of the *o*-diphenylphosphinoferrocene sulfonic acid (**2a**) with (allyl)PdCl dimer and sodium carbonate as the base gave the corresponding chelate (Fc-O,P)Pd(π-allyl) complex **7a** (as a mixture of two isomers). In the presence of pyridine instead of Na_2CO_3 the analogous reaction yielded the square-planar (Fc-O,P)Pd(Cl)pyridine complex **8a**. Both systems were characterized by X-ray diffraction. Reaction of the series of three differently −P(aryl)$_2$-substituted (Fc-O,P)H ligands with $PdMe_2$(tmeda) gave the respective (Fc-O,P)PdMe(pyridine) derivatives (**11**). All three examples **11a,b,c** and one precursor complex, [(Fc-O,P)PdMe]$_2$(tmeda) (**10a**), were characterized by X-ray diffraction. The ligand system *o*-bis-(*o*-anisyl)phosphinoferrocene sulfonic acid (**2b**) formed an active catalyst for ethene/CO nonalternating copolymerization upon treatment with $Pd(OAc)_2$ in methanol. Up to ca. 25% extra ethene incorporation was obtained at an ethene/CO partial pressure ratio of ca. 10:1. This catalyst system and its equivalent derived from the preformed (Fc-O,P)PdMe(pyridine) precursor complex (**11b**) showed reasonable catalyst activities under these conditions.



INTRODUCTION

Homogeneous Ziegler−Natta olefin polymerization catalysis has made some remarkable development in recent decades. A variety of very active and often very selective catalysts were described for the production of various types of 1-alkene-derived polymers and copolymers with catalyst types ranging from selectively designed group 4 metallocenes[1] to Cp/amido complexes[2] of the early transition metals all the way to remarkably well performing "non-metallocene" systems of some late transition metals.[3]

Copolymerization of ethene with polar olefinic monomers had been difficult initially,[4] but meanwhile truly remarkable progress has been achieved combining C_2H_4 with acrylates, metacrylates, (even) acrylonitrile, and other related alkenes bearing reactive functional groups.[5−9] Ethene/carbon monoxide copolymerization is a slightly different case. Seminal work by Drent had shown that cationic chelate bis-phosphine palladium systems produce a strictly alternating "polyketone" (i.e., *alt*-ethene/CO) with high activities.[10] The mechanism of its formation is well understood from the work of a great number of research groups.[11] The *alt*-ethene/CO copolymer formed at this catalyst type has a high melting point, and it is hard to process. Introducing a more than 50% share of the ethylene monomer into the polymer would greatly improve the polymer properties and processability, but achieving substantial deviations from the strictly alternating ethene (or 1-alkene)/CO copolymer formation was difficult initially. A solution was proposed by Drent et al., who showed that an ethene/CO copolymer with up to 20% "extra ethylene" units could be formed with neutral Pd(II) catalyst systems derived from the *o*-diarylphosphinobenzene sulfonate ligand family.[12,13] The bis(*o*-anisyl)phosphino derivate (**1**) is a prominent example (see Chart 1). Ziegler had identified (by DFT calculation) the ability of these systems to allow reversibility of the CO-insertion step to some extent, thereby opening the pathway of multiple consecutive ethene insertions during the polymerization process.[14] Sen et al. later showed that copolymers of almost any ethene/CO ratio could be formed by carefully controlling the specific reaction conditions of the polymerization process, but that a decreasing CO content was achieved at the "prize" of an enormous decrease of the actual polymerization rate.[15]

We recently introduced some novel [3]ferrocenophane-derived bis-phosphine chelate ligands. These made very effective Pd catalysts for *alt*-ethene/CO and for active and highly selective *alt*-propene/CO copolymer formation.[16,17] Therefore, it was tempting to extend the use of novel ferrocene-based ligand systems to the neutral phosphino/sulfonate ligand derived Pd systems. We will here describe the synthesis of a variety of such diarylphosphinoferrocene sulfonate ligands (**2**, see Chart 1), their Pd coordination chemistry, and the successful use of a selected example in catalytic nonalternating ethene/carbon monoxide copolymer formation.

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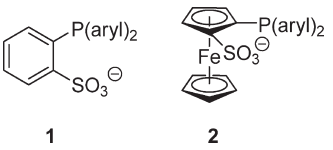
§ X-ray crystal structure analyses.

RESULTS AND DISCUSSION

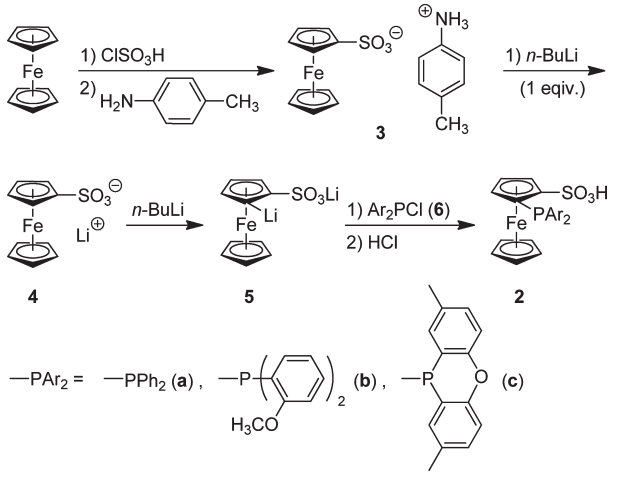
Our synthesis was carried out starting with ferrocene substitution along the lines introduced by Pauson et al.[18] and Schlögl et al.,[19] respectively. Electrophilic "aromatic" substitution of ferrocene with chlorosulfonic acid was followed by treatment with *p*-toluidine to give the toluidinium ferrocene sulfonate salt (**3**), thereby avoiding the problematic isolated free ferrocene sulfonic acid stage. Cation exchange was then carried out by treatment of the toluidinium salt (**3**) with *n*-butyl lithium in THF to yield the corresponding lithium salt (**4**; see Scheme 1).

The ferrocene sulfonate lithium salt **4** then underwent a clean ortho-directed metalation reaction upon treatment with an additional molar equivalent of *n*-butyl lithium to generate the reagent **5**.[20] The in situ generated dilithio ferrocene sulfonate reagent (**5**) was quenched by adding a slight excess of the diarylchlorophosphines **6**(**a**,**b**,**c**) followed by acidification to give the corresponding *o*-diarylphosphinoferrocene sulfonic acids **2a**, **2b**, and **2c**, respectively. These ligand systems were not further purified but used for the subsequent reactions as they were obtained. However, we monitored their ^{31}P NMR resonances [e.g., **2b**: δ −44.2 in d_6-DMSO].

Chart 1



Scheme 1



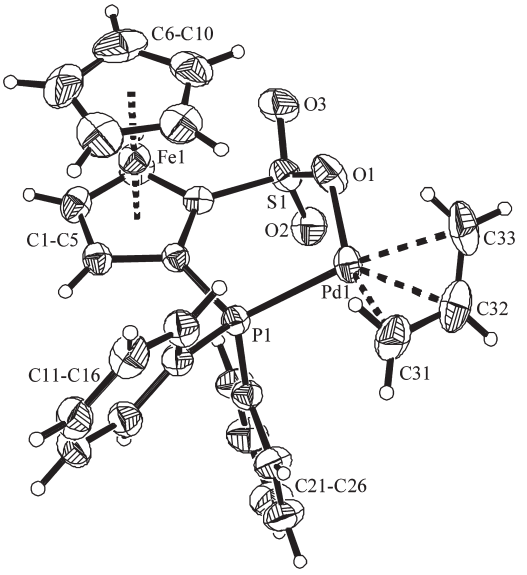


Figure 2. View of the molecular structure of the *anti*-(Fc-O,P)Pd-(π-allyl) complex **7a**.

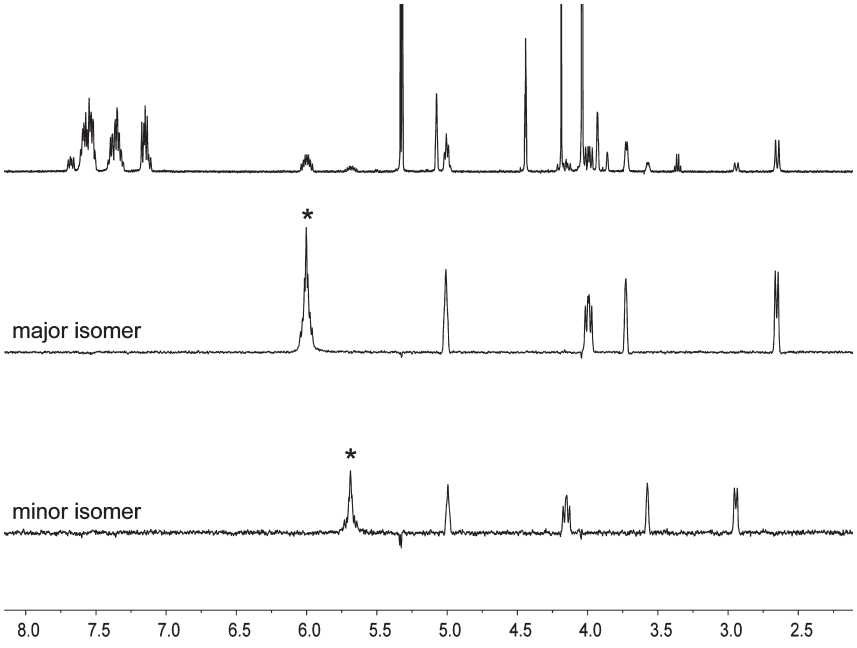


Figure 1. ^{1}H NMR spectra (CD_2Cl_2, 500 MHz, 193 K) of the isomeric mixture of **7a** (top). 1D-TOCSY experiments: Irradiation (*) at the methine proton of the respective π-allyl ligands of both isomers of **7a** [δ^1H = 6.00 (major isomer) and δ^1H = 5.69 (minor isomer)].

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Compound **2a** ["(Fc-O,P)H"] was treated with the (allyl)-PdCl dimer reagent under two different reaction conditions. First we added sodium carbonate as a base. This reaction led to the formation of the (Fc-O,P)Pd(π-allyl) complex **7a**. It was isolated in a total yield of ca. 40% as a mixture of two isomers. These can be described tentatively as the *syn*- and *anti*-π-allyl Pd(Fc-O,P) diastereoisomers **7a**(**A**,**B**). Each features the typical $^{1}H/^{13}C$ NMR signals of a chiral (racemic) Pd(π-allyl) complex (see Figure 1). In solution they were found in a 1:0.3 molar ratio. Single crystals of the product **7a** were obtained from pentane/CH_2Cl_2 by the diffusion method. The X-ray crystal structure analysis shows two crystallographically independent chemically identical molecules in the unit cell. The structure of **7a**, depicted in Figure 2, shows the ortho attachment of the $-SO_3^-$ substituent and the $-PPh_2$ group at the ferrocene nucleus. The Pd atom is coordinated to the sulfonate oxygen and the phosphorus atom. The allyl ligand is bonded in the η^3-mode. In the depicted isomer the internal allyl CH group is oriented away from the ferrocene center (i.e., the **7a**-anti isomer).

Table 1. Selected Bond Lengths (Å) and Angles (deg) of the Pair of Crystallographically Independent 7a(A,B) Molecules in the Crystal

	A	B
Pd−O	2.127(3)	2.129(3)
Pd−P	2.281(1)	2.283(1)
Pd−C(31)	2.101(5)	2.097(5)
Pd−C(32)	2.165(5)	2.156(5)
Pd−C(33)	2.230(5)	2.218(5)
C(31)−C(32)	1.408(8)	1.396(8)
C(32)−C(33)	1.365(8)	1.369(9)

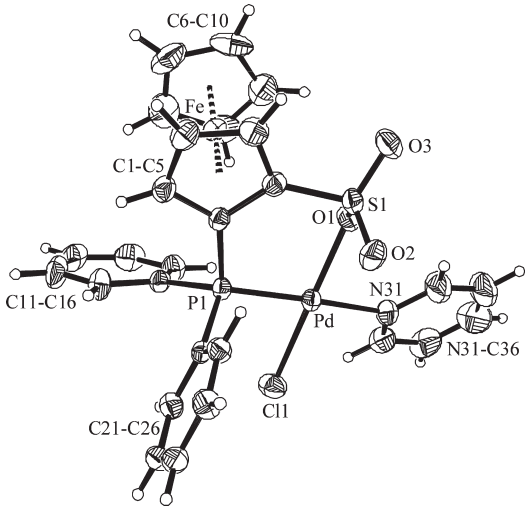


Figure 3. View of the molecular structure of complex **8a**. Selected bond lengths (Å) and angles (deg): Pd−O(1) 2.066(2), Pd−Cl(1) 2.261(1), Pd−N(31) 2.137(3), Pd−P(1) 2.247(1), Cl(1)−Pd−N(31) 91.3(1), Cl(1)−Pd−O(1) 179.3(1), N(31)−Pd−O(1) 88.2(1), Cl(1)−Pd−P(1) 85.2(1), N(31)−Pd−P(1) 175.1(1), O(1)−Pd−P(1) 95.3(1), S(1)−O(1)−Pd 119.6(2).

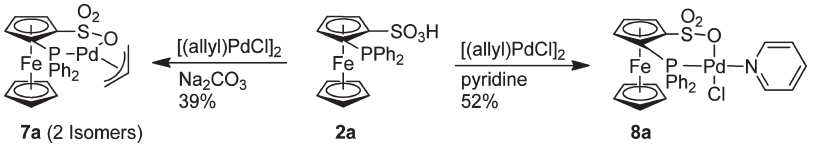
When the reaction of the ferrocene-derived (Fc-O,P) ligand system **2a** with $[Pd(allyl)Cl]_2$ was carried out in the presence of pyridine instead of the sodium carbonate base, we obtained the product **8a**, which was isolated in ca. 50% yield. The X-ray crystal structure analysis (see Figure 3) revealed that the (Fc-O,P) ligand (**2a**) was bonded in the usual cis fashion to palladium and that the Pd center carried a chloride ligand and pyridine bonded to it in a square-planar coordination geometry. The pyridine ligand was found positioned trans to the phosphine and, consequently, chloride was found trans to the sulfonate oxygen atom (see Figure 3 for selected bond lengths and angles).

In solution, complex **8a** features a ^{1}H NMR Cp singlet [δ 4.30, s, 5H (^{13}C: δ 72.8)] and three separate ^{1}H NMR signals of the remaining ferrocene C_5H_3[S][P] moiety (δ 5.18, 4.47, 3.96). We monitored the signals of a $-PPh_2$ substituent (^{31}P NMR: δ 12.5) and the NMR resonances of the Pd-coordinated pyridine ligand [^{1}H NMR: δ 8.90 (*o*), 7.92 (*p*), 7.52 (*m*)].

We next reacted each of the ferrocene-O,P chelate ligand systems **2**(**a**,**b**,**c**) with the (tmeda)$PdMe_2$ reagent (**9**).[21] A typical example is the reaction of **2a** with **9**, which gave the product **10a**. It was isolated in close to 50% yield. Compound **10a** was characterized by C,H,N elemental analysis and by X-ray diffraction before it was used for the subsequent amine displacement reaction with pyridine (see below). In the crystal, complex **10a** was shown to be a dimer, featuring a κN,κN-bridging tetramethylethylenediamine ligand. The κN-amino ligands are oriented trans to phosphorus at each square-planar coordinated Pd atom. The structure of complex **10a** is depicted in the Supporting Information.

The Pd complex **10a** was then subjected to the amine exchange reaction. Treatment with pyridine for 2 h at ambient conditions gave the monomeric (Fc-O,P)Pd(CH_3)(pyridine) complex **11a**, which was isolated from the reaction mixture in close to 50% yield (see Scheme 3). The chelate diarylphosphinoferrocene sulfonate ligands **2b** and **2c** were reacted analogously with the (tmeda)$PdMe_2$ reagent (**9**); only in these cases we did not isolate the respective intermediates (**10b**, **10c**) but subjected them after in situ formation directly to the exchange reaction with pyridine. We isolated the respective products (**11b**, **11c**) in yields of 38% and 61%, respectively. All three products (**11a**,**b**,**c**) were characterized spectroscopically, by C,H,N elemental analysis, and by X-ray diffraction. As a typical example complex **11b** features a broad ^{1}H NMR singlet at δ 0.51 of the [Pd]-CH_3 group [^{13}C NMR feature at δ 0.40] and the signals of a pair of diastereotopic *o*-anisyl groups at phosphorus (OCH_3, ^{1}H NMR: δ 3.54, 3.72; ^{31}P NMR resonance at δ 20.0) and κN pyridine ligand ^{1}H NMR signals at δ 8.89 (*o*), 7.89 (*p*), and 7.52 (*m*).

Scheme 2



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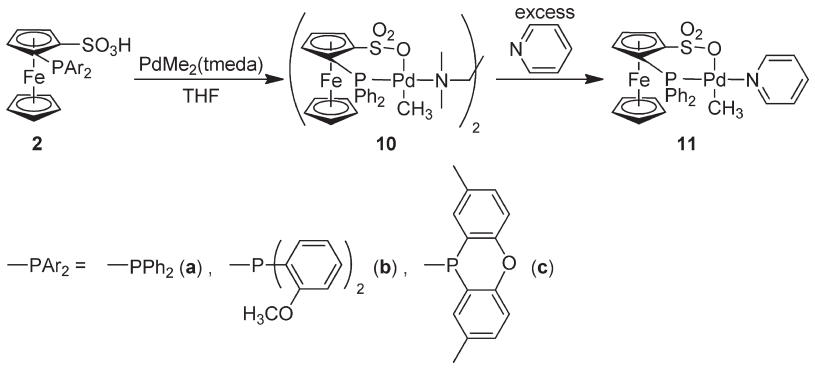
Scheme 3



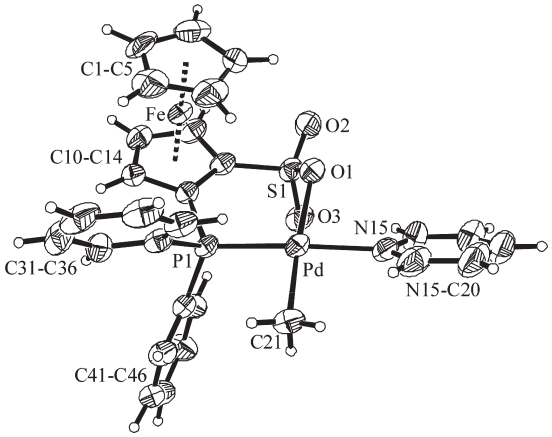


Figure 4. Molecular structure of the Pd complex **11a**.

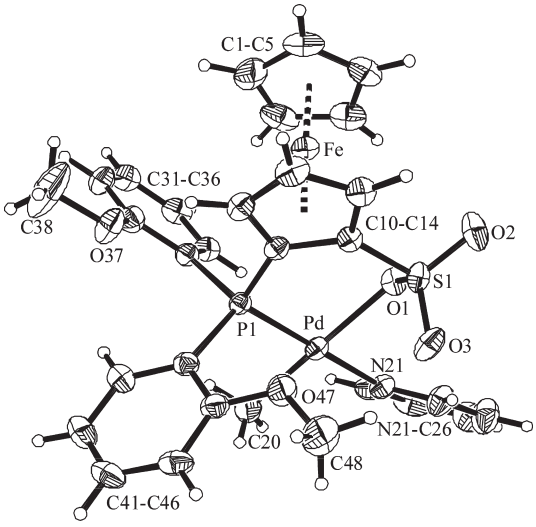


Figure 5. View of the molecular structure of complex **11b**.

The molecular structures of compounds **11a**, **11b**, and **11c** are depicted in Figures 4, 5, and 6. Selected structural data of these (Fc-O,P)PdCH$_3$(pyridine) systems are listed in Table 2, which also contains the data of the parent benzene derivate (**12**)[15] for a comparison (see Chart 2). As a typical example, complex **11b** shows a molecular structure in the crystal that features the pair of $-SO_3^-$ and $-P(anisyl)_2$ substituents at the ferrocene backbone (see Figure 5). The characteristic bonding parameters around the square-planar Pd coordination sphere of **11b** and the ferrocene-free reference compound **12** are quite similar (see Table 2); only the C(Me)−Pd−P and the S−O−Pd angles in **11b** are slightly smaller than in **12**, and the N−Pd−P angle in **11b** is enlarged by ca. 5° relative to this reference.

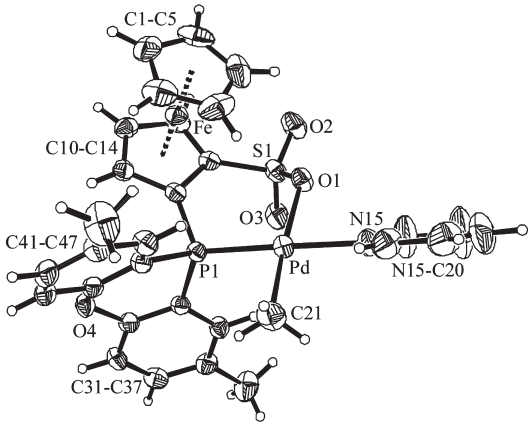


Figure 6. Molecular structure of the (Fc-O,P)PdMe(pyridine) complex **11c**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of the New (Fc-O,P)PdCH$_3$(pyridine) Complexes 11(a,b,c) and (for comparison) of 12[15] (see Chart 2)

	11a	11b	11c	12
Pd−O	2.179(5)	2.161(2)	2.158(2)	2.165(3)
Pd−C(Me)	2.038(8)	2.033(3)	2.021(3)	2.027(5)
Pd−N(Py)	2.126(6)	2.114(2)	2.118(2)	2.108(3)
Pd−P	2.228(2)	2.234(1)	2.205(1)	2.232(1)
C(Me)−Pd−N(Py)	89.5(3)	92.0(1)	90.8(1)	90.8(2)
C(Me)−Pd−O(1)	175.5(3)	176.4(1)	175.4(1)	175.0(2)
N(Py)−Pd−O(1)	86.5(2)	85.4(1)	85.8(1)	84.9(1)
C(Me)−Pd−P(1)	87.6(3)	86.9(1)	86.7(1)	90.0(1)
N(Py)−Pd−P(1)	176.9(2)	177.4(1)	176.5(1)	172.7(1)
O(1)−Pd−P(1)	96.3(1)	95.6(1)	96.9(1)	94.6(1)
S(1)−O(1)−Pd	116.9(3)	117.3(1)	124.3(1)	122.4(2)

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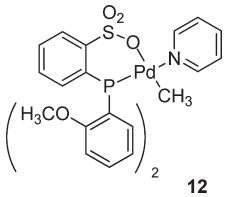
POLYMERIZATION REACTIONS

Ethene/CO copolymerization reactions were carried out in methanol with either the preformed Pd complex or by preparing the active Pd complex in situ by treatment of the respective ligand system **2** with Pd-acetate. In some cases activation by added Lewis acids was probed (see below). Orientating experiments showed that under these conditions the catalysts derived from the diphenylphosphino-substituted (Fc-O,P)H ligand (**2a**) showed only a moderate reactivity and the **2c**-derived system was catalytically inactive. Therefore, we concentrated on the use of the bis(*o*-anisyl)-phosphino-substituted (Fc-O,P)H (**2b**)-derived catalyst systems. As can be seen from Table 3, the catalyst generated in situ from the ligand system **2b** and $Pd(OAc)_2$ in methanol tested under the typical "Drent conditions" (30 bar ethene and 20 bar CO partial pressure)[12] was active but produced only a close to perfectly alternating ethene/CO copolymer. Therefore, we changed the ethene/CO partial pressure ratio in steps to eventually 60/5. This resulted in a reduced catalyst activity, as expected, but the resulting system was still reasonably active. It produced an ethene/CO copolymer that contained substantial amounts of nonalternating sections. The amount of "extra" ethene insertions amounted to ca. 25 mol %. The addition of the Lewis acid activator BF_3 resulted in a small activity increase going along with only a slight decrease in extra ethene insertions (see Table 3, entry 5). From the ^{13}C NMR spectra of the polymer samples (measured in a hexafluoro-2-propanol/d_6-benzene mixture) we could identify the formation of single, double, and potentially triple additional ethene insertion sequences[12,13] (see Scheme 4 and Figure 6).

Chart 2



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We also employed the preformed (Fc-O,P)PdMe(pyridine) system **11b** for the catalyst generation in methanol at elevated temperature. This system performed similarly in ethene/CO nonalternating copolymerization (see Table 4) to the in situ formed catalyst (see above). At an ethene/CO partial pressure ratio of 50/5 we obtained a nonalternating copolymer that contained slightly more than 25% extra ethene insertions. Addition of $B(C_6F_5)_3$ as a Lewis acid activator component resulted in a marked increase in catalyst activity but at the expense of some reduction of the extra ethylene insertion amount (see Table 4). As expected the melting points (1st dsc cycle) were found to decrease markedly with increasing extra ethene insertion.[13,15b]

CONCLUSIONS

The *o*-diarylphosphinoferrocene sulfonates (**2**) are the organometallic analogues of the organic benzene-derived chelate ligand systems **1**. The systems **2** can be prepared by a straightforward synthetic route and form the basis for the preparation of the corresponding neutral Pd(II) chelate complexes **7**, **8**, **10**, and **11**, respectively. The bis(*o*-anisyl)phosphino derivatives are active catalysts for ethene/CO copolymerization. At relatively low ethene/CO ratios they produce nearly alternating ethene/CO copolymers, but at a ca. 10:1 ethene/CO partial pressure ratio substantially nonalternating copolymers were obtained. Of course, the overall catalyst activities decreased with decreasing CO partial pressure,[15] but the resulting activities were still quite remarkable. So, in principle, the new ferrocene-based chelate phosphino/sulfonate catalyst systems (derived from **2**) behaved qualitatively similar to the systems derived from the purely organic ligands **1**. The ferrocene moiety offers quite a variety of possibilities for electronic variation of catalyst systems derived from such chelate ligands. This lets us hope that the described systems are a good start for developing advanced catalyst systems on a ferrocene derivative basis.

EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under a dry argon atmosphere using standard Schlenk techniques or in a glovebox.

Table 3. Ethene/CO Copolymerization at the Catalyst Systems in Situ Prepared from the (Fc-O,P)H Ligand 2b[a]

	entry					
	1	2	3	4	5	6
catalyst	$Pd(OAc)_2$	$Pd(OAc)_2$	$Pd(OAc)_2$	$Pd(OAc)_2$	$Pd(OAc)_2$	$Pd(OTfa)_2$
loading(μmol) [Pd]	10	10	10	10	10	10
loading(μmol) [**2b**]	10	10	10	10	10	10
additive					BF_3	
loading (μL)					10	
loading (μmol)					50	
$p(C_2H_4)$ (bar)	30	50	50	60	60	30
p(CO) (bar)	5	5	5	5	5	20
T (°C)	110	110	90	110	110	110
yield (mg)	220	280	180	210	270	750
activity[b]	22	28	18	21	27	75
extra insertion	5%	12%	12%	25%	23%	1%
Mp(dsc)[c] [°C]	220	206	199	171	182	242

[a] In methanol solution, 1 h reaction time. [b] g (polymer) × mmol[Pd]$^{-1}$ × h^{-1}. [c] Values from the first heating cycle.

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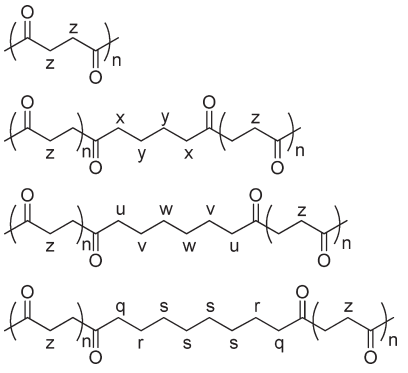
Scheme 4



Solvents (including deuterated solvents used for NMR) were dried and distilled prior to use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a 300, 500, or 600 MHz spectrometer at ambient temperature unless otherwise stated. Chemical shifts are given in ppm relative to solvents (^{1}H and ^{13}C) or to phosphoric acid (85%) as an external standard. Coupling constants are in Hz. Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid. The starting materials di(*o*-anisyl)-phosphine chloride[6a] and Pd(tmeda)Me_2[21] were prepared according to the reported or modified procedure or purchased from Alfa Aeser and Strem.

X-ray single-crystal structure analysis. Data sets were collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods*

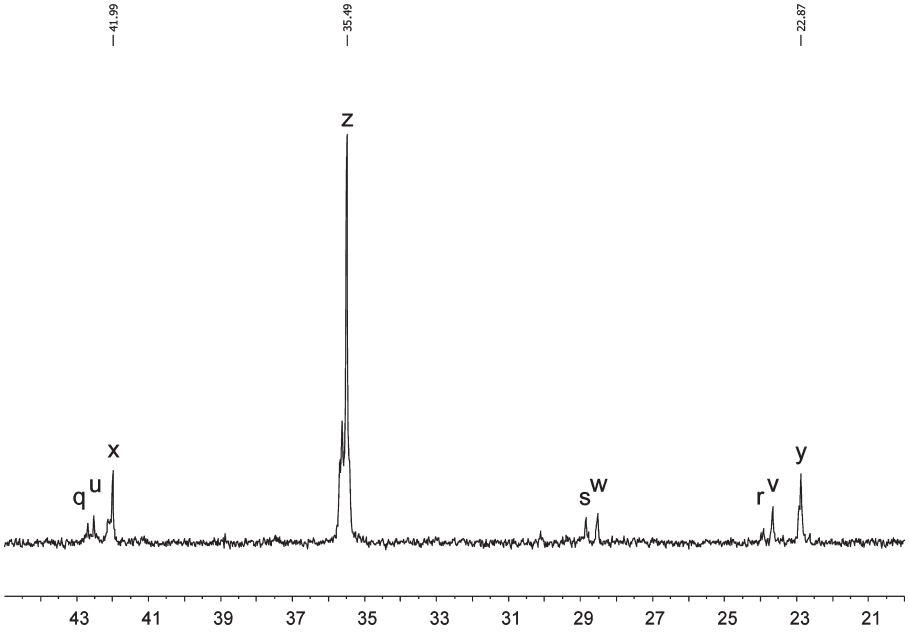


Figure 7. $^{13}C\{^{1}H\}$ NMR (75 MHz, 294 K) spectrum of the ethylene section of the nonalternating copolymer formed at the **2b**/Pd catalyst (entry 5 in Table 3).

Table 4. Nonalternating Ethene/CO Copolymerization with the Catalyst Derived from the Preformed 11b (Fc-O,P)PdMe-(pyridine) System[a]

	entry						
	1	2	3	4	5	6	7
loading (μmol) [Pd]	10	10	10	10	10	10	10
LA[b] additive		$B(C_6F_5)_3$		$B(C_6F_5)_3$		$B(C_6F_5)_3$	
loading (mg) [LA]		11		11		11	
loading (μmol) [LA]		20		20		20	
$p(C_2H_4)$ (bar)	30	30	30	30	50	50	40
p(CO) (bar)	20	20	5	5	5	5	10
T (°C)	110	110	110	110	110	110	110
t (h)	1	1	1	1	1	1	1
yield (mg)	740	1590	250	360	180	320	420
activity [c]	74	159	25	36	18	32	42
extra insertion	3%	1%	15%	10%	27%	17%	8%
Mp(dsc)[d] [°C]	233	242	178	197	167	170	207

[a] In CH_2Cl_2 solution. [b] LA: Lewis acid. [c] g (polymer) × mmol[Pd]$^{-1}$ × h^{-1}. [d] Values from the first heating cycle.

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Enzymol. **1997**, *276*, 307−326), absorption correction SORTAV (R. H. Blessing, *Acta Crystallogr.* **1995**, *A51*, 33−37; R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426) and Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr.* **2003**, *A59*, 228−234), structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467−473), structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112−122), graphics XP (BrukerAXS, 2000). Graphics show the thermal ellipsoids with 50% probability. *R* values are given for the observed reflections; wR^2 values for all reflections.

Preparation of Lithium Ferrocene Sulfonate 3. *Preparation of toluidinium ferrocene sulfonate*:[19] Ferrocene (20 g, 108 mmol) was suspended in acetic anhydride (120 mL) under argon and cooled to 0 °C. Then chlorosulfonic acid was added dropwise over 15 min. After the addition was completed, the mixture was stirred at room temperature for 24 h. The resulting green solution was carefully added to 600 mL of ice. After quenched, the solution was filtered. *p*-Toluidine (12.2 g, 114 mmol) was dissolved in 50 mL of water and concentrated HCl (about 9.0 mL). The two solutions above were cooled to 0 °C and mixed together. A lot of solid was generated. The solid was filtered, pressed, and washed with cooled water (0 °C, 50 mL × 2) and ether (0 °C, 50 mL × 2). The solid was collected and dried under vacuum. The product was obtained as a yellow solid (37 g, 92%). The product was further purified by recrystallization from ethanol. *Lithium ferrocene sulfonate* ***3****:* Toluidinium ferrocene sulfonate (11.2 g, 30.0 mmol) was weighted into a Schlenk tube. The vessel was evacuated and recharged with argon. The cycle was made three times before THF (200 mL) was added under Ar. The suspension was cooled to 0 °C, and *n*-BuLi (1.6 M in hexane, 19 mL, 30.4 mmol) was added dropwise. After the addition was completed, the reaction was allowed to warm to room temperature and stirred overnight. The yellow mixture was filtered under Ar, and the solid was washed with THF (50 mL), dried, and collected in a glovebox. About 10.3 g of product was obtained, and the yield was quantitative.

Preparation of Ligand 2a. Lithium ferrocene sulfonate (1.73 g, 6.3 mmol) was suspended in dry THF (50 mL) under Ar and cooled to 0 °C with an ice bath. Then *n*-BuLi (1.6 M in hexane, 5 mL, 8.0 mmol) was added dropwise. The resulting red solution was stirred for 5.0 h at 0 °C before it was quenched by $ClPPh_2$ (1.7 mL, 8.0 mmol). The mixture was stirred for a further 14 h at room temperature. A 20 mL amount of water and 20 mL of brine were added in one portion to quench the reaction. The organic layer was separated and acidified by 1.5 mL of concentrated HCl in 30 mL of water. The aqueous phase was separated and extracted with THF (30 mL). The organic phases were combined, dried over $MgSO_4$ quickly, and filtered. The filtrate was evaporated to dryness under vacuum. The residue was dispersed with acetone (10 mL) with the assistance of ultrasonic bath. The solution was filtered, and the solid was collected. The product was obtained as a yellow solid (1.0 g, 44%) and was not further purified. ^{31}P NMR (d_6-DMSO, 300 K): δ −18.8.

Preparation of Ligand 2b. *Preparation of dichloro[di(isopropyl)-amido]phosphine*:[22] PCl_3 (12.5 mL, 145 mmol) was dissolved in ether (125 mL) and cooled to 0 °C. Di(isopropyl)amine (37.5 mL, 195 mmol) was slowly added. Then the resulting suspension was allowed to react overnight at RT before it was filtered under Ar. The white solid was washed with ether (2 × 50 mL). The ether solution was combined and evaporated under vacuum. The residue was transferred into a flask via syringe for distillation. The product was obtained as a colorless liquid and slowly crystallized while stored (15.2 mL, 69%). *Preparation of chlorodi(o-anisyl)phosphine:* Anisole (10.8 mL, 100 mmol) and TMEDA (15.0 mL, 100 mmol) were dissolved in pentane (120 mL) under argon and cooled to −78 °C. Then *n*-BuLi (1.6 M in hexane, 64 mL, 102 mmol) was added dropwise. After the addition was completed, the resulting suspension was slowly warmed to RT and stirred for 24 h. Then it was cooled to −78 °C again, and dichloro[di(isopropyl)-amido]phosphine (7.1 mL, 50 mmol) was slowly added. The mixture was warmed to RT and stirred overnight. The reaction was quenched with water (50 mL). The pentane solution was separated. The aqueous phase with lots of solid was extracted with dichloromethane (2 × 50 mL). The organic phases were combined, dried over $MgSO_4$, and filtered. The filtrate was rotatory evaporated to dryness. The residue was purified by recrystallization from hexane to give di(*o*-anisyl)-di-(isopropyl)amido phosphine as a white solid (10.4 g, 60%). The solid was suspended in ether (200 mL) under Ar and cooled to 0 °C. Then HCl etheral solution (2 M, 60 mmol) was added and caused a white precipitation. The suspension was reacted for 12 h at RT and heated to reflux for 1 h. The mixture was filtered, and the solid was washed with ether (200 mL). The ether solution was evaporated to dryness under vacuum, and the product was collected as white solid in a glovebox (7.32 g, 87%). The product, di(*o*-anisyl)phosphine chloride, could be purified by recrystallization from toluene if necessary. *Preparation of ligand* ***2b****:* Lithium ferrocene sulfonate (2.73 g, 10 mmol) was suspended in dry THF (60 mL) under Ar and cooled to 0 °C with an ice bath. Then *n*-BuLi (1.6 M in hexane, 9.5 mL, 15 mmol) was added dropwise. The resulting red solution was stirred for 5 h at 0 °C before it was quenched by $ClPAn_2$ (4.3 g, 15 mmol, dissolved in 20 mL of THF under argon). The mixture was stirred for a further 14 h at room temperature. Sometimes, the mixture should be filtered if some precipitation was produced before being quenched. Then 30 mL of water and 30 mL of brine were added in one portion to quench the reaction. The organic layer was separated and acidified by 2 mL of concentrated HCl in 30 mL of water. The aqueous phase was separated and extracted with THF (2 × 30 mL). The organic phases were combined, dried over $MgSO_4$ quickly, and filtered. The filtrate was evaporated to dryness under vacuum. The residue was dispersed with acetone (10 mL) with the assistance of an ultrasonic bath. The solution was filtered, and the solid was collected. The product was obtained as a yellow solid (2.0 g, 40%) and was not further purified. ^{31}P NMR (d_6-DMSO, 300 K): δ −44.2.

Preparation of Ligand 2c. *Preparation of POPCl [2,8-dimethyl-10-chlorophenoxaphosphine]*:[23] Ditolyl ether (11.9 g, 60 mmol) and $AlCl_3$ (10.7 g, 80 mmol) were dissolved in PCl_3 (40 mL) under argon. The mixture was heated to reflux (ca. 80 °C) for 8 h. Then the mixture was cooled to RT, and exeess PCl_3 was removed under vacuum. To the residue was added toluene (80 mL), and the suspension was stirred thoroughly at 0 °C. Then pyridine was slowly added to produce much solid. After the suspension was stirred for 1 h at room temperature, the solid was filtered off and washed with toluene (50 mL) twice. The toluene solution was combined and evaporated under vacuum. Then 60 mL of toluene was added, and the mixture was heated to reflux. The solution was slowly cooled and kept at −20 °C overnight to give POPCl as a white solid (10.53 g, 74%). *Preparation of ligand* ***2c****:* Lithium ferrocene sulfonate (2.73 g, 10 mmol) was suspended in dry THF (60 mL) under Ar and cooled to 0 °C with an ice bath. Then *t*-BuLi (1.6 M in hexane, 10 mL, 16 mmol) was added dropwise. The resulting red solution was stirred overnight at at room temperature. The reaction was quenched with POPCl (3.15 g, 12 mmol) at 0 °C. The mixture was stirred overnight at room temperature. Then 2.0 mL of concentrated HCl was added followed by 25 mL of water and 25 mL of brine. The aqueous phase was separated and extracted with THF (2 × 20 mL). The organic phases were combined, dried over $MgSO_4$ quickly, and filtered. The filtrate was evaporated to dryness under vacuum. The residue was dispersed with dichloromethane (20 mL) with the assistance of an ultrasonic bath. The solution was filtered, and the solid was collected. The product was obtained as a yellow solid (0.86 g, 17%) and was not further purified.

Preparation of Complex 7a. Ligand **2a** (225 mg, 0.5 mmol) was suspended in CH_2Cl_2 (5 mL) and treated with Na_2CO_3 (210 mg, 2.0 mmol) for 0.5 h. AllylPdCl dimer (90 mg, 0.5 mmol) was added. The mixture was stirred overnight and filtered. The solid was washed with CH_2Cl_2 (5 mL × 2). The solution was combined, layered with ether

(20 mL), and filtered. The product was obtained as a red solid (122 mg, 39%). Anal. Calcd for for $C_{25.5}H_{24}ClFeO_3PPdS$: C 47.91, H 3.78. Found: C 48.79, H 3.97.

Major product (78%): ^{1}H NMR (500 MHz, CD_2Cl_2, 193 K): δ 7.60 (m, 2H, *p*-Ph^b), 7.56 (m, 2H, *o*-Ph^b), 7.53 (m, 2H, *m*-Ph^b), 7.39 (m, 2H, *p*-Ph^a), 7.35 (m, 2H, *m*-Ph^a), 7.15 (m, 2H, *o*-Ph^a), 6.00 (m, 1H, =CH), 5.08 (br, 1H, 5-H), 5.01 (m, 1H, =CH_2^b), 4.44 (m, 1H, 4-H), 4.04 (s, 5H, Cp), 3.99 (m, 1H, =CH_2^b), 3.93 (br, 1H, 3-H), 3.72 (br d, J = 6.5 Hz, 1H, =CH_2^a), 2.65 (br d, J = 11.9 Hz, 1H, =CH_2^a). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 134.1 (d, $^2J_{PC}$ = 14.7 Hz, *o*-Ph^b), 133.0 (d, $^1J_{PC}$ = 46.2 Hz, *i*-Ph^a), 131.6 (br, *p*-Ph^b), 131.1 (d, $^2J_{PC}$ = 12.1 Hz, *o*-Ph^a), 130.7 (d, $^1J_{PC}$ = 52.7 Hz, *i*-Ph^b), 129.8 (br, *p*-Ph^a), 128.6 (d, $^3J_{PC}$ = 11.2 Hz, *m*-Ph^b), 128.3 (d, $^3J_{PC}$ = 11.2 Hz, *m*-Ph^a), 119.5 (m, =CH), 96.3 (d, $^2J_{PC}$ = 17.8 Hz, 1-C), 84.7 (d, J = 27.2 Hz, =CH_2^b), 73.3 (m, 3,5-C), 70.7 (d, J = 5.0 Hz, 4-C), 71.4 (Cp), 67.9 (d, $^1J_{PC}$ = 50.2 Hz, 2-C), 51.3 (=CH_2^a). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 193 K): δ 13.8 ($\nu_{1/2} \approx 2$ Hz). *Minor product (22%)*: ^{1}H NMR (500 MHz, CD_2Cl_2, 193 K): δ 7.68 (m, 2H, *p*-Ph^b), 7.56 (m, 2H, *m*-Ph^b), 7.53 (m, 2H, *o*-Ph^b), 7.39 (m, 2H, *p*-Ph^a), 7.35 (m, 2H, *m*-Ph^a), 7.15 (m, 2H, *o*-Ph^a), 5.69 (m, 1H, =CH), 5.08 (br, 1H, 5-C), 4.99 (m, 1H, =CH_2^b), 4.44 (m, 1H, 4-C), 4.19 (s, 5H, Cp), 4.15 (m, 1H, =CH_2^b), 3.86 (br, 1H, 3-C), 3.57 (br m, 1H, =CH_2^a), 2.94 (br d, J = 11.9 Hz, 1H, =CH_2^a). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ [selected resonances] 119.5 (m, =CH), 84.5 (d, J = 28.8 Hz, =CH_2^b), 71.6 (Cp), 49.2 (=CH_2^a). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 193 K): δ 14.6 ($\nu_{1/2} \approx 2$ Hz).

Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **7a** and CH_2Cl_2. X-ray crystal structure analysis for **7a**·0.5 CH_2Cl_2: formula $C_{25}H_{23}FeO_3PPdS \cdot 1/2CH_2Cl_2$, M = 639.18, yellow crystal 0.30 × 0.10 × 0.05 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.9418(2) Å, b = 14.3677(2) Å, c = 16.6363(3) Å, α = 90.136(1)°, β = 94.013(1)°, γ = 108.473(1)°, V = 2473.69(7) Å^3, D_{calcd} = 1.716 g cm^{-3}, μ = 1.597 mm^{-1}, empirical absorption correction (0.646 ≤ T ≤ 0.924), Z = 4, λ = 0.71073 Å, T = 223 K, ω and φ scans, 22 713 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 11 621 independent (R_{int} = 0.044) and 10 441 observed reflections [$I \geq 2\sigma(I)$], 604 refined parameters, R = 0.049, wR_2 = 0.121, max. residual electron density 1.24 (−1.08) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 8a. Ligand **2a** (225 mg, 0.5 mmol) was suspended in CH_2Cl_2 (10 mL) and treated with pyridine (10 mL) for 1 h. AllylPdCl dimer (90 mg, 0.5 mmol) was added. The mixture was stirred overnight and filtered. The solution was deposited with ether (20 mL) and filtered. Then the solution was slowly evaporated to give the product (175 mg, 52%). Anal. Calcd for $C_{27}H_{23}ClFeNO_3PPdS$: C 48.33, H 3.89, N 1.94. Found: C 48.51, H 3.74, N 1.61. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.90 (d, $^3J_{HH}$ = 4.7 Hz, 2H, *o*-Py), 8.14 (m, 2H, *o*-Ph^a), 7.92 (t, $^3J_{HH}$ = 7.6 Hz, 1H, *p*-Py), 7.70 (m, 1H, *p*-Ph^a), 7.63 (m, 2H, 2H, *m*-Ph^a), 7.61 (m, 2H, 2H, *o*-Ph^b), 7.52 (m, 2H, *m*-Py), 7.52 (m, 1H, *p*-Ph^b), 7.39 (m, 1H, *m*-Ph^b), 5.18 (m, 1H, 5-H), 4.47 (m, 1H, 4-H), 4.30 (s, 5H, Cp), 3.96 (m, 1H, 1H, 3-H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 150.2 (*o*-Py), 139.5 (*p*-Py), 135.5 (d, $^2J_{PC}$ = 11.4 Hz, *o*-Ph^a), 133.6 (d, $^2J_{PC}$ = 10.2 Hz, *o*-Ph^b), 132.6 (d, $^4J_{PC}$ = 2.8 Hz, *p*-Ph^a), 131.7 (d, $^4J_{PC}$ = 3.2 Hz, *p*-Ph^b), 130.8 (d, $^1J_{PC}$ = 58.7 Hz, *i*-Ph^b), 128.7 (d, $^3J_{PC}$ = 10.3 Hz, *m*-Ph^b), 128.6 (d, $^3J_{PC}$ = 10.7 Hz, *m*-Ph^a),128.4 (d, $^1J_{PC}$ = 69.1 Hz, *i*-Ph^a), 125.4 (*m*-Py), 96.5 (d, $^2J_{PC}$ = 15.3 Hz, 1-C), 73.9 (d, $^3J_{PC}$ = 1.7 Hz, 3-C), 73.4 (d, $^3J_{PC}$ = 6.6 Hz, 5-C), 72.8 (Cp), 72.1 (d, $^3J_{PC}$ = 6.7 Hz, 4-C), 69.4 (d, $^1J_{PC}$ = 60.1 Hz, 2-C). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ 12.5 ($\nu_{1/2} \approx 5$ Hz).

Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of ether into a solution of **8** and CH_2Cl_2. X-ray crystal structure analysis of **8**·0.5Et_2O: formula $C_{27}H_{23}FeNO_3PPdS \cdot 1/2\ C_4H_{10}O$, M = 707.25, yellow-organge crystal 0.35 × 0.30 × 0.05 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 17.2424(3) Å, b = 9.4608(2)Å, c = 17.4506(3) Å, β = 92.582 (1)°, V = 2843.8(1) Å^3, D_{calcd} = 1.652 g cm^{-3}, μ = 1.400 mm^{-1}, empirical absorption correction (0.640 ≤ T ≤ 0.933), Z = 4, λ = 0.71073 Å, T = 223 K, ω and φ scans, 17 847 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 6772 independent (R_{int} = 0.055) and 4717 observed reflections [$I \geq 2\sigma(I)$], 358 refined parameters, R = 0.043, wR_2 = 0.104, max. residual electron density 0.80 (−0.78) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 11a. Ligand **2a** (225 mg, 0.5 mmol) was suspended in THF (10 mL), and Pd(tmeda)Me_2 (128 mg, 0.5 mmol) was added at 0 °C. After 5 min the emission of gas ceased and the suspension turned clear. The solution was stirred overnight, and much precipitation was produced again. The solid could be collected via filtration and was characterized as the tmeda-bridged dimer of the Pd complex **10a** (170 mg, 52%). Pyridine (1 mL, excess) was added to the former suspension, giving a solution. After 2 h the mixture was filtered and the residue was washed with dichloromethane (5 mL). The organic phases were combined and deposited with ether (200 mL). Then it was filtered, and the filtrate was kept at −32 °C for 2 days. The crystalline product **11a** was collected via filtration (160 mg, 49%).

*Compound **10a*** was characterized only by elemental analysis and X-ray crystal structure analysis. Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **10** and CH_2Cl_2. Anal. Calcd for $C_{52}H_{58}Fe_2N_2O_6P_2Pd_2S_2$: C 49.66, H 4.65, N 2.23. Found: C 49.54, H 4.49, N 2.09.

X-ray crystal structure analysis for **10a**·2CH_2Cl_2: formula $C_{52}H_{58}Fe_2N_2O_6P_2Pd_2S_2 \cdot 2CH_2Cl_2$, M = 1427.42, yellow crystal 0.50 × 0.10 × 0.05 mm, monoclinic, space group $P2_1/n$ (No. 14), a = 12.0508(2) Å, b = 11.6611(2) Å, c = 24.0288(7) Å, β = 99.615(1)°, V = 3329.23(13) Å^3, D_{calcd} = 1.424 g cm^{-3}, μ = 1.273 mm^{-1}, empirical absorption correction (0.569 ≤ T ≤ 0.939), Z = 2, λ = 0.71073 Å, T = 223 K, ω and φ scans, 21 179 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 7953 independent (R_{int} = 0.067) and 5423 observed reflections [$I \geq 2\sigma(I)$], 355 refined parameters, R = 0.064, wR_2 = 0.223, max. residual electron density 1.70 (−0.73) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*Compound **11a**:* Anal. Calcd for $C_{28}H_{26}FeNO_3PPdS$: C 51.75, H 4.03, N 2.16. Found: C 51.79, H 4.33, N 2.15. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.83 (m, 2H, *o*-Py), 8.00 (m, 2H, *o*-Ph^a), 7.92 (m, 1H, *p*-Py), 7.65 (m, 1H, *p*-Ph^a), 7.62 (m, 2H, *m*-Ph^a), 7.54 (m, 2H, *m*-Py), 7.44 (m, 1H, *o*-Ph^b), 7.42 (m, 1H, *p*-Ph^b), 7.37 (m, 2H, *m*-Ph^b), 5.09 (m, 1H, 5-H), 4.40 (m, 1H, 4-H), 4.21 (s, 5H, Cp), 3.90 (m, 1H, 3-H), 0.67 (d, $^3J_{PH}$ = 2.6 Hz, 3H, $PdCH_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 150.7 (*o*-Py), 138.9 (*p*-Py), 135.8 (d, $^2J_{PC}$ = 13.0 Hz, *o*-Ph^a), 133.6 (d, $^1J_{PC}$ = 52.2 Hz, *i*-Ph^b), 132.5 (d, $^2J_{PC}$ = 10.8 Hz, *o*-Ph^b), 132.1 (d, $^4J_{PC}$ = 2.6 Hz, *p*-Ph^a), 130.5 (d, $^4J_{PC}$ = 2.5 Hz, *p*-Ph^b), 129.7 (d, $^1J_{PC}$ = 60.1 Hz, *i*-Ph^a), 128.9 (d, $^3J_{PC}$ = 11.3 Hz, *m*-Ph^a), 128.7 (d, $^3J_{PC}$ = 10.5 Hz, *m*-Ph^b), 125.6 (*m*-Py), 98.6 (d, $^2J_{PC}$ = 17.2 Hz, 1-C), 73.4 (d, $^3J_{PC}$ = 6.5 Hz, 5-C), 73.3 (d, $^2J_{PC}$ = 1.1 Hz, 3-C), 72.4 (Cp), 71.4 (d, $^3J_{PC}$ = 6.0 Hz, 4-C), 70.9 (d, $^1J_{PC}$ = 55.1 Hz, 2-C), 0.40 (d, $^2J_{PC}$ = 6.5 Hz, $PdCH_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ 24.1 ($\nu_{1/2} \approx 2$ Hz).

Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **11a** and CH_2Cl_2. X-ray crystal structure analysis for **11a**·CH_2Cl_2: formula $C_{28}H_{26}FeNO_3PPdS \cdot CH_2Cl_2$, M = 734.70, yellow crystal 0.20 × 0.15 × 0.05 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 17.8906(7) Å, b = 9.3517(5) Å, c = 17.9434(8) Å, β = 102.814(2)°, V = 2927.3(2) Å^3, D_{calcd} = 1.667 g cm^{-3}, μ = 1.451 mm^{-1}, empirical absorption correction (0.760 ≤ T ≤ 0.931), Z = 4, λ = 0.71073 Å, T = 223 K, ω and φ scans, 19 908 reflections collected (±h, ±k, ±l), [(sin θ)/λ] = 0.66 Å^{-1}, 6629 independent (R_{int} = 0.054) and 4831 observed reflections [$I \geq 2\sigma(I)$], 346 refined parameters, R = 0.077, wR_2 = 0.191, max. residual electron density 1.32 (−1.27) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of the Complex 11b. Ligand **2b** (512 mg, 1.0 mmol) was suspended in THF (10 mL), and Pd(tmeda)Me_2 (256 mg,

1.0 mmol) was added at 0 °C. The suspension was stirred overnight, and then pyridine (1.2 mL, excess) was added to cause some solid to get dissolved. After 2 h the mixture was filtered, and the solid was washed with dichloromethane (5 mL). The organic phases were combined, and the product was precipitated with pentane (200 mL). Then it was filtered, and the filtrate was kept at −32 °C for 2 days. The crystalline product was collected by filtration (266 mg, 38%). Anal. Calcd for $C_{30}H_{30}FeNO_5PPdS$: C 50.76, H 4.26, N 1.97. Found: C 50.39, H 4.07, N 1.82. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 8.89 (m, 2H, *o*-Py), 8.73 (br, 1H, 6-Ar^a), 7.89 (m, 1H, *p*-Py), 7.63 (m, 1H, 4-Ar^a), 7.52 (m, 2H, *m*-Py), 7.35 (m, 1H, 4-Ar^b), 7.23 (m, 1H, 5-Ar^a), 7.09 (m, 1H, 3-Ar^a), 7.06 (m, 1H, 6-Ar^b), 6.87 (m, 1H, 5-Ar^b), 6.84 (m, 1H, 3-Ar^b), 4.97 (m, 1H, 5-H), 4.34 (m, 1H, 4-H), 4.32 (br, 1H, 3-H), 4.04 (s, 5H, Cp), 3.72 (br, 3H, OCH_3^{a}), 3.54 (br, 3H, OCH_3^{b}), 0.51 (br, 3H, $PdCH_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ 161.4 (br d, $^2J_{PC}$ = 0.9 Hz, 2-Ar^a), 160.0 (d, $^2J_{PC}$ = 4.5 Hz, 2-Ar^b), 150.9 (*o*-Py), 140.7 (br d, $^2J_{PC}$ = 24.0 Hz, 6-Ar^a), 138.6 (*p*-Py), 133.8 (d, $^4J_{PC}$ = 0.9 Hz, 4-Ar^a), 133.4 (d, $^2J_{PC}$ = 7.0 Hz, 6-Ar^b), 131.6 (d, $^4J_{PC}$ = 1.5 Hz, 4-Ar^b), 125.4 (*m*-Py), 121.7 (br d, $^1J_{PC}$ = 57.8 Hz, 1-Ar^b), 120.9 (d, $^3J_{PC}$ = 13.4 Hz, 5-Ar^a), 120.3 (br d, $^3J_{PC}$ = 10.2 Hz, 5-Ar^b), 118.8 (d, $^1J_{PC}$ = 57.2 Hz, 1-Ar^a), 111.4 (d, $^3J_{PC}$ = 4.2 Hz, 3-Ar^a), 111.3 (br, 3-Ar^b), 98.0 (d, $^2J_{PC}$ = 18.8 Hz, 1-C), 74.3 (d, $^2J_{PC}$ = 1.0 Hz, 3-C), 73.8 (br d, $^1J_{PC}$ = 56.2 Hz, 2-C), 72.1 (Cp), 71.9 (d, $^3J_{PC}$ = 6.7 Hz, 5-C), 70.8 (d, $^3J_{PC}$ = 6.3 Hz, 4-C), 55.4 (br, OCH_3^{b}), 55.3 (OCH_3^{a}), 0.40 ($PdCH_3$). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298 K): δ 20.0 ($\nu_{1/2} \approx$ 150 Hz).

Single crystals suitable for the X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **11b** and CH_2Cl_2. X-ray crystal structure analysis for **11b**: formula $C_{30}H_{30}FeNO_5PPdS$, M = 709.83, organge crystal 0.50 × 0.30 × 0.15 mm, monoclinic, space group $P2_1/c$ (No. 14), a = 14.5221(2) Å, b = 10.9631(2) Å, c = 18.2341(3) Å, β = 97.508(1)°, V = 2878.11(8) Å^3, D_{calcd} = 1.638 g cm^{-3}, μ = 1.298 mm^{-1}, empirical absorption correction (0.563 ≤ T ≤ 0.829), Z = 4, λ = 0.71073 Å, T = 223 K, ω and φ scans, 26 492 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 6897 independent (R_{int} = 0.042) and 5703 observed reflections [$I \geq 2\sigma(I)$], 364 refined parameters, R = 0.029, wR_2 = 0.078, max. residual electron density 0.59 (−0.62) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of Complex 11c. Ligand **2c** (248 mg, 0.5 mmol) was suspended in CH_2Cl_2 (5 mL), and Pd(tmeda)Me_2 (126 mg, 0.5 mmol) was added at 0 °C. The suspension turned clear initially and formed a suspension again in 0.5 h. Then pyridine (1 mL, excess) was added to cause some solid to dissolve. After 2 h the mixture was filtered and the solid was washed with dichloromethane (5 mL). The organic phases were combined and deposited with ether (90 mL). Then it was filtered, and the filtrate was kept at −32 °C for 2 days. The crystalline product was collected by filtration (236 mg, 61%). Anal. Calcd for $C_{30}H_{28}FeNO_4PPdS \cdot 0.5CH_2Cl_2$: C 49.89, H 3.98, N 1.91. Found: C 50.34, H 3.79, N 1.98. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ 8.93 (m, 2H, *o*-Py), 8.14 (dm, $^3J_{PH}$ = 15.5 Hz, 1H, 9-POP), 8.07 (dm, $^3J_{PH}$ = 15.2 Hz, 1H, 1-POP), 7.97 (m, 1H, *p*-Py), 7.60 (m, 2H, *m*-Py), 7.48 (dm, $^3J_{HH}$ = 8.4 Hz, 1H, 3-POP), 7.29 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 3.9 Hz, 1H, 4-POP), 7.25 (dm, $^3J_{HH}$ = 8.2 Hz, 1H, 7-POP), 7.08 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{PH}$ = 3.9 Hz, 1H, 6-POP), 4.89 (br m, 1H, 5-H), 4.31 (s, 5H, Cp), 4.19 (br t, $^3J_{HH}$ = 2.5 Hz, 1H, 4-H), 3.68 (br m, 1H, 3-H), 2.54 (s, 3H, 2-Me^{POP}), 2.35 (s, 3H, 8-Me^{POP}), 0.55 (d, $^3J_{PH}$ = 3.5 Hz, 1H, $PdCH_3$). ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ 155.3 (d, $^2J_{PC}$ = 1.3 Hz, 4a-POP), 153.0 (d, $^2J_{PC}$ = 1.4 Hz, 5a-POP), 150.6 (*o*-Py), 139.0 (*p*-Py), 135.9 (d, $^2J_{PC}$ = 17.3 Hz, 1-POP), 135.8 (d, $^2J_{PC}$ = 18.2 Hz, 9-POP), 134.6 (d, $^4J_{PC}$ = 2.0 Hz, 3-POP), 134.5 (d, $^3J_{PC}$ = 13.1 Hz, 8-POP), 134.0 (d, $^4J_{PC}$ = 2.1 Hz, 7-POP), 133.97 (d, $^3J_{PC}$ = 12.6 Hz, 2-POP), 125.7 (*m*-Py), 118.2 (d, $^3J_{PC}$ = 4.0 Hz, 4-POP), 117.7 (d, $^3J_{PC}$ = 3.8 Hz, 6-POP), 114.7 (d, $^1J_{PC}$ = 56.1 Hz, 9a-POP), 110.6 (d, $^1J_{PC}$ = 63.4 Hz, 10a-POP), 97.0 (d, $^2J_{PC}$ = 19.2 Hz, 1-C), 74.9 (d, $^1J_{PC}$ = 50.2 Hz, 2-C), 72.9 (d, $^3J_{PC}$ = 6.6 Hz, 5-C), 72.1 (Cp), 72.1 (3-C), 70.9 (d, $^3J_{PC}$ = 6.3 Hz, 4-C), 20.9 (2-Me^{POP}), 20.8 (8-Me^{POP}), 0.93 (d, $^2J_{PC}$ = 6.3 Hz, $PdCH_3$). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, 298 K): δ −10.7 ($\nu_{1/2} \approx$ 3 Hz).

Single crystals suitable for X-ray crystal structure analysis were obtained by slow diffusion of pentane into a solution of **11c** and CH_2Cl_2. X-ray crystal structure analysis for **11c**·CH_2Cl_2: formula $C_{30}H_{28}FeNO_4PPdS \cdot CH_2Cl_2$, M = 776.74, yellow crystal 0.30 × 0.15 × 0.10 mm, triclinic, space group $P\bar{1}$ (No. 2), a = 10.2911(2) Å, b = 11.3479(2) Å, c = 15.2349(3) Å, α = 71.626(1)°, β = 72.345 (1)°, γ = 71.369(1)°, V = 1558.86 (5) Å^3, D_{calcd} = 1.655 g cm^{-3}, μ = 1.369 mm^{-1}, empirical absorption correction (0.684 ≤ T ≤ 0.875), Z = 2, λ = 0.71073 Å, T = 223 K, ω and φ scans, 16 046 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sin θ)/λ] = 0.66 Å^{-1}, 7381 independent (R_{int} = 0.048) and 6108 observed reflections [$I \geq 2\sigma(I)$], 404 refined parameters, R = 0.037, wR_2 = 0.096, max. residual electron density 0.71 (−1.06) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

In Situ Copolymerizations. In a typical reaction, 10 μmol (2.3 mg) of $Pd(OAc)_2$, 10 μmol of ligand **2b**, and 25 mL of MeOH were transferred to a 100 mL (Roth) or 250 mL stainless steel autoclave. The autoclave was quickly closed and purged with argon and then charged with ethylene until a pressure of 30 bar was reached. Subsequently, CO was introduced to reach the respective pressure, e.g., 50 bar (C_2H_4:CO ≈ 30:20). After the solution was completely saturated with gas (15 min), the 100 or 250 mL autoclave was heated using a mantel for the indicated time (usually 1 h). After this time the cooled contents were filtered and the solid was washed with methanol (50 mL) and dried overnight.

Copolymerization Using 11b. In a typical reaction, 10 μmol of complex **11b** and 25 mL of dichloromethane were transferred to a 100 mL (Roth) or 250 mL stainless steel autoclave. The autoclave was quickly closed and purged with argon and then charged with ethylene until a pressure of 30 bar was reached. Subsequently, CO was introduced to reach the respective pressure, e.g., of 50 bar (C_2H_4:CO ≈ 30:20). After the solution was completely saturated with gas (15 min), the 100 or 250 mL autoclave was heated using a mantel for the indicated time. Afterward the cooled contents were deposited with methanol (50 mL), filtered, washed with methanol (50 mL), and dried overnight.

■ ASSOCIATED CONTENT

Supporting Information. Text and figures giving further experimental and spectroscopic details and crystallographic data (CIF files) for **7a**, **8a**, **10**, and **11a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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