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Palladium(II) Complexes with Phosphanylferrocenecarboxylate Ligands and Their Use as Catalyst Precursors for Semialternating CO–Ethylene Copolymerization

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Neutral [Pd(κ*P*,κ*O*-P~O)(κ^3*C*,*C*,*C*-carbocycloenyl)] complexes, where P~O is a chiral or achiral chelating phosphanylferrocenecarboxylate ligand, were synthesized and characterized by multinuclear NMR spectroscopy. The crystal structure of a representative complex was determined by single-crystal X-ray diffraction analysis. In all complexes, the palladium(II) ion is located at the centre of a square plane formed by the P and O donor atoms from an anionic P~O$^-$ ligand, a σ-carbon atom and a C–C double bond from a carbocycloenyl ligand. Neutral methyl complexes with the formulas [PdCl(Me)(κ*P*,κ*H*-P~OH)] and [Pd(Me)(OTs)(κ*P*,κ*H*-P~OH)] were also synthesized and characterized. On the basis of IR, NMR and MS–FAB data, the methyl complexes are proposed to be formulated with the fourth coordination position occupied by an agostic O–H···Pd interaction from a free carboxylic acid moiety [P~OH = 1′-(diphenylphosphanyl)ferrocenecarboxylic acid] or a solvent molecule. Selected complexes were employed as catalyst precursors for CO–ethylene copolymerization in MeOH in the presence of an excess of *p*-toluenesulfonic acid. In all cases, low molecular weight semialternating polyketones were produced. The catalytic activities were rather low and the extra-ethylene insertion reached a maximum value of 4.3 %. An operando high-pressure NMR experiment with [Pd(Me)(S)$_2$(κ*P*-P~OH)]OTs (S = solvent, adventitious water) precursor showed that this monocationic Pd^{II} alkyl complex is readily converted into a catalytically inactive binuclear carbonyl-bridged Pd^{I} compound, which, however, regenerates catalytically active Pd^{II}–H species by reaction with TsOH and that β-chelates of the formula [Pd(CH$_2$CH$_2$C(O)P)(S)(κ*P*-P~OH)]OTs (P = propagating polyketone chain) are catalyst resting states. For the first time, β-chelate propagating species have been intercepted in a CO–olefin copolymerization assisted by catalysts devoid of a chelating ligand.

Introduction

The organometallic chemistry of functionalized phosphanes modified with an additional (non-phosphane) donor group is attracting considerable attention, predominantly because of its successful and varied applications in homogeneous catalysis.[1] As a contribution to this area, some of us have designed and synthesized several phoshanylferrocenecarboxylic acid ligands (Scheme 1) and studied their ability to coordinate to transition metals, with the ultimate goal of utilizing the obtained compounds in catalysis.[2] The **HLa** ligand (Scheme 1) and some of its functional derivatives have been used in palladium-catalyzed Suzuki cross-coupling reactions[3] and as modifiers to MCM-41-supported ruthenium catalysts in condensation reactions to yield 2-oxopropyl benzoate.[4] In addition, rhodium(I) complexes containing **La**$^-$ as a chelating phosphanyl-carboxylate ligand have been shown to efficiently catalyze the hydroformylation of 1-hexene.[5] These positive results prompted us to scrutinize phosphanylferrocenecarboxylic acid ligands in different types of C–C bond-forming reactions catalyzed by palladium compounds.

In this paper, we describe the synthesis and characterization of new alkyl palladium(II) complexes with chelating phosphanylferrocenecarboxylate ligands (Scheme 1) and report on their use as catalyst precursors for the imperfectly alternating (semialternating) CO–C_2H_4 copolymerization (Scheme 2, a) either in batch reactors or in high-pressure NMR (HPNMR) sapphire tubes.

The semialternating CO–C_2H_4 copolymerization is a reaction of much current academic and industrial interest.[6,7] Indeed, the stereoelectronic factors favouring semialter-

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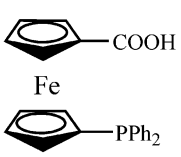
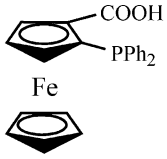
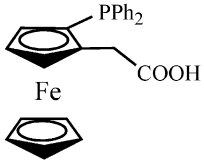


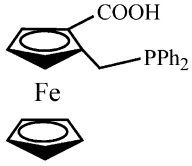
1' -(diphenylphosphanyl)ferrocenecarboxylic acid
HLa



(*Sp*)-2-(diphenylphosphanyl)ferrocenecarboxylic acid
HLb

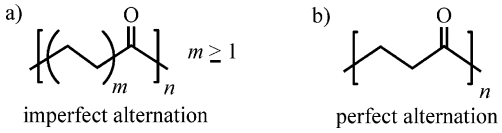


rac-[2-(diphenylphosphanyl)ferrocenyl]acetic acid
HLc



rac-[2-(diphenylphosphanyl)methyl]ferrocenecarboxylic acid
HLd

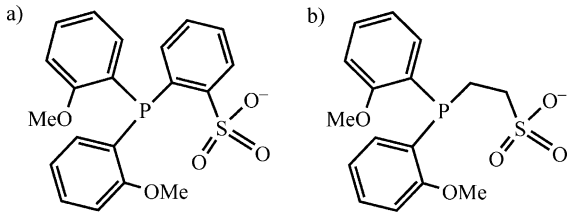
Scheme 1.



Scheme 2.

nation over perfect alternation (Scheme 2, b) are still at the centre of an intense debate. In addition, semialternating polyketones, featuring improved rheological properties relative to perfectly alternating polyketones, are receiving increasing attention as thermoplastics, compatibilizers and glue components.

Semialternating polyketones can be obtained by either free radical[6] or insertion polymerization reactions.[7] Drent and coworkers have demonstrated that palladium(II) salts modified with anionic chelating ligands bearing phosphorus and oxygen donor atoms (P~O$^-$) constitute effective catalysts for the synthesis of semialternating polyketones by insertion polymerization.[7a] It is also agreed that nonalternation is promoted by high temperatures (>100 °C), low partial pressures of CO in the feed and appropriate substituents on the P-aryl rings of the supporting P~O$^-$ ligand.[7] Two examples of these ligands are shown in Scheme 3.



Scheme 3.

Following Drent's discovery, other authors have demonstrated the effectiveness of P~O$^-$ ligands in nonalternating CO–C_2H_4 copolymerization, and their studies—both experimental[7b–7d] and theoretical[7e,7f]—have helped to shed light on the mechanism of semialternation. However, much remains to be elucidated, especially in regard to the species that do control the extra-ethylene insertion.

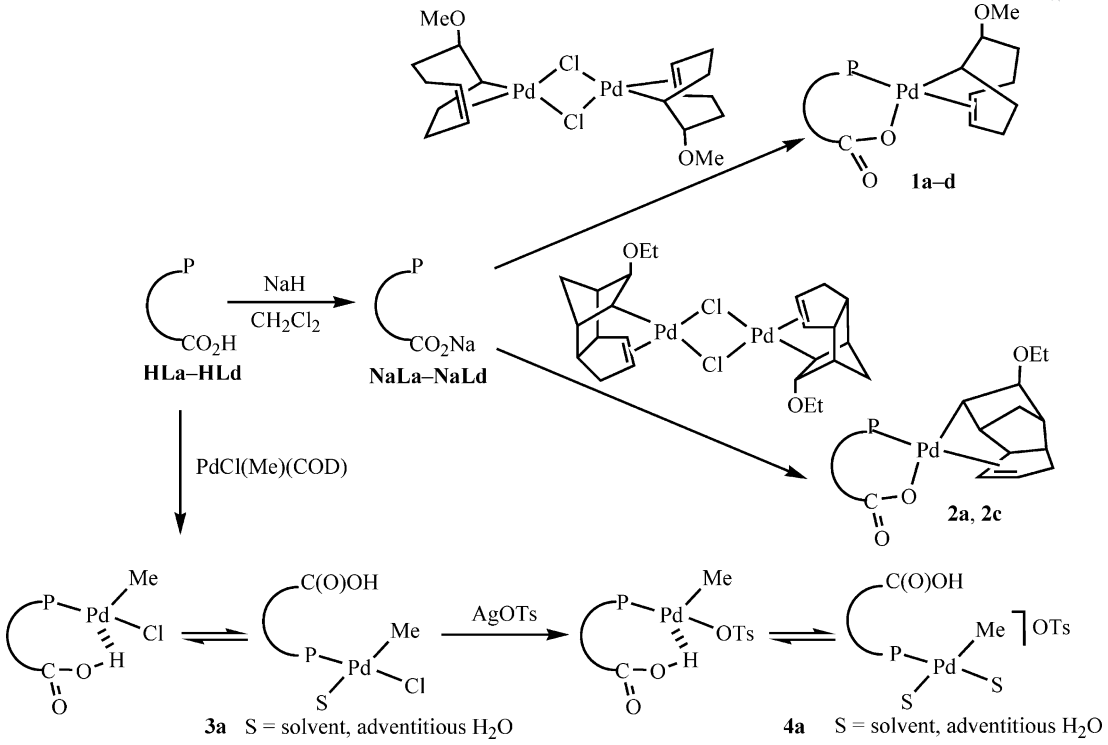
Some authors have suggested that semialternation is a result of the facile decarbonylation of Pd acyl species with no intermediacy of β-chelates,[7e,7f] whereas others have proposed that multiple-ethylene insertion is just facilitated by the destabilization of neutral β-chelates.[7a,7d] More recently, on the basis of operando HPNMR and model organometallic studies, it has been demonstrated that i) Pd^{II} β-chelates are key intermediates in the catalysis cycle of semialternation and their opening is a viable process by either comonomer and ii) Pd^{II}(P~O) fragments do not form stable carbonyl complexes.[7c]

Since the known catalysts for semialternating copolymerization are nearly two orders of magnitude less active than those producing strictly alternating copolymers, an increasing amount of studies is being directed towards the design of more active catalytic systems.

Results and Discussion

Synthesis of Palladium(II) Complexes

The reaction between sodium phosphanylferrocenecarboxylates, prepared in situ by reacting NaH with **HLa**, **HLb**, **HLc** or **HLd** in CH_2Cl_2, and [PdCl(COD^{OMe})]$_2$ (COD = cycloocta-1,5-diene) gave the following neutral palladium(II) phosphanyl-carboxylate complexes: [1′-(diphenylphosphanyl-κ*P*)ferrocenecarboxylato-κ*O*](1η:5–6η-2-methoxycyclooct-5-en-1-yl)palladium (**1a**), (S_p)-[2-(diphenylphosphanyl-κ*P*)ferrocenecarboxylato-κ^2*O*,*P*](1η:5-6η-2-methoxycyclooct-5-en-1-yl)palladium (**1b**), *rac*-[2-(diphenylphosphanyl-κ*P*)ferrocenylacetato-κ*O*](1η:5-6η-2-methoxycyclooct-5-en-1-yl)palladium (**1c**), and *rac*-{2-[(diphenylphosphanyl-κ*P*)methyl]ferrocenecarboxylato-κ*O*}-(1η:5-6η-2-methoxycyclooct-5-en-1-yl)palladium (**1d**) (Scheme 4).



Scheme 4.

Analogous reactions of **NaLa** and **NaLc** with [PdCl(Dicp^{OEt})]$_2$ (Dicp = dihydrodicyclopentadiene) gave [1′-(diphenylphosphanyl-κ*P*)ferrocenylacetato-κ*O*](1-2η,5η-6-ethoxy-3a,4,5,6,7,7a-hexahydro-4,7-methanoindene)palladium (**2a**) and *rac*-[2-(diphenylphosphanyl-κ*P*)ferrocenylacetato-κ*O*](1-2η,5η-6-ethoxy-3a,4,5,6,7,7a-hexahydro-4,7-methanoindene)palladium (**2c**) (Scheme 4).

The reaction between **HLa** and the [PdCl(Me)(η^2:η^2-COD)] mononuclear precursor in CH_2Cl_2 yielded the neutral chloro[1′-(diphenylphosphanyl)ferrocenylcarboxylic acid](methyl)palladium complex, [PdCl(Me)(κ*P*,κ*H*-**HLa**)] (**3a**), as an orange semicrystalline compound. Analogous reactions with **HLb**, **HLc** and **HLd** also gave the corresponding (chloro)methyl complexes, although these were highly contaminated by unidentified species. Therefore, after several unsuccessful synthesis attempts, these reactions were not investigated further.

Treatment of **3a** with AgOTs in CH_2Cl_2 followed by the addition of a mixture of diethyl ether and *n*-hexane to the reaction solution led to the precipitation of the neutral methyl derivative, [Pd(Me)(OTs)(κ*P*,κ*H*-**HLa**)] (**4a**), as a yellow-orange powder.

All the new palladium complexes were characterized by NMR and IR spectroscopy and elemental analysis. In addition, the solid-state structure of **2c** was determined by single-crystal X-ray diffraction analysis. Single crystals of **2c** were obtained by the slow evaporation of a CH_2Cl_2 solution of the crude reaction product at room temperature. An ORTEP drawing of the molecular structure of **2c** is shown in Figure 1, and selected bond lengths and angles are listed in Table 1.

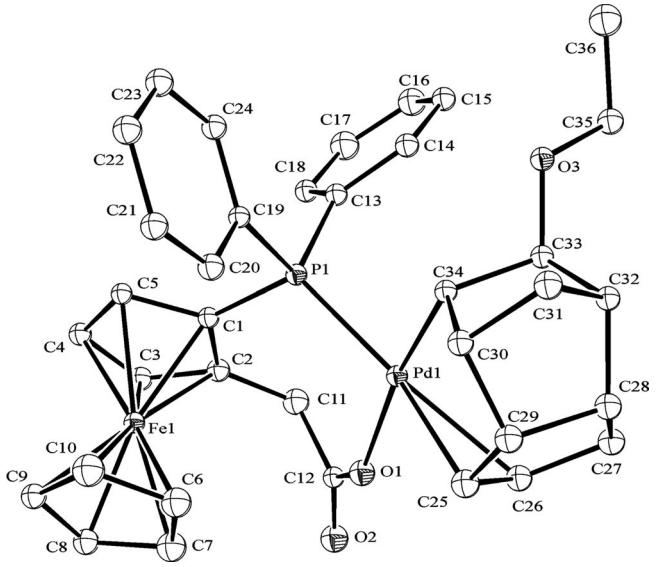


Figure 1. ORTEP plot of **2c**. Hydrogen atoms were omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

The palladium atom is positioned at the centre of a square plane defined by the P(1) and O(1) atoms from the chelating **Lc**$^-$ ligand, the C(34) carbon atom and by the C(25)–C(26) double bond from the 6-ethoxy-*exo*-5,6-dihydrodicyclopentadienyl ligand. The maximum deviation from the least-squares plane defined by these atoms is 0.091(1) Å for C(26). The P(1)–Pd(1)–O(1) bite angle of 99.97(9)° is slightly larger than that in the related **Lc**$^-$ complex, {2-[(dimethylamino-κ*N*)methyl]phenyl-κ*C*^{1}}{*rac*-[2-

Table 1. Selected bond lengths [Å] and angles [°] for **2c**.[a]

Bond or angle	Bond lengths [Å] and angles [°]
Pd(1)–P(1)	2.262(1)
Pd(1)–O(1)	2.152(3)
Pd(1)–C(25)	2.273(4)
Pd(1)–C(26)	2.409(4)
Pd(1)–C(34)	2.046(4)
C(25)–C(26)	1.357(6)
C(12)–O(1)	1.277(5)
C(12)–O(2)	1.232(6)
Fe(1)–Cg(1)	1.649(1)
Fe(1)–Cg(2)	1.652(1)
P(1)–Pd(1)–O(1)	99.97(9)
P(1)–Pd(1)–C(34)	88.94(12)
O(1)–Pd(1)–C(25)	89.56(14)
O(1)–Pd(1)–C(26)	78.73(13)
C(25)–Pd(1)–C(34)	81.48(16)
C(26)–Pd(1)–C(34)	92.76(15)
Cp(1), Cp(2)	2.75(26)

[a] Definitions of the ring planes: Cp(1) = C(1–5), Cp(2) = C(6–10). Cg(1) and Cg(2) are the respective ring centroids.

(diphenylphosphanyl-κ*P*)ferrocenyl]acetate-κO^2}palladium [97.65(3)°].[8a] The carboxylate oxygen atom O(1) is *trans* to the σ-bonded C(34) atom with a O(1)–Pd(1)–C(34) angle of 170.89(14)° and, consequently, the phosphorus donor atom is *trans* to the C–C double bond. The latter shows an interplanar angle of 70.83(19)° with the least-squares plane defined by the Pd(1), P(1), O(1) and C(34) atoms. The *trans* disposition of the phosphorus donor atom and the C–C double bond of the organyl ligand is consistent with the $^2J_{C,P}$ value observed in the $^{13}C\{^1H\}$ NMR spectrum.[8]

The geometry of the ferrocenyl backbone is quite regular, with the two cyclopentadienyl rings nearly coplanar and close to a *syn*-eclipsed conformation (the torsion angle is ca. 11°). The Fe–Cg distances (the Cg's are the centroids of the Cp rings, as defined in Table 1) are 1.649(1) and 1.652(1) Å for Cg(1) and Cg(2), respectively. The coordination of the carboxylate moiety to palladium leads to a significant elongation of the C=O double bond from 1.211(2) (free ligand) to 1.232(6) Å, while the C–O single bond shortens from 1.320(2) (free ligand) to 1.277(5) Å.[8a]

Unfortunately, no crystal of **3a** suitable for X-ray analysis was obtained. The structure of this compound, as shown in Scheme 4, was therefore proposed on the basis of indirect evidence as well as some precedents in the literature. The FAB-MS spectra in 2-nitrobenzyl alcohol matrix were consistent with the formula PdCl(Me)(**HLa**) with no other ligands. The solid IR spectrum (KBr, Nujol mull) showed a ν(C=O) band at 1678 cm^{-1} with a shoulder at 1717 cm^{-1}, whereas the IR spectrum in CH_2Cl_2 contained a single band at 1682 cm^{-1} [ν(C=O) bands at 1669 and 1677 cm^{-1} are observed for the free **HLa** ligand in the solid- and solution-state spectra, respectively]. The ^1H NMR spectra in [D_4]-MeOH or CD_2Cl_2 showed a doublet at δ = 0.68 or 0.80 ppm with a $^3J_{H,P}$ value of 1.9 or 2.4 Hz, respectively, for the CH_3 ligand, which should therefore be located *cis* to the phosphorus atom.[9] The methyl group appeared as a broad singlet at δ = 4.87 ppm in the $^{13}C\{^1H\}$ NMR spectrum in [D_4]MeOH. The broadness of this resonance may be due to the formation of different dynamic species where the fourth coordination position at palladium may be occupied by an agostic H atom or, much more likely, by CH_3OH or adventitious water. Consistent with this hypothesis, the same spectrum in CD_2Cl_2 showed a very sharp methyl resonance at δ = 6.92 ppm. The $^{31}P\{^1H\}$ NMR spectra in [D_4]MeOH or CD_2Cl_2 exhibited a singlet at δ = 30.9 or 28.16 ppm, respectively, which is in line with the low *trans* influence of the chloride atom. Indeed, *trans*-[$PdCl_2$(**HLa**)$_2$] shows a $^{31}P\{^1H\}$ NMR chemical shift of 15.8 ppm.[10] Taken altogether, the spectroscopic characteristics of **3a** are indicative of a primary T-shaped coordination geometry, either in the solid state or in apolar solvents, where the Pd^{II} centre is surrounded by P, C(methyl) and Cl atoms. Such Pd^{II} compounds are known in the literature to be stabilized by bulky ligands capable of realizing agostic H-bonds to the metal centre.[9] In this respect, the free carboxylic acid moiety of **HLa** is an excellent candidate to bring about such an intramolecular interaction. On the other hand, in polar and/or coordinating solvents like methanol, it is much more likely that the fourth position at palladium be occupied by the solvent itself to give a complex with the formula [PdCl(Me)(S)(κ*P*-**HLa**)] (S = solvent, adventitious H_2O).

Like for **3a**, the characterization data for **4a** are indicative of a T-shaped coordination in both the solid state and in apolar solvents with the palladium centre surrounded by Me and OTs groups and with **HLa** behaving as a "*P,H*-bidentate" ligand. CH_2Cl_2 solutions of **4a** do not conduct, whereas this complex behaves as a 1:1 electrolyte in either nitroethane or MeOH. Therefore, **4a** was tentatively assigned the formula [Pd(Me)(S)$_2$(κ*P*-**HLa**)]OTs in methanol (S = methanol, adventitious H_2O). The ^1H and $^{13}C\{^1H\}$ NMR spectra showed **4a** to have a *cis* arrangement of the P and C(methyl) atoms.

Catalytic Study

The neutral palladium complexes **1a**–**1d** and **4a** were employed as precatalysts for CO–C_2H_4 copolymerization in MeOH in the presence of different gas blends at a fixed overall pressure of 800 psi and coreagents such as TsOH or 1,4-benzoquinone (BQ). The results of the catalytic study are summarized in Table 2.

The copolymer products showed keto and ester end groups in a 1:1 ratio and, most importantly, featured the imperfect alternation of CO and ethylene units. The molecular weights of the copolymers ranged from 13.4 to 2.5 $kg\,mol^{-1}$; this was dependent on the ethylene partial pressure and the reaction temperature. Increasing the latter led to a significant decrease in the average molecular weight of the copolymers, likely because of acceleration of the chain transfer reactions.[11]

In the absence of TsOH, no polyketone was produced because of the intrinsic instability of all catalyst precursors that underwent irreversible degradation to palladium black (entries 1, 14 and 18 in Table 2).

The beneficial action of strong protic acids on the activity of CO–olefin copolymerization catalysts is well

Table 2. Nonalternating CO–ethylene copolymerization in MeOH, catalyzed by the neutral palladium precursors **1a**–**1d** and **4a**.

Entry[a]	Precursor	TsOH (equiv.)	CO/C_2H_4 ratio	t [h]	Prod.[b]	M_n [kg mol^{-1}]	% Extra C_2H_4
1	**1a**	0	1:3	11	0.0		
2	**1a**	10	1:3	11	5.3	7.6	1.3
3[c]	**1a**	10	1:3	11	2.5	7.2	1.2
4	**1a**	19	1:3	3	2.4		
5	**1a**	19	1:3	6	2.9		
6	**1a**	19	1:3	11	10.2	6.4	1.7
7[d]	**1a**	19	1:3	11	2.7		
8[e]	**1a**	19	1:3	11	0.8	3.4	2.2
9[f]	**1a**	19	1:3	11	0.6		
10	**1a**	19	1:3	17	9.9	6.4	1.8
11	**1a**	38	1:3	11	3.5	7.2	2.3
12	**1a**	19	1:1	11	3.4	13.4	1.5
13	**1a**	19	1:6	11	1.5	5.2	2.4
14	**4a**	0	1:3	11	0.0		
15	**4a**	18	1:3	6	2.9		
16	**4a**	18	1:3	11	10.1	6.2	1.8
17	**4a**	18	1:3	17	9.9		
18	**1b**	0	1:3	11	0.0		
19	**1b**	10	1:3	11	3.0		
20	**1b**	19	1:3	6	2.9		
21	**1b**	19	1:3	11	4.5	6.9	2.2
22[d]	**1b**	19	1:3	11	1.3		
23[e]	**1b**	19	1:3	11	1.9		
24	**1b**	19	1:3	17	3.4	2.5	4.3
25	**1b**	38	1:3	11	2.4	2.4	2.9
26	**1b**	19	1:1	11	1.4	9.5	1.8
27	**1c**	19	1:3	11	0.1		
28	**1d**	19	1:3	11	0.1		

[a] Reaction conditions: precursor (0.012 mmol), MeOH (50 mL), 100 °C, total pressure p at reaction temperature: p = 800 psi. [b] Productivity expressed as (grams polyketone)/(mmole Pd)×hour. [c] NaOTs (9 equiv.). [d] BQ (40 equiv.). [e] 120 °C. [f] 80 °C.

known. Besides neutralizing anionic nucleophiles that may compete with monomers or with the MeOH required to activate the precursors,[11] strong protic acids convert inactive Pd^0 species into active Pd^{II}–H initiators. Accordingly, a partial substitution of TsOH with its sodium salt led to a remarkable decrease in productivity (entry 2 vs. entries 3 and 6 in Table 2). In the present catalytic systems, TsOH has the additional role of transforming neutral compounds into cationic ones with a phosphanyl-carboxylic acid ligand (see below).

The palladium precursors with **La**$^-$ and **Lb**$^-$ showed a maximum activity in the presence of 18–19 equiv. of acid and a 1:3 CO/C_2H_4 ratio (entries 6, 16 and 21 in Table 2). Increasing the amount of TsOH to 38 equiv. (entries 11 and 25 in Table 2) significantly decreased the productivity, which suggests that too large a concentration of *p*-toluenesulfonate ions in the reaction mixture disfavours monomer coordination to palladium.[11] Under comparable conditions, **1c** and **1d** yielded only traces of polymeric material along with extensive catalyst degradation to palladium black (entries 27 and 28 in Table 2).

The catalytic activity of **1a** and **1b** increased significantly with time (entries 4–6, 15,16, 20 and 21 in Table 2). This finding is quite interesting as Pd^{II}-catalyzed CO–ethylene copolymerization reactions suffer from catalyst deactivation, with a consequent decrease in productivity.[11] Under the experimental conditions, no catalyst deactivation apparently occurred, and a nonlinear increase in productivity was observed, which is hard to rationalize. The most straightforward interpretation is to think of a long induction period required to convert the precursor into catalytically active species that seem to change with time. Indeed, a nonlinear increase in productivity [(gram polyketone)/(mmole Pd)×hour] with time was observed: 2.4 after 3 h, 2.9 after 6 h and 10.2 after 11 h for **1a**. Unfortunately, at the reaction temperature, no species were seen on the NMR timescale, which indicates the occurrence of fast equilibria between different species. However, after activation and catalysis, a unique β-chelate catalyst resting state was formed (see below). In no case, however, was the productivity in nonalternating polyketones comparable to that obtained with the phosphane-sulfonate Pd^{II} catalysts reported by Drent that are active even in the absence of added TsOH.[7a]

Notably, the use of **4a** as precursor (entries 14–17) in the place of **1a** (entries 1, 5, 6 and 10) gave almost identical results, which suggests that **1a** and **4a** generate the same catalyst. This evidence is also an indirect confirmation that TsOH protonates the bonded carboxylate group in **1a**, which results in the formation of a free –C(O)OH moiety.

To our surprise, the addition of an organic oxidant such as BQ to the reaction mixtures decreased the catalytic productivity (entries 7 and 22 vs. 6 and 21, respectively). Indeed, like protic acids, BQ is a coreagent that almost invariably increases the productivity of Pd^{II}-assisted CO–olefin copolymerization reactions by oxidizing inactive low valent Pd species. On the other hand, it is known that BQ also has the effect of converting Pd^{II}–H into Pd^{II}–OMe initiators.[11] Thus, this experimental evidence could be the indirect confirmation that the CO–ethylene copolymerization mechanism with the phosphanylferrocenecarboxylic acid/palladium catalysts involves Pd^{II}–H initiators and that chain transfers occur by methanolysis.[11]

The catalytic activities of **1a** and **1b** were also influenced by the gas blend, with the optimum CO/C_2H_4 ratio being 1:3. Indeed, analogous catalytic reactions carried out in the presence of either 1:1 or 1:6 gas mixtures gave a lower productivity. In general, a high concentration of CO stabilizes Pd(acyl)(CO) species, while a low concentration can slow down the rate of β-chelate opening, which is a key step of chain propagation (see below).[11,12]

The degree of extra-ethylene insertion as well as the occurrence of double ethylene insertions in the polymeric chain were monitored by $^{13}C\{^1H\}$ NMR measurements in a (1:1, v/v) solvent mixture of 1,1,1,3,3,3-[D_2]hexafluoro-2-propanol (HFIP) and C_6D_6. In addition to signals due to perfectly alternating copolymers, the spectra showed three additional singlets at δ 21.55, 40.14 and 212.50 ppm due to extra-ethylene insertion.[7a] In agreement with previous reports, we have found that higher temperatures and lower partial pressures of CO, at constant total pressure, favour the extra enchainment of ethylene. The maximum extra insertion was around 4.3% for **1b** at 100 °C (entry 24 in Table 2). The amount of added TsOH did not significantly

influence the amount of extra-ethylene insertion (entries 2, 6 and 11 or 21 and 25).

Some reactions with precatalysts **1a** and **1b** were performed in the presence of only ethylene (i.e., without CO). Only traces of but-1-ene and *cis*/*trans*-but-2-ene were obtained, which suggests that only double ethylene insertion is actually promoted by the present catalysts.

Operando $^{31}P\{^1H\}$ HPNMR Study

In an attempt to intercept some intermediates that might help to clarify the mechanism by which the phosphanylferrocenecarboxylate catalysts operate to produce nonalternating polyketones, an operando HPNMR experiment was carried out using **4a** as precursor with a 1:3 CO/C_2H_4 mixture at an overall pressure of 800 psi. The reactions were followed by variable-temperature $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. Selected $^{31}P\{^1H\}$ NMR spectra are reported in Figure 2.

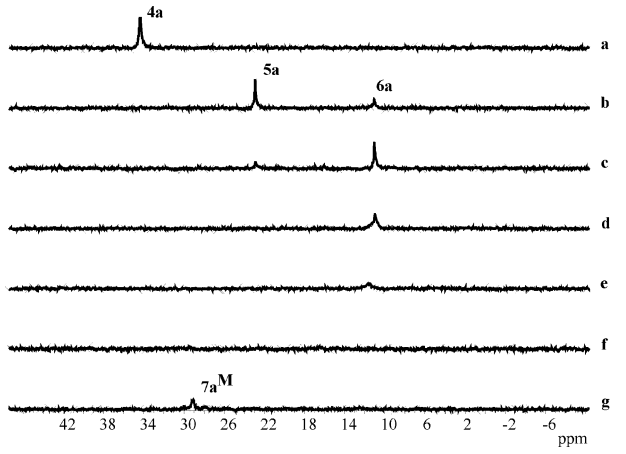
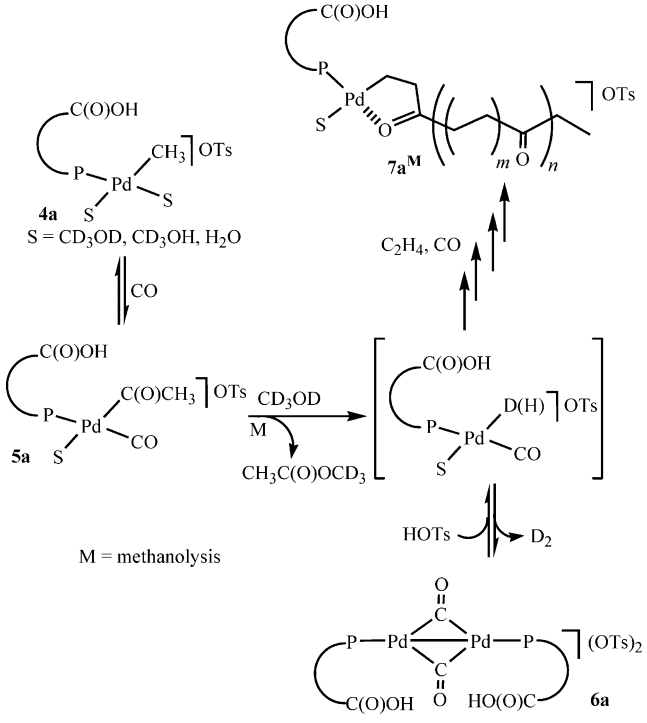


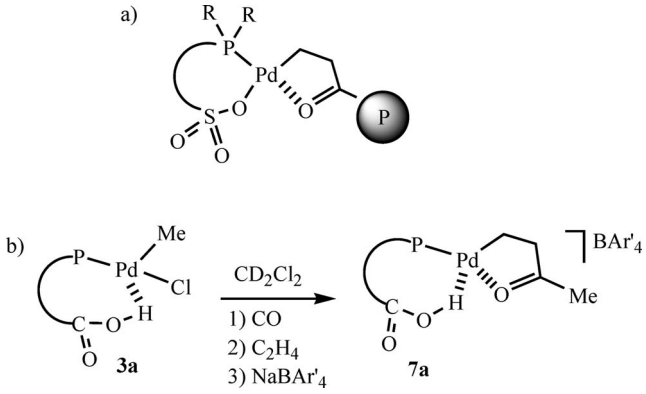
Figure 2. Variable-temperature $^{31}P\{^1H\}$ HPNMR study of the CO–C_2H_4 copolymerization reaction with **4a**/TsOH [sapphire tube, $[D_4]$MeOH, TsOH (18 equiv.), 81.01 MHz]: (a) **4a**/TsOH at room temperature; (b) immediately after charging with CO (200 psi); (c) after 20 min under CO; (d) immediately after charging with C_2H_4 (600 psi); (e) at 50 °C; (f) after 30 min at 100 °C; (g) after cooling to room temperature.

To a $[D_4]$MeOH solution of **4a** ($^{31}P\{^1H\}$ NMR: δ = 32.90 ppm) was added TsOH (18 equiv.), and the resulting mixture was transferred into a 10 mm HPNMR sapphire tube under nitrogen ($^{31}P\{^1H\}$ NMR singlet at δ = 33.50 ppm; Figure 2, trace a). On pressurizing the sapphire tube with CO (200 psi) at room temperature, two new $^{31}P\{^1H\}$ NMR singlets appeared (Figure 2, trace b). One is at δ = 22.80 ppm and we attribute it to the acyl complex **5a** on the basis of a multinuclear NMR analysis (Scheme 5). The identification of the species responsible for the second peak at δ = 11.05 ppm was less straightforward. We are inclined to assign this singlet to a binuclear CO-bridged Pd^I complex (**6a**) on the basis of its high-field ^{31}P NMR resonance as well as the detection of a unique $^{13}C\{^1H\}$ NMR carbonyl resonance at δ = 222.48 ppm (obtained by using a 1:9 $^{13}CO/^{12}CO$ mixture at 200 psi in an independent experiment). Within 20 min at room temperature, **5a** was converted almost completely into **6a** (Figure 2, trace c) with formation of the $CH_3C(O)OCD_3$ ester (GC-MS evidence), hence through a reaction sequence involving the methanolysis of **5a** to yield a transient Pd-H species (Scheme 5). At this stage, the HPNMR tube was pressurized with ethylene (600 psi) at room temperature (1:3 CO/C_2H_4 mixture), but no change was observed (Figure 2, trace d). Only upon heating to 50 °C did **6a** disappear, and no trace of this compound was seen after 30 min at 100 °C. During this time, copolymer formation occurred (Figure 2, traces e and f). After the sapphire tube was cooled to room temperature, the spectrum showed a new broad singlet at δ = 29.20 ppm (Figure 2, trace g).



Scheme 5. Cationic palladium complexes observed by operando HPNMR spectroscopy in the CO–C_2H_4 copolymerization reaction catalyzed by **4a**/TsOH in $[D_4]$MeOH.

The identification of the species responsible for the singlet at δ = 29.20 ppm, quoted as **7a^M**, was carried out in an indirect way. Some previous studies of nonalternating CO–C_2H_4 copolymerization catalyzed by Pd^{II}(P~O) complexes {P~O = 2-[bis(*o*-methoxyphenyl)phosphanyl]phenylenesulfonate and 2-[bis(*o*-methoxyphenyl)phosphanyl]ethylenesulfonate, Scheme 3} had revealed that the catalyst resting state consisted of β-chelate species of the type shown in part a of Scheme 6 (P = propagating chain).[7c] With this in mind, we synthesized in situ the first-generation β-chelate complex {Pd[$CH_2CH_2C(O)CH_3$]($\kappa P,\kappa H$-**HLa**)}BAr'_4 [Ar′ = 3,5-bis(trifluoromethyl)phenyl] (**7a**) from **3a** by a well-known stepwise process involving the carbonylation of the starting compound in CD_2Cl_2, followed by treatment of the acyl product with a chloride scavenger ($NaBAr'_4$) under an ethylene atmosphere (Scheme 6, b).



Scheme 6.

Compound **7a** was characterized in situ by ^{1}H NMR and IR spectroscopy. A *cis* arrangement of the P and C atoms bound to palladium was established by NMR spectroscopy, while the IR spectrum showed the presence of a coordinated C=O group.[11,12] Like **3a** and **4a** in apolar solvents, **7a** is drawn with a proposed Pd–H interaction.[9] As expected, **7a** and **7a^M** in [D$_4$]MeOH showed the same ^{31}P{^{1}H} NMR spectra corresponding to structures where **HLa** behaves as a monodentate ligand through its phosphorus atom. Obviously, **7a^M** represents a family of β-chelates containing propagating chains of different lengths (Scheme 5).

At the end of the HPNMR experiment illustrated in Figure 2, the sapphire tube was vented with a nitrogen flow to remove all unreacted gases, and a thin layer of semialternating polyketone was collected at the gas–liquid interphase. A GC-MS analysis of the reaction solution showed the formation of $CH_3C(O)OCD_3$ which resulted from the methanolysis of **5a** (Scheme 5).

Conclusions

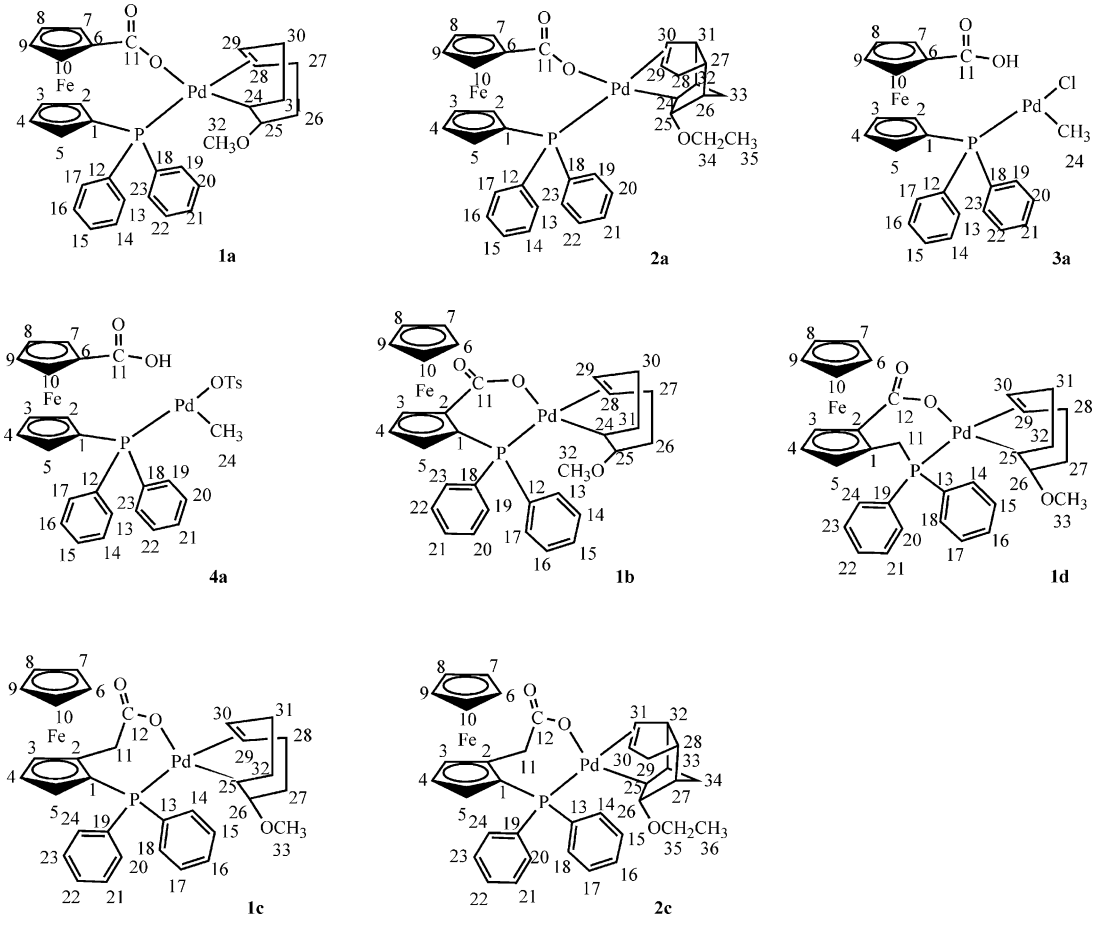
New neutral Pd^{II} complexes containing either chelating phosphanylferrocenecarboxylate or monodentate phosphanylferrocenecarboxylic acid ligands were synthesized and characterized. Selected complexes were used as precatalysts for the CO–C_2H_4 copolymerization in MeOH in the presence of an excess of TsOH with different gas blends, and at a fixed overall pressure of 800 psi and temperatures ≥100 °C. Under these experimental conditions, semialternating polyketones with extra-ethylene incorporation up to 4.3% were obtained. The productivities were quite modest: an order of magnitude lower than those obtainable with Pd^{II} catalysts supported by chelating phosphanylphenylenesulfonate ligands.[7a–7c] Surprisingly, however, the productivities increased with time, which may be due to a very long induction period required for the conversion of the precursors into more than one catalytically active species. An operando HPNMR study has revealed that the neutral precursors are converted into cationic monophosphane alkyl complexes by protonation of the carboxylate group. More importantly, the operando experiment has shown the formation of β-chelates as catalyst resting states, which confirms the key role of such species in the nonalternating CO–C_2H_4 copolymerization reaction.[7a,7c,7d] Finally, it is worth stressing that this paper reports the first evidence of β-chelate Pd^{II} complexes derived from CO and ethylene with no need of a chelating ligand.

In an attempt to avoid the formation of monodentate phosphane ligands, which may be responsible for the low catalytic activity observed, studies are in progress in our laboratories aimed at replacing the –C(O)OH moiety in the phosphanylferrocene ligands with a functional group featuring a stronger Brønsted acidity.

Experimental Section

General Procedures: All reactions and manipulations were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Solvents were distilled from suitable dehydrating reagents and were deoxygenated before use. Reagents were used as received from Aldrich or Fluka, unless stated otherwise. Compounds **HLa**,[13a] **HLb**,[13b] **HLc**,[8a] **HLd**,[13c] [PdCl(COD^{OMe})]$_2$,[14a] [PdCl(Dicp^{OEt})]$_2$,[14b] PdCl(Me)(COD)[14c] and NaBAr′$_4$[15] were prepared according to the literature methods. Copolymerization reactions were performed in a 200 mL stainless steel autoclave constructed at ICCOM-CNR (Florence, Italy) and equipped with a magnetic drive stirrer and a homemade temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain constant pressure during the catalytic reactions. GC-MS analyses were performed with a Shimadzu QP2100S apparatus equipped with a SPB-1 Supelco fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness). Deuterated solvents for routine NMR measurements were dried with activated molecular sieves. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were obtained with either a Bruker ACP 200 (200.13, 50.32 and 81.01 MHz, respectively) or a Bruker Avance DRX-400 spectrometer (400.13, 100.62 and 161.98 MHz, respectively). Chemical shifts (δ) are reported in ppm relative to TMS, and referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C NMR) or 85% H_3PO_4 (^{31}P NMR). The assignment of ^{1}H and ^{13}C signals is based on 2D NMR experiments (^{1}H COSY and ^{1}H–^{13}C HMQC). See Scheme 7 for the atom labeling of palladium complexes **1a**–**1d**, **2a**, **2c**, **3a** and **4a**. HPNMR experiments were carried out with a Bruker ACP 200 using a 10 mm sapphire NMR tube (Saphikon, Milford, NH) equipped with a titanium high-pressure charging head constructed at the ICCOM-CNR (Florence, Italy).[16] Elemental analyses were performed using a Carlo–Erba Model 1106 elemental analyzer. The conductivity measurement was carried out with an Orion model 101 conductivity meter with a 10^{-3} M MeOH solution.[17] Infrared spectra were recorded with an FT-IR Perkin–Elmer Spectrum GX instrument. FAB-MS measurements were carried out with a Finnigan MAT-95 instrument.

Synthesis of 1a: Solid sodium hydride (3.9 mg, 0.17 mmol) was added to a solution of **HLa** (70.3 mg, 0.17 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred for 30 min while the orange precipitate of **NaLa** separated. A solution of [PdCl(COD^{OMe})]$_2$ (44.9 mg, 0.08 mmol) in CH_2Cl_2 (2 mL) was added, and the resulting mixture was stirred at room temperature for 1 h and then filtered through a plug of Celite to remove NaCl. The filtrate was concentrated to a small volume (ca. 4 mL). Addition of diethyl ether led to the precipitation of **1a** as a brown microcrystalline solid, which was filtered, washed with diethyl ether and dried in a stream of nitrogen. Yield 89.5 mg (80%).



Scheme 7. Atom labeling of isolated palladium complexes **1a**–**1d**, **2a**, **2c**, **3a** and **4a**.

$C_{32}H_{33}FeO_3PPd$ (658.6): calcd. C 58.36, H 5.01; found C 58.67, H 5.10. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.80 (m, 1 H, 31-H), 1.95–2.15 (m, 2 H, 26-H), 2.20–2.40 (m; 4 H; 24-H, 30-H and 31′-H), 2.46 (s, 3 H, 32-H), 2.80 (m, 2 H, 27-H), 2.91 (br. s, 1 H, 25-H), 4.23 and 4.27 (s, 2 H, 8-H and 9-H), 4.31 (s, 1 H, 2-H), 4.36 (s, 1 H, 5-H), 4.54 (s, 1 H, 3-H), 4.64 (s, 1 H, 4-H), 4.71 and 4.75 (s, 2 H, 7-H and 10-H), 6.62 (m, 1 H, 29-H), 6.98 (m, 1 H, 28-H), 7.48 (m; 6 H; 14-H, 15-H, 16-H, 20-H, 21-H and 22-H), 7.60–7.69 (dd; $^3J_{H,H}$ = 8.0 and $^3J_{P,H}$ = 10.6 Hz; 4 H; 13-H, 17-H, 19-H and 23-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.28 (s, C-30), 28.37 (s, C-27), 31.55 (s, C-26), 35.65 (s, C-31), 43.41 (s, C-24), 55.17 (s, C-32), 70.85 (s, C-8 and C-9), 71.80 (br. s, C-3), 72.12 and 73.59 (s, C-7 and C-10), 72.93 (d, $^3J_{C,P}$ = 6.8 Hz, C-4), 74.96 (d, $^2J_{C,P}$ = 8.1 Hz, C-2), 76.22 (d, $^2J_{C,P}$ = 15.1 Hz, C-5), 81.47 (s, C-25), 120.56 (br. s, C-28), 123.31 (br. s, C-29), 128.53 (s; C-14, C-16, C-20 and C-22), 130.74 (s, C-15 and C-21), 131.69 (d, $^1J_{C,P}$ = 4.3 Hz, C-12 and C-18), 133.89 (br. s; C-13, C-17, C-19 and C-23), 175.31 (s, C-11) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 19.93 ppm.

Synthesis of 2a: Solid sodium hydride (3.9 mg, 0.17 mmol) was added to a solution of **HLa** (70.3 mg, 0.17 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 30 min while the orange precipitate of **NaLa** separated. Addition of a solution of $[PdCl(Dicp^{OEt})]_2$ (51.0 mg, 0.08 mmol) in CH_2Cl_2 (2 mL) to the obtained suspension afforded an orange solution, which was stirred at room temperature for 2 h, filtered through a plug of Celite to remove NaCl and concentrated to a small volume (4 mL). Addition of diethyl ether led to the precipitation of **2a** as orange-brown microcrystals, which were filtered, washed with diethyl ether and dried in a stream of nitrogen. Yield 94.7 mg (80%). $C_{35}H_{33}FeO_3PPd$ (696.6): calcd. C 60.35, H 5.02; found C 60.53, H 5.08. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 0.99 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, 35-H), 1.10 (d, $^2J_{H,H}$ = 9.7 Hz, 1 H, 28-H), 1.29 (d, $^2J_{H,H}$ = 9.7 Hz, 1 H, 28′-H), 1.69 (dd, $^3J_{H,H}$ = 15.6 and 3.8 Hz, 1 H, 31-H), 2.37 (d, $^3J_{H,H}$ = 4.9 Hz, 1 H, 32-H), 2.43 (m, 1 H, 33-H), 2.74–2.81 (m, 2 H, 26-H and 33′-H), 2.87 (m, 1 H, 27-H), 3.04 (m, 1 H, 25-H), 3.20 (m, 1 H, 34-H), 3.42 (m, 1 H, 34-H), 3.81 (d, $^2J_{H,H}$ = 6.5 Hz, 24-H), 4.17 (br. s, 1 H, 2-H), 4.22 (br. s, 1 H, 7-H), 4.30 (br. s, 1 H, 10-H), 4.42 (br. s, 1 H, 5-H), 4.53 (br. s, 1 H, 3-H), 4.58 (br. s, 1 H, 4-H), 4.78 (br. s, 1 H, 8-H), 4.97 (br. s, 1 H, 9-H), 6.74 (br. s, 1 H, 29-H), 7.44 and 7.78 (m, 13-H–17-H and 19-H–23-H), 7.65 (br. s, 1 H, 30-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 15.32 (s, C-35), 31.76 (s, C-33), 35.64 (s, C-28), 39.32 (s, C-26), 41.73 (s, C-32), 52.00 (s, C-24), 53.00 (s, C-31), 57.75 (s, C-27), 63.79 (s, C-34), 70.40 (s, C-7), 70.52 (s, C-10), 71.30 (d, $^1J_{P,C}$ = 37.9 Hz, C-1), 71.80 (d, $^3J_{P,C}$ = 5.7 Hz), 72.40 (d, $^3J_{P,C}$ = 8.3 Hz, C-4), 72.50 (s, C-9), 73.00 (s, C-8), 75.10 (d, $^2J_{P,C}$ = 8.4 Hz, C-2), 75.60 (d, $^2J_{P,C}$ = 15.0 Hz, C-5), 81.08 (s, C-25), 81.12 (s, C-6), 128.29 (d; $^3J_{P,C}$ = 10.5 Hz; C-14, C-16, C-20 and C-22), 130.20 (s, C-15 and C-21), 130.28 (s, C-29), 130.80 (s, C-30), 132.88 (d, $^1J_{P,C}$ = 47.2 Hz, C-12 and C-18), 132.91, 135.10 (d; $^3J_{P,C}$ = 11.7 Hz; C-13, C-17, C-19 and C-23), 174.67 (s, C-11) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 21.37 ppm.

Synthesis of 3a: A solid sample of PdCl(Me)(COD) (63.6 mg, 0.24 mmol) was added to a solution of **HLa** (100.0 mg, 0.24 mmol) in CH_2Cl_2 (7 mL). The reaction mixture was stirred for 1 h and

concentrated to half of its original volume. The addition of diethyl ether (12 mL) to this precipitated **3a** as an orange microcrystalline solid, which was filtered, washed with diethyl ether (2 × 6 mL) and dried in a stream of nitrogen. Yield 109.6 mg (80%). $C_{24}H_{22}ClFeO_2PPd$ (570.9): calcd. C 50.49, H 3.85; found C 50.66, H 3.92. ^{1}H NMR (400.13 MHz, [D$_4$]MeOH, 25 °C): δ = 0.68 (d, $^3J_{H,P}$ = 1.9 Hz, 3 H, 24-H), 4.48 (s, 2 H, 2-H and 5-H), 4.53 (s, 2 H, 3-H and 4-H), 4.75 (s, 2 H, 8-H and 9-H), 4.95 (s, 2 H, 7-H and 10-H), 7.43 (t; $^3J_{H,H}$ = 6.4 Hz; 4 H; 14-H, 16-H, 20-H and 22-H), 7.48 (m, $^3J_{H,H}$ = 6.7 and $^4J_{H,H}$ = 6.1 Hz, 2 H, 15-H and 21-H), 7.59 (dd; $^3J_{H,P}$ = 11.4 and $^3J_{H,H}$ = 7.6 Hz; 4 H; 13-H, 17-H, 19-H and 23-H) ppm. ^{13}C{^{1}H}NMR (100.62 MHz, [D$_4$]MeOH, 25 °C): δ = 4.87 (br. s, C-24), 71.83 (s, C-7 and C-10), 72.47 (s, C-6), 73.61 (d, $^3J_{C,P}$ = 7.3 Hz, C-3 and C-4), 74.70 (s, C-8 and C-9), 75.08 (d, $^1J_{C,P}$ = 27.9 Hz, C-1), 75.43 (d, $^2J_{C,P}$ = 10.8 Hz, C-2 and C-5), 127.86 (d; $^3J_{C,P}$ = 10.8 Hz; C-14, C-16, C-20 and C-22), 130.36 (s, C-15 and C-21), 131.92 (d, $^1J_{C,P}$ = 53.3 Hz, C-12 and C-18), 133.61 (d; $^2J_{C,P}$ = 11.5 Hz; C-13, C-17, C-19 and C-23), 173.38 (s, C-11) ppm. ^{31}P{^{1}H} NMR (161.98 MHz, [D$_4$]MeOH, 25 °C): δ = 30.90 ppm. IR (KBr, Nujol mull): $\tilde{\nu}$ = ν(C=O) 1678, 1717 (sh) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(C=O) 1682 cm^{-1}. FAB-MS: *m*/*z* (%) = 568.63 (100), 570.63 (90) [M].

Synthesis of 4a: Solid Ag(OTs) (22.4 mg, 0.08 mmol) was added to a solution of **3a** (45.6 mg, 0.08 mmol) in deaerated CH_2Cl_2 (10 mL). The suspension was stirred at room temperature for 10 min, and filtered through a plug of Celite. The orange solution was then concentrated to half of its original volume (5 mL), and the addition of a 1:1 (v/v) mixture of diethyl ether and *n*-hexane caused the precipitation of a yellow-orange powder, which was filtered off, washed with diethyl ether (3 mL) and dried in a stream of nitrogen. Yield 45.9 mg (85%). $C_{31}H_{29}FeO_5PPd$ (674.5): calcd. C 55.20, H 4.30; found C 55.10, H 4.15. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 0.64 (d, $^3J_{H,P}$ = 1.6 Hz, 3 H, 24-H), 2.42 (s, 3 H, Ar-CH_3), 4.39 (m, 2 H, 2-H and 5-H), 4.63 (s, 2 H, 3-H and 4-H), 4.73 (s, 4 H, 7-H–10-H), 7.28 (d, $^3J_{H,H}$ = 10.8 Hz, 2 H, Ar-H), 7.42–7.64 (m, 10 H, 13-H–17-H and 19-H–23-H), 7.81 (d, $^3J_{H,H}$ = 10.8 Hz, 2 H, Ar-H) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 7.20 (s, C-24), 21.11 (s, Ar-CH_3), 73.44 (s, C-7 and C-10), 73.66 (s, C-6), 73.80 (d, $^3J_{C,P}$ = 10.0 Hz, C-3 and C-4), 73.97 (s, C-8 and C-9), 74.50 (d, $^1J_{C,P}$ = 62.6 Hz, C-1), 78.17 (d, $^2J_{C,P}$ = 17.0 Hz, C-2 and C-5), 126.1 (s, Ar-C) 128.39 (d; $^3J_{C,P}$ = 15.0 Hz; C-14, C-16, C-20 and C-22), 129.0 (s, Ar-C), 131.08 (s, C-15 and C-21), 131.22 (d, $^1J_{C,P}$ = 76.5 Hz, C-12 and C-18), 133.98 (d; $^2J_{C,P}$ = 16.1 Hz; C-13, C-17, C-19 and C-23), 140.71 (s, Ar-C), 141.27 (s, Ar-C), 181.02 (s, C-11) ppm. ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 33.08 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(C=O) 1683 cm^{-1}. Λ_M (nitroethane): 57 Ω^{-1} cm^2 mol^{-1}.

In Situ Synthesis of 4a in [D$_4$]MeOH: Solid Ag(OTs) (5.6 mg, 0.02 mmol) was added to a solution of **3a** (11.4 mg, 0.02 mmol) in [D$_4$]MeOH (2 mL). The suspension was stirred at room temperature for 10 min, and then filtered through a plug of Celite. The filtrate was then transferred under nitrogen into a 5 mm NMR tube. Selected NMR spectroscopic data: ^{1}H NMR (400.13 MHz, [D$_4$]MeOH, 25 °C): δ = 0.78 (d, $^2J_{H,P}$ = 0.7 Hz, 3 H, PdCH_3) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, [D$_4$]MeOH, 25 °C): δ = 0.26 (d, $^2J_{C,P}$ = 4.6 Hz, PdCH_3) ppm. ^{31}P{^{1}H} NMR (161.98 MHz, [D$_4$]MeOH, 25 °C): δ = 32.9 (s) ppm. Λ_M (MeOH): 67 Ω^{-1} cm^2 mol^{-1}.

In Situ Synthesis of 5a and 6a: A solution of **4a** (0.02 mmol) in [D$_4$]MeOH (2 mL) prepared as described above was transferred into a 10 mm HPNMR tube under nitrogen at room temperature. The tube was then charged with a (1:9) ^{13}CO/^{12}CO mixture to a pressure of 200 psi. Analysis by multinuclear NMR spectroscopy at room temperature showed the presence of $CH_3C(O)OCD_3$ and the two complexes {Pd(CO)[C(O)CH$_3$}(**HLa**)]OTs (**5a**) and [Pd(CO)(**HLa**)]$_2$OTs (**6a**). The transformation of **5a** into **6a** was complete within 2 h at room temperature. Selected NMR spectroscopic data for **5a**: ^{1}H NMR (200.13 MHz, [D$_4$]MeOH, 25 °C): δ = 2.11 [d, $^4J_{H,P}$ = 1.82 Hz, 3 H, PdC(O)CH$_3$] ppm. ^{13}C{^{1}H} NMR (50.32 MHz, [D$_4$]MeOH, 25 °C): δ = 31.50 [d, $^3J_{C,P}$ = 28.8 Hz, PdC(O)*C*H$_3$], 219.81 [s, Pd*C*(O)CH$_3$], 228.50 (d, $^2J_{C,P}$ = 78 Hz, PdCO) ppm. ^{31}P{^{1}H} NMR (81.01 MHz, [D$_4$]MeOH, 25 °C): δ = 22.85 (s) ppm. Selected NMR spectroscopic data for **6a**: ^{13}C{^{1}H} NMR (50.32 MHz, [D$_4$]MeOH, 25 °C): δ = 222.48 (s, PdCO) ppm. ^{31}P{^{1}H} NMR (81.01 MHz, [D$_4$]MeOH, 25 °C): δ = 11.02 (s) ppm.

In situ Synthesis of 7a: CO was bubbled through a solution of **3a** (22.8 mg, 0.04 mmol) in CD_2Cl_2 (1.2 mL) in a Schlenk tube for 10 min at room temperature. After nitrogen was bubbled through the resulting solution to eliminate excess CO, ethylene was bubbled through it, and then a solid sample of NaBAr′$_4$ (44.3 mg, 0.05 mmol) was added to the solution to scavenge the chloride ligand from Pd. The suspension was stirred for 2 min and filtered under nitrogen, and the filtrate was transferred into a 5 mm NMR tube. The atom labelling of the hydrogen atoms of the Cp rings corresponds to that applied for **3a** and **4a**. ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.85 (s, 2 H, PdCH_2), 2.49 [s, 3 H, C(O)CH_3], 2.95 (br. s, 2 H, CH_2CO), 4.35 (br. s, 2 H, 2-H and 5-H), 4.70 (br. s; 4 H; 3-H, 4-H, 8-H and 9-H), 5.45 (br. s, 2 H, 7-H and 10-H), 7.35–7.90 (m, 22 H, Ar-H) ppm. ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 29.6 (s) ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = ν(C=O) 1636 [C(O)CH_3], 1655 [C(O)OH] cm^{-1}.

Synthesis of 1b: A procedure analogous to that described above for **1a** that substituted **HLb** for **HLa** was followed to give **1b** as a brown crystalline solid. Yield 91.8 mg (82%). $C_{32}H_{33}FeO_3PPd$ (658.6): calcd. C 58.36, H 5.01; found C 58.45, H 5.08. Diastereoisomer ratio A/B = 1:1. **Diasteroisomer A:** ^{1}H NMR, (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.80–3.60 (9 H; 24-H, 26-H, 27-H, 30-H and 31-H), 2.72 (s, 3 H, 32-H), 2.92 (m, 1 H, 25-H), 3.95 (q, $^4J_{P,H}$ = 3.9 and $^3J_{H,H}$ = 2.4 Hz, 1 H, 3-H), 4.42 (s, 5 H, 6-H–10-H), 4.56 (t, $^3J_{H,H}$ = 2.6 Hz, 1 H, 4-H), 5.20 (m, 1 H, 5-H), 6.22 (m, 1 H, 29-H), 6.65 (m, 1 H, 28-H), 7.30–7.88 (m, overlapping signals with diastereoisomer B, 13-H–17-H and 19-H–23-H) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.49 (s, C-30), 29.04 (s, C-27), 31.42 (s, C-26), 35.88 (s, C-31), 40.43 (s, C-24), 55.31 (s, C-32), 70.71 (d, $^1J_{C,P}$ = 53.8 Hz, C-1) (C-2 overlapped), 71.61 (s, C-6–C-10), 72.70 (d, $^3J_{C,P}$ = 6.2 Hz, C-4), 73.81 (s, C-3), 75.78 (d, $^2J_{C,P}$ = 6.8 Hz, C-5), 82.75 (s, C-25), 119.15 (d, $^2J_{C,P}$ = 8.1 Hz, C-28), 124.52 (d, $^2J_{C,P}$ = 9.4 Hz, C-29), 127.89 (d, $^1J_{C,P}$ = 51.9 Hz, C-12 and C-18), 128.77 and 128.92 (d; $^3J_{C,P}$ = 10.6 and 11.3 Hz, respectively; C-14, C-16, C-20 and C-22), 130.42 and 131.04 (d, $^4J_{C,P}$ = 1.5 Hz, C-15 and C-21), 132.91 and 133.20 (d; $^2J_{C,P}$ = 12.8 and 11.3 Hz, respectively; C-13, C-17, C-19 and C-23), 171.74 (s, C-11) ppm. ^{31}P{^{1}H} NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 16.20 ppm. **Diasteroisomer B:** ^{1}H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.80–3.60 (9 H; 24-H, 26-H, 27-H, 30-H and 31-H), 2.85 (s, 3 H, 32-H), 3.52 (m, 1 H, 25-H), 4.03 (q, $^4J_{P,H}$ = 3.9 and $^3J_{H,H}$ = 2.4 Hz, 1 H, 3-H), 4.19 (s, 5 H, 6-H–10-H), 4.53 (t, $^3J_{H,H}$ = 2.6 Hz, 1 H, 4-H), 5.21 (m, 1 H, 5-H), 6.27 (m, 1 H, 29-H), 6.75 (m, 1 H, 28-H), 7.30–7.88 (m, overlapping signals with diastereoisomer A, 13-H–17-H and 19-H–23-H) ppm. ^{13}C{^{1}H} NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.62 (s, C-30), 28.11 (s, C-27), 30.48 (s, C-26), 34.97 (s, C-31), 37.23 (s, C-24), 55.79 (s, C-32), 69.92 (d, $^1J_{C,P}$ = 54.8 Hz, C-1) (C-2 overlapped), 71.31 (s, C-6–C-10), 72.99 (d, $^3J_{C,P}$ = 6.3 Hz, C-4), 73.98 (s, C-3), 74.54 (d, $^2J_{C,P}$ = 7.2 Hz, C-5), 82.75 (s, C-25), 122.02 (d, $^2J_{C,P}$ = 7.8 Hz, C-28), 124.11 (d, $^2J_{C,P}$ = 9.4 Hz, C-29), 128.77 and 129.02 (d; $^3J_{C,P}$ =

10.6 Hz; C-14, C-16, C-20 and C-22), 129.6 (d, $^1J_{C,P}$ = 58.5 Hz, C-12 and C-18), 131.37 and 131.70 (d; $^4J_{C,P}$ = 1.5 and 2.1 Hz, respectively; C-15 and C-21), 132.17 and 134.17 (d; $^2J_{C,P}$ = 11.9 and 12.2 Hz, respectively; C-13, C-17, C-19 and C-23), 172.05 (s, C-11) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 16.79 ppm.

Synthesis of 1c: A procedure analogous to that described above for **1a** that used **HLc** instead of **HLa** was employed to give **1c** as an orange crystalline solid. Yield 99.5 mg (74%). $C_{33}H_{35}FeO_3PPd$ (672.6): calcd. C 58.93, H 5.20; found C 59.02, H 5.31. Diastereoisomer ratio A/B = 3:2. **Diasteroisomer A:** ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.80–2.85 (9 H; 25-H, 27-H, 28-H, 31-H and 32-H), 2.58 (s, 3 H, 33-H), 3.22 (d, $^2J_{H,H}$ = 12.7 Hz, 1 H, 11-H), 3.66 (d, $^2J_{H,H}$ = 12.7 Hz, 1 H, 11′-H), 3.89 (s, 5 H, 6-H–10-H), 4.02 (m, 1 H, 4-H), 4.34 (m, 1 H, 5-H), 4.55 (m, 1 H, 3-H), 6.16 (m 1 H, 30-H), 6.77 (m, 1 H, 29-H), 7.24–8.20 (m, overlapping signals, 14-H–18-H and 20-H–24-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.09 (s, C-31), 28.09 (s, C-28), 30.93 (s, C-27), 35.76 (s, C-32), 39.34 (s, C-11), 42.82 (s, C-25), 55.73 (s, C-33), 69.33 (d, $^2J_{C,P}$ = 5.2 Hz, C-5), 70.18 (d, $^1J_{C,P}$ = 51.1 Hz, C-1), 70.44 (s, C-4), 71.07 (s, C-6–C-10), 74.75 (d, $^3J_{C,P}$ = 8.5 Hz, C-3), 81.37 (s, C-26), 89.54 (d, $^2J_{C,P}$ = 18.9 Hz, C-2), 121.39 (d, $^2J_{C,P}$ = 7.6 Hz, C-30), 124.55 (d, $^2J_{C,P}$ = 9.7 Hz, C-29), 128.34 and 128.92 (d; $^3J_{C,P}$ = 9.9 and 11.6 Hz, respectively; C-15, C-17, C-21 and C-23), 129.70 and 131.84 (d, $^1J_{C,P}$ = 1.5 Hz, C-16 and C-22), 130.98 and 133.45 (d; $^1J_{C,P}$ = 51.5 and 48.1 Hz, respectively; C-13 and C-19), 131.87 and 135.64 (d; $^2J_{C,P}$ = 14.4 Hz; C-14, C-18, C-20 and C-24), 175.09 (s, C-12) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 15.52 ppm. **Diasteroisomer B:** ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.80–2.85 (9 H; 25-H, 27-H, 28-H, 31-H and 32-H), 2.59 (s, 3 H, 33-H), 3.01 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, 11-H), 3.11 (d, $^2J_{H,H}$ = 13.1 Hz, 1 H, 11′-H), 4.02 (m, 1 H, 4-H), 4.21 (s, 5 H, 6-H–10-H), 4.34 (m, 1 H, 5-H), 4.52 (m, 1 H, 3-H), 6.43 (m, 1 H, 30-H), 6.61 (m, 1 H, 29-H), 7.24–8.20 (m, overlapping signals, 14-H–18-H and 20-H–24-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.30 (s, C-31), 28.57 (s, C-28), 31.37 (s, C-27), 35.22 (s, C-32), 38.02 (s, C-11), 40.48 (s, C-25), 55.40 (s, C-33), 68.64 (d, $^2J_{C,P}$ = 5.6 Hz, C-5), 71.25 (s, C-6–C-10), 71.48 (s, C-4), 74.39 (d, $^3J_{C,P}$ = 8.5 Hz, C-3), 81.37 (s, C-26), 89.02 (d, $^2J_{C,P}$ = 21.0 Hz, C-2), 122.16 (d, $^2J_{C,P}$ = 8.3 Hz, C-30), 124.00 (d, $^2J_{C,P}$ = 8.5 Hz, C-29), 128.64 and 128.78 (d; $^3J_{C,P}$ = 14.4 and 11.6 Hz, respectively; C-15, C-17, C-21 and C-23), 130.85 and 131.12 (d, $^4J_{C,P}$ = 1.5 Hz, C-16 and C-22), 131.12 (d, $J_{C,P}$ = 1.9 Hz, CH_p PPh_2), 133.36 and 133.70 (d; $^2J_{C,P}$ = 11.9 and 14.4 Hz, respectively; C-14, C-18, C-20 and C-24), 133.71 (d, $^1J_{C,P}$ = 46.3 Hz, C-13 and C-19), 175.09 (s, C-12) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 17.34 ppm.

Synthesis of 2c: A procedure analogous to that described above for **2a** with **HLc** instead of **HLa** was employed to give **2c** as an orange crystalline solid. Yield 110.4 mg (74%). $C_{36}H_{37}FeO_3PPd$ (710.9): calcd. C 60.85, H 5.21; found C 60.98, H 5.34. Diastereoisomer ratio A/B = 3:1. **Diasteroisomer A:** ^1H NMR (400.16 MHz, CD_2Cl_2, 25 °C): δ = 1.05 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, 36-H), 1.18 (dd, $^2J_{H,H}$ = 7.2 and $^3J_{H,H}$ = 1.2 Hz, 1 H, 29-H), 1.37 (dd, $^2J_{H,H}$ = 9.9 and $^3J_{H,H}$ = 1.5 Hz, 1 H, 29′-H), 1.91 (m, 2 H, 32-H), 2.38 (d, $^2J_{H,H}$ = 5.5 Hz, 33-H), 2.70–2.92 (5 H, 11-H, 27-H and 34-H), 2.94 (m, 1 H, 28-H), 3.04 (m, 1 H, 26-H), 3.19 (m, 1 H, 35-H), 3.38 (m, 1 H, 35′-H), 3.52 (m, 1 H, 3-H), 3.61 (m, 1 H, 25-H), 4.12 (s, 5 H, 6-H–10-H), 4.28 (t, $^3J_{H,H}$ = 2.5 Hz, 1 H, 4-H), 4.55 (m, 1 H, 5-H), 6.55 (m, 1 H, 31-H), 7.57 (m, 1 H, 30-H), 7.35–7.75 (m, overlapping signals, 14-H–18-H and 20-H–24-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 15.47 (s, C-36), 31.82 (s, C-34), 35.63 (s, C-29), 37.90 (s, C-27), 39.29 (s, C-11), 41.88 (s, C-33), 51.04 (s, C-32), 53.0 (s, C-26), 57.27 (s, C-28), 63.73 (s, C-35), 68.58 (d, $^3J_{P,C}$ = 5.6 Hz, C-4) (C-1 partially overlapped), 71.79 (d, $^3J_{P,C}$ = 5.6 Hz, C-3), 74.81 (d, $^2J_{P,C}$ = 7.8 Hz, C-5), 80.57 (s, C-25), 89.19 (d, $^2J_{P,C}$ = 20.0 Hz, C-2), 127.99 (d, $^2J_{P,C}$ = 7.4 Hz, C-30), 128.44 (d; $^3J_{P,C}$ = 10.7 Hz; C-15, C-17, C-21 and C-23), 130.43 and 131.07 (d; $^4J_{P,C}$ = 1.9 and 1.5 Hz, respectively; C-16 and C-22), 130.61 (d, $^1J_{P,C}$ = 50.0 Hz, C-13 and C-19), 133.16 and 134.13 (d; $^2J_{P,C}$ = 12.2 and 12.6 Hz, respectively; C-14, C-18, C-20 and C-24), 133.21 (d, $^2J_{P,C}$ = 8.9 Hz, C-31), 174.38 (s, C-12) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 18.32 ppm. **Diasteroisomer B:** ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 0.87 (t, $^3J_{H,H}$ = 7.0 Hz, 3 H, 36-H), 1.11 (dd, $^2J_{H,H}$ = 7.2 and $^3J_{H,H}$ = 1.2 Hz, 1 H, 29-H), 1.38 (dd, $^2J_{H,H}$ = 9.9 and $^3J_{H,H}$ = 1.6 Hz, 1 H, 29′-H), 1.86 (m, 2 H, 32-H), 2.38 (d, $^2J_{H,H}$ = 5.5 Hz, 33-H), 2.70–2.92 (5 H; 11-H, 28-H and 34-H), 2.92–3.02 (2 H, 26-H and 27-H), 3.15 (m, 1 H, 35-H), 3.36 (m, 1 H, 35′-H), 3.61 (m, 1 H, 25-H), 3.74 (m, 1 H, 3-H), 4.04 (s, 5 H, 6-H–10-H), 4.29 (t, $^3J_{H,H}$ = 2.4 Hz, 1 H, 4-H), 4.55 (m, 1 H, 5-H), 6.69 (m, 1 H, 31-H), 7.10 (m, 1 H, 30-H), 7.45–7.98 (m, overlapping signals, 14-H–18-H and 20-H–24-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 15.23 (s, C-36), 31.95 (s, C-34), 35.47 (s, C-29), 39.15 (s, C-27), 39.29 (s, C-11), 41.22 (s, C-33), 51.17 (s, C-32), 53.0 (s, C-26), 57.27 (s, C-28), 63.49 (s, C-35), 68.91 (d, $^3J_{P,C}$ = 5.7 Hz, C-4), 70.05 (C-1, partially overlapped), 70.70 (br, C-3), 74.34 (d, $^2J_{P,C}$ = 8.2 Hz, C-5), 81.30 (s, C-25), 89.35 (d, $^2J_{P,C}$ = 20 Hz, C-2), 126.03 (d, $^2J_{P,C}$ = 7.2 Hz, C-30), 128.16 and 128.27 (d; $^3J_{P,C}$ = 10.7 and 11.5 Hz, respectively; C-15, C-17, C-21 and C-23), 130.02 and 131.15 (d, $^4J_{P,C}$ = 1.5 Hz, C-16 and C-22), 130.61 (d, $^1J_{P,C}$ = 50.0 Hz, C-13 and C-19), 132.40 (d, $^2J_{P,C}$ = 8.9 Hz, C-31), 133.09 and 134.78 (d; $^2J_{P,C}$ = 11.5 and 13.3 Hz, respectively; C-14, C-18, C-20 and C-24), 174.63 (s, C-12) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 16.84 ppm.

Synthesis of 1d: A procedure analogous to that described above for **1a** that used **HLd** instead of **HLa** was employed to give **1d** as orange microcrystals. Yield 151.3 mg (75%). $C_{33}H_{35}FeO_3PPd$ (672.6): calcd. C 58.93, H 5.20; found C 59.05, H 5.41. Diastereoisomer ratio A/B = 4:3. **Diasteroisomer A:** ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.68–2.68 (9 H, 25-H, 27-H, 28-H, 31-H and 32-H), 2.71 (s, 3 H, 33-H), 3.14 (dd, $^2J_{H,P}$ = 14.4 and $^2J_{H,H}$ = 12.8 Hz, 1 H, 11-H), 3.86 (br. s, 1 H, 5-H) (5-H, overlapped signal), 4.11 (s, 5 H, 6-H–10-H), 4.33 (dd, $^2J_{H,P}$ = 5.6 and $^2J_{H,H}$ = 12.8 Hz, 1 H, 11′-H), 4.71 (br. s, 1 H, 3-H), 6.48 (m 1 H, 30-H), (29-H, overlapped signal), 7.22–7.92 (m, 14-H–18-H and 20-H–24-H) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.28 (s, C-31), 28.06 (s, C-28), 30.20 (s, C-27), 30.73 (d, $^1J_{C,P}$ = 22.9 Hz, C-11), 35.60 (s, C-32), 38.89 (s, C-25), 55.83 (s, C-33), 67.42 (s, C-3), 70.24 (s, C-6–C-10), 71.48 (s, C-4), 72.39 (s, C-5), 78.83 (d, $^3J_{C,P}$ = 4.1 Hz, C-2), 81.86 (s, C-26) (C-1, overlapped signal), 122.37 (d, $^2J_{C,P}$ = 7.3 Hz, C-30), 124.57 (d, $^2J_{C,P}$ = 4.8 Hz, C-29), 128.67 and 128.03 (d; $^3J_{C,P}$ = 10.9 and $^3J_{C,P}$ = 9.7 Hz, respectively; C-15, C-17, C-21 and C-23), 130.52 (br. s, C-16 and C-22), 131.40 and 134.80 (d; $^2J_{C,P}$ = 10.3 and 12.9 Hz, respectively; C-14, C-18, C-20 and C-24) (C-13 and C-19, overlapped signals), 176.29 (s, C-12) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 30.17 ppm. **Diasteroisomer B:** ^1H NMR (400.13 MHz, CD_2Cl_2, 25 °C): δ = 1.68–2.68 (9 H; 25-H, 27-H, 28-H, 31-H and 32-H), 2.41 (s, 3 H, 33-H), 3.30 (dd, $^2J_{H,P}$ = 14.4 and $^2J_{H,H}$ = 13.0 Hz, 1 H, 11-H), 3.96 (s, 1 H, 4-H), 4.03 (dd, $^2J_{H,P}$ = 7.4 and $^2J_{H,H}$ = 13.0 Hz, 1 H, 11′-H), 4.13 (s, 5 H, 6-H–10-H), 4.16 (br. s, 1 H, 5-H), 4.90 (br. s, 1 H, 3-H), 6.26 (m, 1 H, 30-H) (29-H, overlapped signal), 7.22–7.92 (m, 14-H–18-H and 20-H–24-H) ppm.$^{13}C\{^1H\}$ NMR (100.62 MHz, CD_2Cl_2, 25 °C): δ = 25.28 (s, C-31), 28.53 (s, C-28), 30.79 (s, C-27), 31.34 (d, $^1J_{P,C}$ = 23.7 Hz, C-11), 35.15 (s, C-32), 38.35 (s, C-25), 55.18 (s, C-33), 67.47 (s, C-3), 70.45 (s, C-6–C-10), 71.91 (s, C-4), 72.89 (s, C-5), 78.84 (d, $^3J_{C,P}$ = 4.1 Hz, C-2), 81.69 (s, C-26) (C-

1, overlapped signal), 120.79 (d, $^2J_{C,P}$ = 7.3 Hz, C-30), 124.65 (d, $^2J_{C,P}$ = 5.6 Hz, C-29), 128.39 and 129.27 (d; $^3J_{C,P}$ = 9.7 and10.3 Hz, respectively; C-15, C-17, C-21 and C-23), 130.81 (br. s, C-16 and C-22), 132.90 and 133.66 (d; $^2J_{C,P}$ = 10.3 and 12.9 Hz, respectively; C-14, C-18, C-20 and C-24) (C-13 and C-19, overlapped signals), 176.29 (s, C-12) ppm. $^{31}P\{^1H\}$ NMR (161.98 MHz, CD_2Cl_2, 25 °C): δ = 30.25 ppm.

Operando HPNMR Experiments: To a solution of compound **4a** (13.5 mg, 0.02 mmol) in [D_4]MeOH (2 mL) was added TsOH (68.4 mg, 0.36 mmol). The acidic methanol solution was transferred under nitrogen into a 10 mm sapphire tube that was placed into an NMR probe head at room temperature, and the $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired at this same temperature. Then the sapphire tube was removed from the NMR probe and charged with CO (200 psi), and the $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired again at room temperature. Afterwards, the sapphire tube was removed from the NMR probe and charged with ethylene (600 psi) at room temperature, before the $^{31}P\{^1H\}$ and ^1H NMR spectra were again acquired. Then the sapphire tube was heated in the NMR probe from room temperature to 100 °C, while the $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired at temperature intervals of 10 °C. Once the reaction temperature of 100 °C was reached, the sapphire tube was continuously heated for half an hour, before the $^{31}P\{^1H\}$ and ^1H NMR spectra were acquired. Then the sapphire tube was cooled to room temperature, and the $^{31}P\{^1H\}$ and ^1H NMR spectra were again acquired. Afterwards, the sapphire tube was removed from the NMR probe, the gases were vented off and the reaction solution was analyzed by GC-MS.

Catalytic Copolymerization Reaction in MeOH: In a typical experiment, MeOH (50 mL) was introduced into an autoclave (200 mL) which had been previously evacuated by a vacuum pump and charged with the catalyst precursor (0.012 mmol) and the desired amounts of TsOH and/or BQ. Then, the autoclave was charged with the appropriate CO/ethylene gas ratio to a total pressure of 400 psi at room temperature. The autoclave was then heated by means of a silicon oil bath. Once the desired reaction temperature was reached, the total pressure of the appropriate gas mixture was adjusted to 800 psi, and stirring was started (1200 rpm). After the desired reaction time, the autoclave was cooled by means of an ice-water bath, and unreacted gases were vented off. The polymeric material was filtered off, washed with MeOH (3 × 20 mL) and dried under vacuum at 50 °C until a constant weight was obtained.

Characterization of the Copolymers: The polyketone products were analyzed by IR as well as ^1H and $^{13}C\{^1H\}$ NMR spectroscopy.[7a] The NMR measurements, performed in a 1:1 (v/v) mixture of [D_2]-HFIP and C_6D_6, showed an imperfectly alternating structure originating from double ethylene insertion. All of the polymer samples featured ketone and ester end groups in a 1:1 molar ratio. The number-average molecular weights (M_n) of the copolymers were determined by ^1H NMR spectroscopy, while the degree of extra-ethylene insertion was determined by ^{13}C NMR using an inverse-gated decoupling pulse sequence. Typical analytical data: ^1H NMR (400.13 MHz, 294K): δ = 0.82 [t, $^3J_{H,H}$ = 7.2 Hz, C(O)CH_2CH_3], 2.03 [q, $^3J_{H,H}$ = 7.2 Hz, C(O)CH_2CH$_3$], 2.38 [br. s, CH_2C(O)CH_2], [C(O)CH$_2$CH_2CH_2CH$_2$C(O), overlapped signal], 2.68 [t, $^3J_{H,H}$ = 9.2 Hz, C(O)CH_2CH$_2$CH$_2$CH_2C(O)], 3.35 (s, OCH_3) ppm. $^{13}C\{^1H\}$ NMR (100.62 MHz, 294K): δ = 6.71 [s, C(O)CH$_2$CH$_3$], 21.69 [s, C(O)CH$_2$CH$_2$CH$_2$CH$_2$C(O)], 35.27 [s, CH$_2$C(O)CH$_2$], 40.25 [s, C(O)CH$_2$CH$_2$CH$_2$CH$_2$C(O)], 51.62 (s, OCH_3), 175.39 [s, C(O)-OCH_3], 211.44 [s, CH$_2$C(O)CH$_2$], 212.52 [s, (CH$_2$CH$_2$)$_2$C(O)-CH$_2$CH$_2$], 215.07 [s, C(O)CH$_2$CH$_3$] ppm. IR (KBr): $\tilde{\nu}$ = 3392 (w), 2911 (m), 1695 (vs), 1407 (s), 1334 (s), 1258 (m), 1197 (w), 1175 (w), 1056 (s), 810 (m), 592 (m) cm^{-1}.

Crystal Structure Determination of 2c: X-ray diffraction intensity data were collected at 150 K on an Oxford Diffraction CCD diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) using ω-scans. Cell refinement, data reduction and the empirical absorption correction were carried out with the Oxford diffraction software and SADABS.[18a] All structure determination calculations were performed with the WINGX package[18b] with SIR-97,[18c] SHELXL-97[18d] and ORTEP-3 programs.[18e] Final refinements based on F^2 were carried out with anisotropic thermal parameters for all non-hydrogen atoms, while the hydrogen atoms were included in calculated positions and refined using a riding model with isotropic U_{iso}(H) values dependent on the U_{eq}(C) of the adjacent carbon atoms. The highest residual electron density of 1.7 e Å^{-3} is located close to C(32), which shows a distance of 1.547 Å to this latter atom. The rather poor crystal quality of compound **2c** accounts for the observed residual electron density. Relevant crystallographic data are summarized in Table 3.

Table 3. Crystallographic data and structure refinement details for **2c**.

Formula	$C_{36}H_{37}FeO_3PPd$
Molecular weight [g mol^{-1}]	710.88
Crystal habit	orange prism
Crystal size [mm]	0.6 × 0.4 × 0.2
Temperature [K]	150.0(2)
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a [Å]	15.425(5)
b [Å]	11.189(5)
c [Å]	17.980(5)
β [°]	110.557(5)
V [Å^3]	2905.6(2)
Z	4
Density (calculated) [g cm^{-3}]	1.625
F(000)	1456
θ range [°]	4.16–32.14
Absorption coefficient [mm^{-1}]	1.211
Range of transmission factors	0.565–0.785
Reflections collected	9406
Independent reflections	9406
Parameters	380
Gof on F^2	1.103
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0797, 0.1375
$R1$, $wR2$ (all data)	0.1022, 0.1473
$\Delta\rho$ [e Å^{-3}]	1.719/–1.168

CCDC-649696 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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