Methoxycarbonylation of Ethene by Palladium(II) Complexes with 1,1′-Bis(diphenylphosphino)ferrocene (dppf) and 1,1′-Bis(diphenylphosphino)octamethylferrocene (dppomf)

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The square-planar bis(aquo) palladium(II) complexes $[Pd(H_2O)_2(dppf)](OTs)_2$ and $[Pd(H_2O)_2(dppomf)](OTs)_2$ are effective catalysts for the methoxycarbonylation of ethene, yet they exhibit quite different selectivity: the dppf-modified catalyst produces several low molecular weight oxygenates, spanning from methyl propanoate to alternating oligomers of carbon monoxide and ethene, while the dppomf catalyst yields exclusively methyl propanoate (dppf = 1,1′-bis(diphenylphosphino)ferrocene; dppomf = 1,1′-bis(diphenylphosphino)octamethylferrocene; OTs = *p*-toluenesulfonate). In an attempt to rationalize the different selectivities of the two catalytic systems, the methoxycarbonylation of ethene has been carried out under various experimental conditions in both autoclaves and high-pressure NMR tubes. Also, a number of model compounds have been synthesized with the aim of elucidating the structure of intermediate species observed by NMR during catalysis. Model reactions for the initiation, propagation, and chain-transfer steps in either alternating copolymerization or selective production of methyl propanoate have been performed. On the basis of all of these studies, it can be concluded that the behavior of the dppf precursor is similar to that of any other Pd^{II} catalyst modified with a chelating diphosphine. In particular, the formation of β-chelate intermediates from either Pd−H or Pd−OMe and their importance in controlling the perfect alternation of monomers have been experimentally demonstrated. The selective production of methyl propanoate with the use of the dppomf-modified catalyst has been attributed to the greater propensity of dppomf versus dppf to form Pd^{II} complexes with a dative Fe−Pd bond, which forces the P atoms to be *trans* to each other, yielding Pd-acyl species that do not react with ethene in MeOH. β-Chelate species are not formed by the dppomf-modified catalyst.

Introduction

The methoxycarbonylation of ethene catalyzed by the bis(aquo) palladium(II) complexes $[Pd(H_2O)_2(dppf)](OTs)_2$ (**1**) and $[Pd(H_2O)_2(dppomf)](OTs)_2$ (**2**) has been recently investigated by some of us (dppf = 1,1′-bis(diphenylphosphino)ferrocene; dppomf = 1,1′-bis(diphenylphosphino)octamethylferrocene; OTs = *p*-toluenesulfonate).[1]

It was found that the dppf catalyst leads to a variety of low molecular weight oxygenates spanning from methyl propanoate to perfectly alternating oligoketones, while dppomf generates a selective catalyst for methyl propanoate (Scheme 1).

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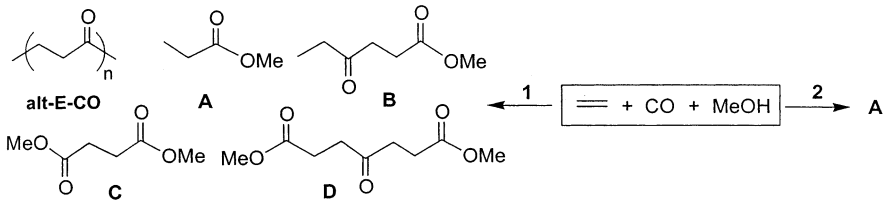
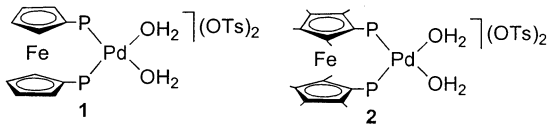
Scheme 1



No attempt was made to rationalize the different selectivity of the two catalytic systems, apart from suggesting a correlation between chemoselectivity and P−Pd−P bite angles in the bis(aquo) precursors. Single-crystal X-ray analyses showed a significantly larger P−Pd−P bite angle for $[Pd(H_2O)_2(dppomf)]^{2+}$ (101.32(5)°) as compared to $[Pd(H_2O)_2(dppf)]^{2+}$ (96.38(4)°).[1] Therefore, we decided to study the mechanistic aspects of the methoxycarbonylation of ethene using **1** and **2** by in situ NMR spectroscopy in conjunction with the isolation and characterization of intermediates and resting states related to catalysis. The results of this investigation are reported in this paper. We are confident to have elucidated the role of the dppf and dppomf ligands in governing the chemoselectivity of the ethene methoxycarbonylation catalyzed by **1** and **2**. Our study may also contribute to a better understanding of the general mechanisms involved in the alkoxycarbonylation of olefins[2] by diphosphine-palladium(II) complexes and expand the knowledge of the coordination chemistry of 1,1′-bis(diorganylphosphino)ferrocenes,[3] whose applications in metal-catalyzed homogeneous reactions are increasingly numerous and successful.[1,4]



Results

Carbonylation of Ethene in Methanol with the Catalyst Precursors 1 and 2. To achieve a more profound knowledge of the catalytic activity of **1** and **2**, the methoxycarbonylation of ethene with these two catalyst precursors was reinvestigated using a wider range of experimental conditions than previously done. Common to all reactions were a constant 600 psi pressure of 1:1 CO/C_2H_4, 85 °C, and a catalyst concentration of 10^{-4} M. Under these typical conditions,[1,2,5] **1** and **2** generated catalytic systems with almost constant activity within 1 h of reaction time. At longer reaction times, the conversion of ethene, estimated experimentally by measuring the gas uptake, slowed regularly, but all the systems were still active after 3 h. Appreciable formation of inactive Pd metal, as a black powder, was observed in all reactions lasting more than 1 h.

Table 1 reports data for reactions carried out in the presence of *p*-toluenesulfonic acid (TsOH) varying from 0 to 160 equiv with respect to palladium. In some reactions, the oxidant *p*-benzoquinone (BQ) was employed, alone or in conjunction with TsOH.[2] The promoting effects of protic acids and oxidants in olefin alkoxycarbonylation catalyzed by Pd^{II} complexes with chelating diphosphines are well known.[2,5c,d,g] Strong protic acids with weakly coordinating conjugated bases such as TsOH serve to remove strongly bound ligands from palladium, oxidize Pd^0 species to Pd^{II} species, and deliver active Pd^{II} that might have been entrapped into less active compounds, such as μ-hydroxo complexes $[Pd(\mu\text{-}OH)(P-P)]_2^{2+}$ (P−P = chelating diphosphines) into the catalytic cycle. The formation of the latter complexes is generally observed in reactions performed in reagent

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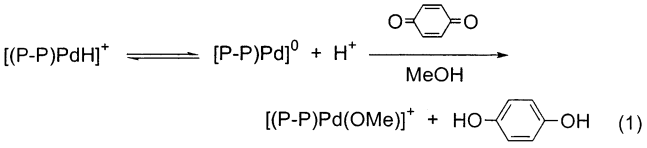
Table 1. Methoxycarbonylation of Ethene Catalyzed by Pd^{II} Complexes with dppf or Dppomf Ligands[a]

entry no.	precursor	amt of TsOH (equiv)	amt of BQ (equiv)	**alt-E-CO** productivity/TOF[b]	TOF[b] A	B	C	D[e]
1[f]	1	0	0	110/214	340	406	5	411
2[f]	1	20	0	580/1069	1378	1780	29	1887
3	1	40[c]	0	949/1804	2264	2994	72	3679
4	1	80[c]	0	1107/2103	2610	3210	60	2905
5	1	160[c]	0	1748/3321	2838	1664	35	1478
6	1	0	80	263/500	194	104	21	107
7[f]	1	20	80	940/1785	1085	1274	40	1280
8	1[d]	20	0	326/619	749	541	20	650
9	1[d]	20	80	470/893	825	1234	62	1851
10	3	0	0	traces	69	23	traces	53
11	3	20	0	338/643	1170	1187	17	299
12	3	0	80	0	171	79	traces	286
13	3	20	80	376/714	1224	1632	63	2210
14[f]	2	0	0	0	139	0	0	0
15[f]	2	20	0	0	550	0	0	0
16	2	40	0	0	732	0	0	0
17	2	80	0	0	1202	0	0	0
18	2	160	0	0	1665	0	0	0
19	2	0	80	0	95	0	0	0
20[f]	2	20	80	0	513	0	0	0
21	2[d]	20	0	0	370	0	0	0
22	2[d]	20	80	0	460	0	0	0
23	4	0	0	0	131	0	0	0
24	4	20	0	0	560	0	0	0

[a] Catalyst (0.01 mmol); 1:1 CO/C_2H_4 (600 psi); MeOH (100 mL); 85 °C; 1 h; 1400 rpm. [b] Productivity as g of product (g of Pd × h)$^{-1}$; TOF as moles of ethene incorporated (moles of cat × h)$^{-1}$. [c] This reaction produced also diethyl ketone. [d] 3 h. [e] Three higher homologues of **D** are also included (overall 20% of **D**). [f] Reference 1.

grade methanol, especially when the catalyst precursors contain water molecules, as is the case of **1** and **2**.[2,3f,n,5a,6]

The organic oxidant, here BQ, is commonly used to oxidize inactive Pd^{I} or Pd^{0}, which may form during the catalysis,[2,5a,d,g] to Pd^{II} and also transform (P−P)Pd^{II}-H into (P−P)Pd^{II}-OMe (eq 1). Protons are consumed in the course of the latter process.



(1)

The catalytic activities of **1** and **2** increased steadily with the TsOH concentration with no significant change in the chemoselectivity up to 80 equiv of acid (entries 1−4 and 14−17). The dppf-based catalysts gave several carbonylation products (Scheme 1), from alternating oligoketones (**alt-E-CO**) to a variety of low molecular weight oxygenates including methyl propanoate (**A**), methyl 4-oxohexanoate (**B**), dimethyl succinate (**C**), and dimethyl 4-oxoheptanedioate (**D**). Three other oligomeric diesters with higher molecular weight were also detected by GC in small amounts (overall 20% of **D**). In contrast, the dppomf-based catalyst produced **A** exclusively. Irrespective of the reaction conditions, the overall TOFs (moles of ethene incorporated (moles of cat × h)$^{-1}$) obtained with the dppf-modified catalysts were significantly higher than those with dppomf.

In the case of **1**, the production of diethyl ketone was observed under acidic conditions only, with a maximum TOF of 190 in the presence of 160 equiv of TsOH. The addition of BQ decreased the activity of **1** (entries 6 and 7 vs 1 and 2), yet the organic oxidant improved the selectivity in **alt-E-CO** as well as the catalyst stability, as is evident from a comparison between reactions lasting 1 h (entries 2 and 7) and 3 h (entries 8 and 9).

Some reactions were also carried out using the μ-hydroxo complex [Pd(μ-OH)(dppf)]$_2$(OTs)$_2$ (**3**), which was shown to be a chain-transfer product by in situ HPNMR spectroscopy (see below).[3f,n] Complex **3** generated an effective catalyst only in the presence of TsOH as co-reagent (entry 11), while the concomitant presence of both acid and organic oxidant gave an overall TOF that was almost twice as high. Recent studies have shown that μ-hydroxo Pd^{II} complexes with chelating diphosphines are active catalyst precursors for the alternating CO/C_2H_4 copolymerization due to their capability to react with CO, forming mononuclear Pd^{II}-H moieties via a water gas shift mechanism.[5a,7]

In the absence of BQ, with or without TsOH, the oligoketone products were featured by a 1:1 ratio between ketone and ester end groups and an average molecular weight of ca. 0.5 kg mol^{-1} (^{1}H and ^{13}C{^{1}H} NMR analysis). When BQ was used in conjunction with the acid (entry 7), a slight prevalence of ester over ketone end groups (6:4 ratio) was observed (molecular weight of 0.6 kg mol^{-1}), while, in the presence of 80 equiv of BQ with no added acid (entry 6), the end groups were prevalently constituted by ester groups (8:2 ratio) and the average molecular weight was 0.7 kg mol^{-1}.

Like observed for **1**, the catalytic activity of **2** did not improve by using BQ as co-reagent (entries 19, 20), yet the presence of the organic oxidant improved the catalyst stability (entries 15, 20 vs entries 21, 22).

The last two entries of Table 1 refer to reactions performed with the catalyst precursor [Pd_2(μ-H)(μ-CO)-(dppomf)$_2$]OTs (**4**), which was actually intercepted by NMR spectroscopy during the methoxycarbonylation

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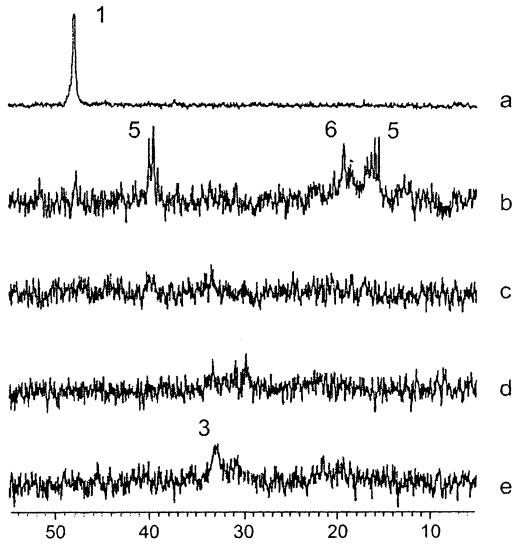
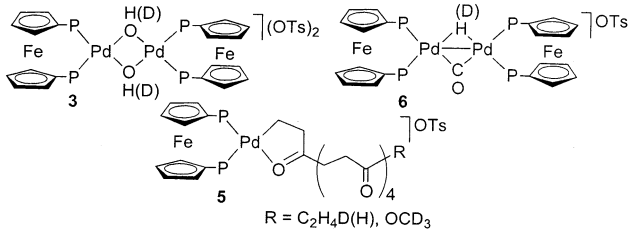


Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, MeOH-d_4, 81.01 MHz) of the carbonylation reaction of ethene catalyzed by **1**: (a) dissolving **1** in MeOH-d_4 under nitrogen at room temperature; (b) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1) at room temperature; (c) after 10 min at 50 °C; (d) after 10 min at 70 °C; (e) after the tube was cooled to room temperature.

Chart 1. Complexes Seen in the HPNMR Study of the Methoxycarbonylation of Ethene Catalyzed by 1



reactions catalyzed by **2** (see below).[6b,8−12] Precursor **4** was as efficient and selective as the parent complex **2** under comparable experimental conditions. A few reports showing a catalytic role for μ-H(μ-CO) Pd^I complexes in alkene carbonylation reactions have appeared in the relevant literature.[6b,8b]

In Situ High-Pressure NMR Study of the Methoxycarbonylation of Ethene Catalyzed by 1. The reaction catalyzed by **1** was followed by variable-temperature $^{31}P\{^1H\}$ and ^1H HPNMR spectroscopy in MeOH-d_4. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 1.

A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **1** in MeOH-d_4 and then placed into the NMR probe at room temperature (δ 47.9, trace a). Pressurizing with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature (trace b) converted **1** into the β-chelate complexes [Pd(CH_2CH_2C(O)(CH_2CH_2C(O))$_n$R)(dppf)]OTs (**5**; doublets at ca. δ 40 and 16 with J(PP) of ca. 36 Hz) (Chart 1). R in **5** may be either OCD_3 or $C_2H_4D(H)$ depending on whether the reaction starts with Pd-D/H or Pd-OCD_3, respectively. The average repeating units of the chain in **5** were estimated to be ca. 4 by ^1H NMR integration.[2,3f,5c,12−19] A minor species (5−10%) featured by a broad signal at δ 19.6 was also observed that was assigned to the μ-hydrido-μ-carbonyl complex [Pd_2(μ-D/H)(μ-CO)(dppf)$_2$]OTs (**6**) (Chart 1).[6b,8−12] In addition to the formation of these well-defined species, appreciable catalyst degradation occurred, as shown by the high noise level of the baseline and the appearance of traces of black palladium in the NMR tube. The ^1H NMR spectrum of **6** contained a weak, yet unambiguously identifiable signal due to the μ-H hydrogen (quintet at δ −6.01), which suggests the involvement of the water molecules contained in both **1** and solvent in the formation of Pd-H moieties. Alternatively, the proton may stem from H/D scrambling with ethene via β-hydride elimination of palladium alkyl intermediates. Increasing the temperature led to the disappearance of **5** and **6**; species in fast dynamic exchange were formed in their place (see the spectra recorded in the temperature range from 50 to 70 °C, traces c and d). After 30 min at 70 °C, the probe-head was cooled to room temperature. The $^{31}P\{^1H\}$ NMR spectrum at this temperature showed the formation of a mixture of products that denied first-order analysis. The only complex that we could assign was the known μ-OH(OD) complex **3** (Chart 1) (trace e, singlet at δ 33.1).[3f,n] Analysis of the solution by GC showed the formation of deuterated samples of **A**, **B**, **C**, and **D**. The formed co-oligomer was similar to the samples obtained in the batch experiments under comparable experimental conditions with $\tilde{n}$ values of ca. 8 and both ketonic and ester end groups.[1]

A different $^{31}P\{^1H\}$ NMR picture was observed when the methoxycarbonylation of ethene was performed in the presence of 16 equiv of BQ with respect to the catalyst. In this case the Pd^I-Pd^I complex **6** did not form at any stage of the reaction, while the μ-OH species was again seen at the end of the reaction. Along the whole experiment, the spectral noise was much lower than that observed in the absence of oxidant, which reflects a minor degradation of the Pd^{II} catalyst to palladium metal.

In the reaction performed in the presence of 4 equiv of TsOH, no other palladium complex than **1** was seen by NMR spectroscopy, besides the protonolysis termination product **3**.[3f] Moreover, the signal of the precursor **1** persisted up to 50 °C. Apparently, the formation of the β-chelates **5** from either Pd-H or Pd-OMe is inhibited at room temperature by the tosylate ions, which may compete with monomers for coordination to palladium. Above 50 °C, when the methoxycarbonylation products started to form, all the species were in rapid chemical exchange on the NMR time scale and therefore undetectable.

Synthesis and Characterization of Intermediates and Resting States in the Methoxycarbonylation of Ethene Catalyzed by 1. The model β-chelate complex [Pd(CH_2CH_2C(O)Me)(dppf)]OTf[3f,12] (**7**) was synthesized by sequential bubbling of CO and ethene into a solution of [PdMe(NCMe)(dppf)]OTf[3l] in CH_2Cl_2

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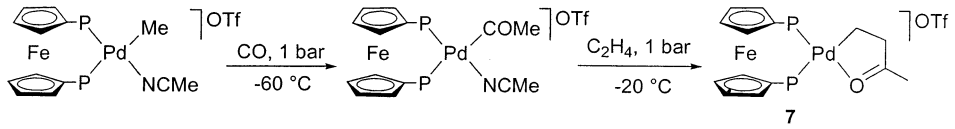
Scheme 2



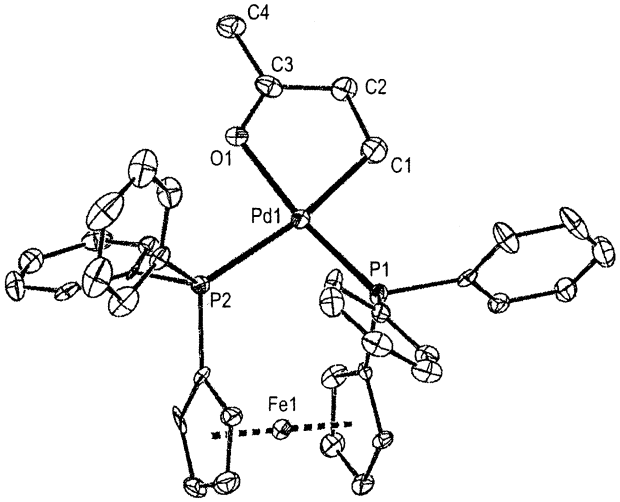


Figure 2. ORTEP drawing (30% displacement ellipsoids) of the cation of **7**·0.5CH_2Cl_2. Hydrogen atoms, triflate anion, and CH_2Cl_2 have been omitted for clarity.

Table 2. Selected Geometrical Parameters for 7·0.5CH_2Cl_2

bond lengths (Å)		bond angles (deg)	
Pd−P1	2.220(3)	P1−Pd−P2	98.47(9)
Pd−P2	2.395(3)	P2−Pd−O1	89.9(2)
Pd−O1	2.123(7)	P1−Pd−C1	90.5(3)
Pd−C1	2.032(12)	O1−Pd−C1	81.1(4)
C1−C2	1.490(15)	O1−C3−C2	119.9(9)
C2−C3	1.476(16)	O1−C3−C4	119.5(10)
C3−C4	1.466(14)	Pd−O1−C3	114.1(7)
C3−O1	1.229(13)	C1−C2−C3	113.3(10)
		Pd−C1−C2	110.3(8)

at low temperature, followed by solvent evaporation (Scheme 2).

The coordination of the β-keto group was inferred by the low-field $^{13}C\{^1H\}$ NMR signal of the carbonyl carbon atom (δ 238.9) and the low-frequency ν(CO) stretch (1630 cm^{-1}).[15−19] Conclusive evidence of the β-chelate structure was obtained by a single-crystal X-ray analysis of **7**·0.5CH_2Cl_2 (Figure 2 and Table 2).

The structure consists of $[Pd(CH_2CH_2C(O)Me)(dppf)]^+$ complex cations and triflate counteranions with interspersed CH_2Cl_2 molecules. The metal center exhibits a square-planar geometry with *cis* coordinating phosphorus atoms (P1−Pd−P2 angle of 98.47(9)°). This P1−Pd−P2 angle is similar to that of other palladium complexes of dppf.[20] The structure shows the chelate ring with the oxygen atom of the carbonyl group coordinated to the metal center. The Pd−P1 distance is much shorter (2.220(3) Å) than the Pd−P2 distance (2.395(3) Å), as this bond is *trans*-located to the Pd−alkyl bond, whereas the P2 phosphorus is *trans*-coordinated to the coordinating oxygen atom. The Pd−O bond length of 2.123(4) Å is in accordance with a dative bond.[19,21]

The (carbonyl)acyl complex $[Pd(CO)(C(O)CH_2CH_2C(O)Me)(dppf)]OTf$ (**8**) and the β-ketoalkyl derivative $[Pd(CH_2CH_2C(O)CH_2CH_2C(O)Me)(dppf)]OTf$ (**9**) were prepared in CD_2Cl_2 and characterized by NMR spectroscopy at low temperature. The reaction of CO with **7** gave the carbonyl(acyl) **8**, which was transformed into the β-chelate **9** by reaction with ethene (Scheme 3). In the reaction leading to **9**, the formation of a minor species featured by two doublets with chemical shifts and coupling constants (δ 39.1 and 15.4, $^2J(PP) = 35.8$ Hz) very close to those of **9** (δ 38.7 and 15.8, $^2J(PP) = 35.7$ Hz) was observed. On the basis of these NMR data and the presence of two IR bands at 1629 and 1710 cm^{-1}, which are typical of coordinated and free carbonyl groups, respectively,[22] we suggest that this minor species is a higher β-ketoalkyl homologue of **9** formed by reaction of the latter with residual CO and ethene in the solution.

Multinuclear NMR analysis allowed for the identification of the acyl(carbonyl) complex **8**; in particular, the $^{13}C\{^1H\}$ NMR spectrum showed an acyl carbon signal at δ 229.3 (d, $^2J(CP) = 86.7$ Hz) and ketone carbon signal at δ 208.1 (s).

The μ-H, μ-CO complex **6** was independently synthesized by two different methods, involving either the treatment of the aquo complex **1** with CO in CH_2Cl_2 (water-gas shift reaction)[2] (route a in Scheme 4) or the methanolysis of the Pd-acetyl complex $[Pd(COMe)(NCMe)(dppf)]OTs$[3l] under a CO atmosphere (route b). The NMR features of **6** are in line with those of other μ-hydrido, μ-carbonyl binuclear Pd[8−12] and Pt[23] complexes stabilized by phosphine ligands.

The synthesis of **6** from an acetyl complex in the presence of CO (route b) resembles closely the chain-transfer mechanism by methanolysis in real copolymerization reactions catalyzed by Pd^{II} precursors with chelating diphosphines where the acetyl group is sub-

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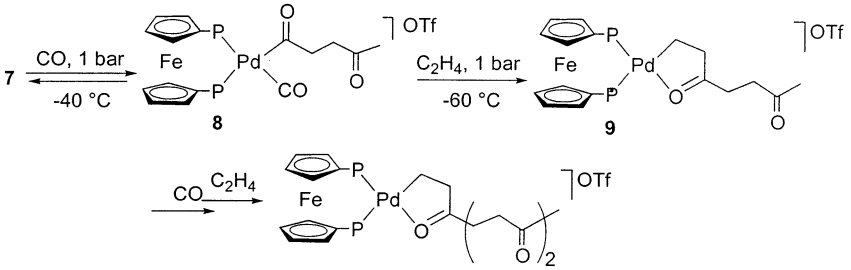
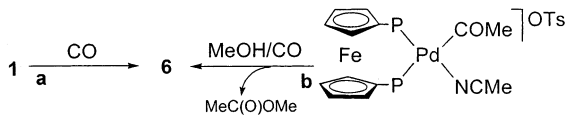
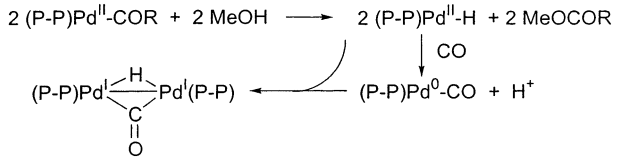
Scheme 3



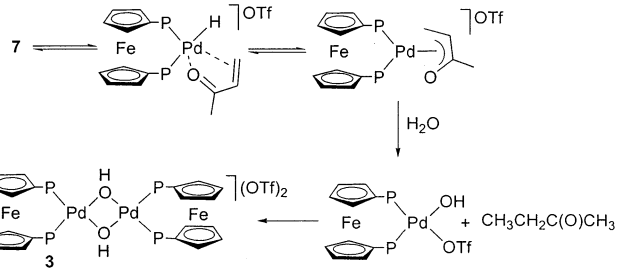
Scheme 4



Scheme 5



Scheme 6

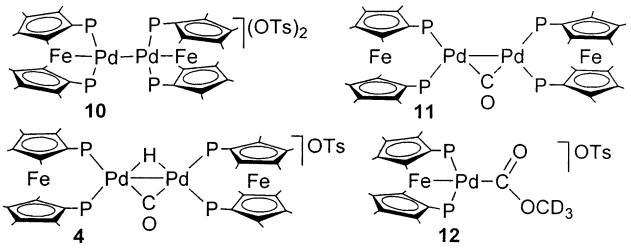


stituted by a generic acyl group (Scheme 5).[2] Following the methanolysis of Pd-COR with production of the corresponding ester, the resultant [$Pd^{II}H(P-P)$] fragment is not stable in the presence of CO.[2,9a,24] Part of it disproportionates to give H^+ and [$Pd^0(CO)(P-P)$]. The combination of the latter Pd^0 fragment with residual [$Pd^{II}H(P-P)$] eventually generates the Pd^I-Pd^I μ-H, μ-CO species.

The μ-OH complex **3** was previously synthesized by Longato[3n] and later shown by van Leeuwen to be the chain-transfer product by protonolysis with water in CO/C_2H_4 copolymerizations catalyzed by Pd^{II}-dppf complexes.[3f] The formation of **3** involves β-chelates, structurally similar to **6**, that isomerize to enolates prior to undergoing regioselective attack by water at the C_2 carbon atom. This mechanism is exemplified for **7** in Scheme 6.[3f]

Stability of 2 in Methanol. Synthesis and Characterization of [Pd(dppomf)]$_2$(OTs)$_2$. The starting solution employed in this study was obtained by dissolving a sample of **2** in MeOH-d_4 at room temperature. Within a few minutes, the green solution of **2** turned brownish red. The reaction was followed by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. The first $^{31}P\{^1H\}$ NMR spectrum showed a 14% conversion of the precursor (δ 71.6) into the palladium(I) binuclear complex [Pd(dppomf)]$_2$(OTs)$_2$ (**10**) (δ −1.3) (Chart 2).[11,25,26] Additional NMR spectra were acquired every 30 min at room temperature. The ratio between **2** and **10** did not appreciably vary with time, yet the concentration of these two compounds slowly decreased, becoming, altogether, one-fifth of the initial one over 2 days. The ^1H NMR spectra acquired during this experiment showed a small downfield shift of the resonances of both *p*-toluenesulfonate ions and adventitious water, which is consistent with the presence of protons in solution (vide infra). In separate NMR experiments, treating a freshly prepared solution containing **2** and **10** with 4 equiv of either TsOH or BQ resulted in re-formation of **2** as the exclusive complex.

Chart 2. Complexes Seen in the HPNMR Study of the Methoxycarbonylation of Ethene Catalyzed by 2



In Situ High-Pressure NMR Study of the Methoxycarbonylation of Ethene Catalyzed by 2 without Co-reagent. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution prepared by dissolving a solid sample of **2** in MeOH-d_4 and then placed into the NMR probe at room temperature. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 3.

As already observed in the stability study of **2** in methanol, the first spectrum (trace a) showed the partial conversion (15%) of the precursor into **10**. The NMR tube was pressurized with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature (trace b) and then heated to 40 °C. As shown by the first spectrum acquired at this temperature (trace c), both complexes converted into a new complex featured by a singlet at δ 5.6, which we suggest to be the Pd^0 μ-CO binuclear complex Pd_2-(μ-CO)(dppomf)$_2$ (**11**) (Chart 2) on the basis of its NMR characteristics (see below).[27] Increasing progressively the temperature to 50 (trace d), 60 (trace e), and 70 °C (trace f) decreased the concentration of **11**; in its place

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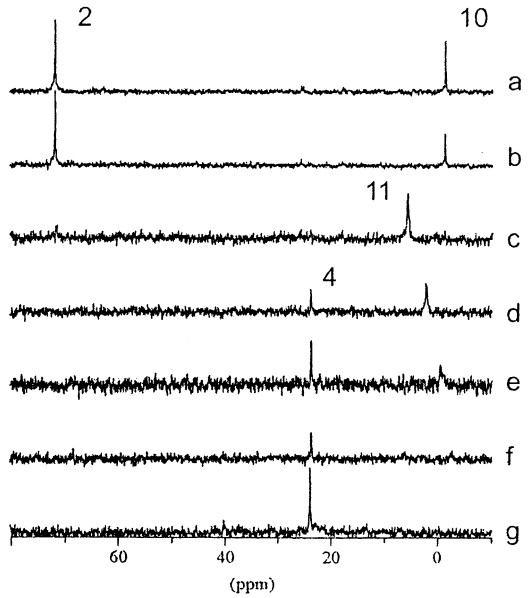


Figure 3. Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, MeOH-d_4, 81.01 MHz) of the carbonylation reaction of ethene catalyzed by **2**: (a) dissolving **2** in MeOH-d_4 under nitrogen at room temperature; (b) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1) at room temperature; (c) at 40 °C; (d) at 50 °C; (e) at 60 °C; (f) at 70 °C; (g) after the tube was cooled to room temperature.

a new complex was formed (singlet at δ 23.7) featured by a quintet at δ −6.31 (J(HP) = 42.1 Hz) in the ^1H NMR spectrum. On the basis of an independent synthesis, the new complex was identified as the μ-hydrido, μ-carbonyl complex [$Pd_2(\mu$-H)(μ-CO)(dppomf)$_2$]OTs (**4**) (Chart 2). After 30 min at 70 °C, the probe-head was cooled to room temperature. The $^{31}P\{^1H\}$ NMR spectrum at this temperature showed that compound **4** was the only phosphorus-containing species visible in solution (trace g). Palladium metal in the tube indicated the occurrence of partial catalyst decomposition. ^1H NMR spectra acquired during the experiment showed that the formation of methyl propanoate-d_4 (multiplets at δ 1.05 and 2.27) had started at ca. 60 °C.

In Situ High-Pressure NMR Study of the Methoxycarbonylation of Ethene Catalyzed by 2 in the Presence of 16 Equiv of BQ. A sequence of selected $^{31}P\{^1H\}$ NMR spectra is reported in Figure 4. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **2** in MeOH-d_4 and then placed into the NMR probe at room temperature.

As in the previous experiment, the first spectrum (trace a) showed the presence of both **2** and **10** in a ca. 5:1 ratio. Adding BQ (16 equiv) led to the immediate oxidative conversion of **10** into **2** (trace b). Pressurizing with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature caused the complete transformation of **2** into a new complex featured by a $^{31}P\{^1H\}$ NMR resonance at δ −19.1 (trace c). On the basis of an in situ NMR characterization in methanol (see below) this complex was assigned the η^1-carbomethoxy complex [Pd(C(O)OCD$_3$)(dppomf)]OTs (**12**), where the metal center is coordinated in a square-planar environment by two *trans* phosphorus atoms from dppomf, a carbomethoxy group, and a dative Fe−Pd bond (Chart 2).[1,3a,c,k] Increasing the temperature to 40 °C caused the consumption of BQ (eq 1) with concomitant transformation of

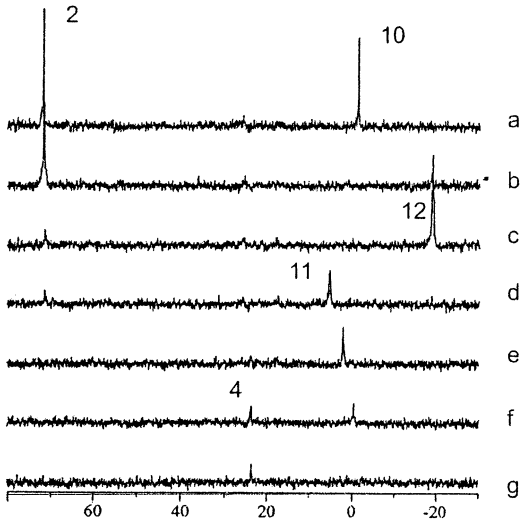


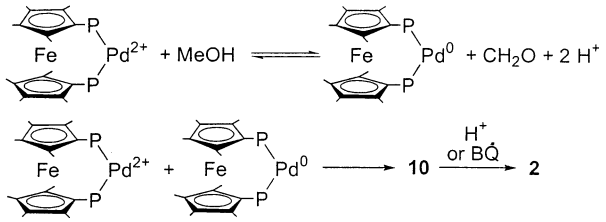
Figure 4. Variable-temperature $^{31}P\{^1H\}$ NMR study (sapphire tube, MeOH-d_4, 81.01 MHz) of the carbonylation reaction of ethene catalyzed by **2**: (a) dissolving **2** in MeOH-d_4 under nitrogen at room temperature; (b) after the addition of 16 equiv of BQ; (c) after the tube was pressurized with 40 bar of CO/C_2H_4 (1:1) at room temperature; (d) at 40 °C; (e) at 50 °C; (f) at 60 °C; (g) at 70 °C.

12 into the μ-CO dimer **11** (trace d). Upon a further increase of the temperature to 70 °C, **11** converted to the μ-hydride, μ-CO complex **4** (traces e−g), while methyl propanoate began to form. After 30 min at 70 °C, the tube was allowed to cool to room temperature. The $^{31}P\{^1H\}$ NMR spectrum at this temperature showed exclusively **4**, yet traces of black palladium metal proved the occurrence of some catalyst degradation. ^1H NMR and GC/MS analyses confirmed the formation of methyl propanoate-d_4.

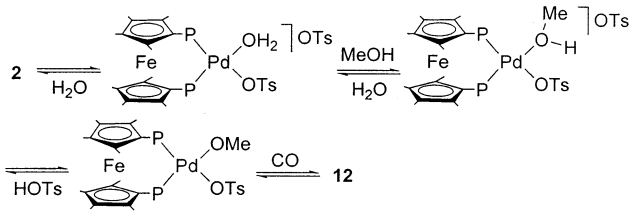
In Situ High-Pressure NMR Study of the Methoxycarbonylation of Ethene Catalyzed by 2 in the Presence of 4 Equiv of TsOH. A 10 mm sapphire HPNMR tube was charged with a solution of **2** in MeOH-d_4 under nitrogen. The first spectrum at room temperature showed the presence of both **2** and **10** in a ca. 5:1 ratio. Upon addition of TsOH (4 equiv), **10** converted immediately to **2** completely. Pressurizing with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature caused the quantitative formation of the μ-hydride, μ-CO complex **4**, which was also the only phosphorus-containing complex visible on the NMR time scale during the carbonylation reaction (1 h, 50−70 °C). After 30 min at 70 °C, the probe-head was cooled to room temperature. The $^{31}P\{^1H\}$ NMR spectrum at this temperature showed only **4**, while ^1H NMR and GC/MS analyses revealed the formation of methyl propanoate-d_4.

In Situ High-Pressure NMR Study of the Methoxycarbonylation of Ethene Catalyzed by 2 in the Presence of 4 Equiv of TsOH and 16 Equiv of BQ. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **2**, TsOH (4 equiv), and BQ (16 equiv) in MeOH-d_4 (2 mL) and then placed into the NMR probe at room temperature. The first spectrum showed only **2**. Pressurizing to 40 bar with a 1:1 mixture of CO/C_2H_4 at room temperature caused no change in both the ^1H and $^{31}P\{^1H\}$ NMR spectra. However, increasing the temperature to 50 °C decreased the

Scheme 7



Scheme 8



concentration of **2** and gave both **11** and **4**, albeit in small amounts. At 60 °C, only **11** and **4** were visible, with a higher concentration of the former complex. With time, the signal of **11** decreased in intensity. At 70 °C, **4** was the only visible phosphorus-containing species during the carbonylation reaction. After 30 min at 70 °C, the probe-head was cooled to room temperature. The $^{31}P\{^1H\}$ NMR spectrum at this temperature showed the exclusive presence of **4**. As usual, palladium metal deposited on the bottom of the NMR tube. ^1H NMR and GC/MS analyses showed the formation of methyl propanoate-d_4.

Synthesis and Characterization of Intermediates and Termination Products of the Methoxycarbonylation of Ethene by 2. Complex **10** was obtained by simply dissolving **2** in methanol. After 5 min, ca. 14% **2** converted to **10**, while the color of the solution turned from green to brownish red. An in situ experiment monitored by NMR spectroscopy showed that both **2** and **10** were intrinsically unstable in methanol under N_2, where they decomposed with time to unknown species, under release of protons. During this decomposition, the **2**/**10** ratio remained constant. All our attempts to isolate a sample of **10** by fractional crystallization were unsuccessful. Likewise, we were unable to develop an independent synthetic procedure to this Pd^I-Pd^I dimer. Therefore, **10** was characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy in situ. Two magnetically equivalent phosphorus atoms and two largely separated signals for the methyl hydrogen atoms of the Cp* rings ($\Delta\delta = 1.35$) are strongly diagnostic for a structure in which the phosphorus atoms are *trans* to each other, and iron forms a dative bond to palladium using its e_{2g} electron density.[3a,c,k] Recent studies have demonstrated that the formation of dative iron−palladium bonds in dppf and dppomf palladium complexes causes a tilting of the Cp rings. As a consequence of this tilting, the ^1H NMR $\Delta\delta$ of the α- and *β*-hydrogen atoms (H in Cp, Me in Cp*) is larger than that in the free ligand.[3a,c,k]

Indirect support for the proposed structure for **10** was provided by its reactivity toward protic acids and oxidants. Indeed, treatment of methanol solutions of **10** with either TsOH or BQ regenerated **2** cleanly.

The dissolution of mononuclear (P−P)Pd^{II} complexes in MeOH (P−P = chelating diphosphine) is a known procedure to prepare binuclear Pd^I complexes structurally similar to **10**.[11,25,26] The formation of these Pd^I-Pd^I compounds has been proposed to involve the coupling of (P−P)Pd^{II} and (P−P)Pd^0 moieties, the latter being generated by palladium-promoted methanol oxidation to formaldehyde.[9,25] Scheme 7 illustrates this process for **10**.

The protons formed during the oxidation of methanol, converting **10** into **2**, are likely to be responsible for the constant **2**/**10** ratio observed in the stability experiment described above.

Like **10**, the *μ*-CO binuclear complex **11** was neither isolated nor prepared through an independent procedure. All our efforts to prepare **11** led to the formation of either unidentified species or well-defined (dppomf)-Pd^0 complexes, such as [Pd(dppomf)$_2$] and the bis(carbonyl) complex [Pd(CO)$_2$(dppomf)],[28] none of which showing the spectral characteristics of **11**. Indirect support for the proposed structure of **11** was provided by the following experiment: a 10 mm sapphire HP-NMR tube was charged under nitrogen with a solution of **2** in MeOH-d_4 and pressurized to 40 bar with 1:1 CO/C_2H_4 at room temperature. The tube was introduced into a spectrometer and heated to 40 °C. Already the first spectrum at this temperature showed the quantitative formation of **11** (see Figure 3, trace c). The tube was then removed from the probe head, frozen in liquid nitrogen, and subjected to vacuum to remove the gaseous phase. One equivalent of TsOH was added to the frozen solution. The tube was allowed to reach room temperature, where the quantitative formation of the *μ*-hydride, *μ*-CO complex **4** was observed by NMR spectroscopy.

Complex **4** was synthesized by the procedure described above for the dppf derivative **6**, namely, the reaction of the aquo complex **2** with CO in CH_2Cl_2. Alternatively, **4** was prepared by pressurizing a mixture of **2** and TsOH (4 equiv) in methanol with 1:1 CO/C_2H_4 in a HPNMR tube. Under these conditions, **4** can form according to the reaction sequence proposed in Scheme 5 for the dppf analogue **6**, i.e., partial disproportionation of the Pd^{II} system [PdH(dppomf)]$^+$ in the presence of CO to give H^+ and [Pd(CO)(dppomf)], followed by combination of the latter Pd^0 fragment with residual [PdH(dppomf)]$^+$.

Like **6** and other *μ*-hydrido, *μ*-carbonyl binuclear Pd complexes with chelating diphosphines, **4** is fluxional on the NMR time scale: the hydride resonance in the ^1H NMR spectrum appears as a quintet with δ −6.02 (J(HP) = 42.6 Hz) at 20 °C and as a triplet of triplets with δ −5.72 (^2J(HP) = 80.8, 5.2 Hz) at −70 °C.[8,12]

Pressurizing a methanol solution of **2** with CO gave the carbomethoxy complex **12** quantitatively, likely through CO insertion into a Pd^{II} methoxy intermediate that was not intercepted (Scheme 8).[2,29]

A carbon resonance at 209.9 in the $^{13}C\{^1H\}$ NMR spectrum was diagnostic for the presence of a carbomethoxy group in **12**, while the lack of additional P−C couplings in the $^{31}P\{^1H\}$ NMR spectrum, when ^{13}CO was used in the place of ^{12}CO, was consistent with a *trans* arrangement of the phosphorus atoms.[3a,c,k] Fi-

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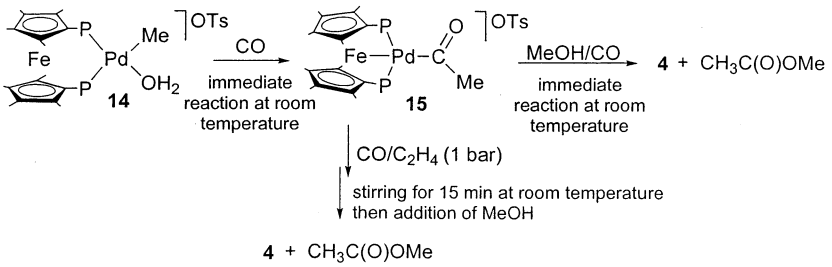
Scheme 9



nally, a strong argument in favor of the η^3-*P,P,Fe* bonding mode of dppomf in **12** was provided by the large difference between the chemical shifts of the α and β methyl hydrogen atoms of the Cp* rings ($\Delta\delta = 0.87$).[3a,c,k]

Under CO atmosphere, **12** underwent methanolysis at room temperature very slowly ($t_{1/2}$ ca. 12 h), yielding dimethyl carbonate (GC/MS analysis) and the (hydrido)-carbonyl complex **4**.

Some possible intermediates in Scheme 8 have been represented with arbitrary molecular structures. Our preference for a chelating η^2-*P,P* dppomf ligand in these compounds stems from the nature of the co-ligands, which are neither sterically demanding nor electron-withdrawing (H, OMe, OTs). Indeed, both characteristics disfavor the formation of a dative Fe−Pd, which requires either bulky or electron-withdrawing co-ligands.[3a,c]

Model Study of the Methoxycarbonylation of Ethene by Pd^{II}-dppomf Catalysis. The methyl complex [Pd(Me)(H_2O)(dppomf)]OTs (**14**) was straightforwardly prepared by reaction of [PdCl(Me)(dppomf)] (**13**) with AgOTs in CH_2Cl_2 solution. In the presence of 1 bar of CO at room temperature, **14** converted immediately into the acyl complex [Pd(COMe)(dppomf)]OTs (**15**) (Scheme 9). The different hapticity of dppomf in **14** and **15** was unequivocally put in evidence by the corresponding $^{31}P\{^1H\}$ NMR patterns: AM system with δ 48.8 (br) and 12.6 (^2J(PP) = 20.5 Hz), and A_2 system with δ −13.3, respectively. The ^1H NMR resonances of the Cp* methyl groups were in line with the different hapticity of dppomf in the two compounds, showing four close signals for **14** and two well-separated signals for **15**.

The acyl complex **15** in CD_2Cl_2 underwent fast methanolysis at room temperature, yielding the μ-hydride, μ-CO complex **4** (see Scheme 5) and methyl acetate (Scheme 9). Complex **4** and methyl acetate were selectively produced also when MeOH was added to a CD_2Cl_2 solution of **15** previously saturated with a 1:1 CO/C_2H_4 mixture at room temperature. It is worth noticing that the carbomethoxy complex **12**, containing a dative Fe−Pd bond like **15**, undergoes alcoholysis very slowly even in neat MeOH (vide infra), which reflects the lower electrophilic character of the CO_2R carbon atom as compared to the COR carbon atom.

Discussion

The overall mechanism accounting for the nature of the oxygenated products obtained by methoxycarbonylation of ethene with **1** and **2** (Scheme 1) has been reported previously.[1] The results of the present study highlight mechanistic details regarding the propagation and termination steps of the alternating copolymerization catalyzed by **1** as well as rationalize the different selectivity of the dppf and dppomf catalysts.

Scheme 10 shows mechanistic details for the reactions assisted by the dppf-modified catalyst.

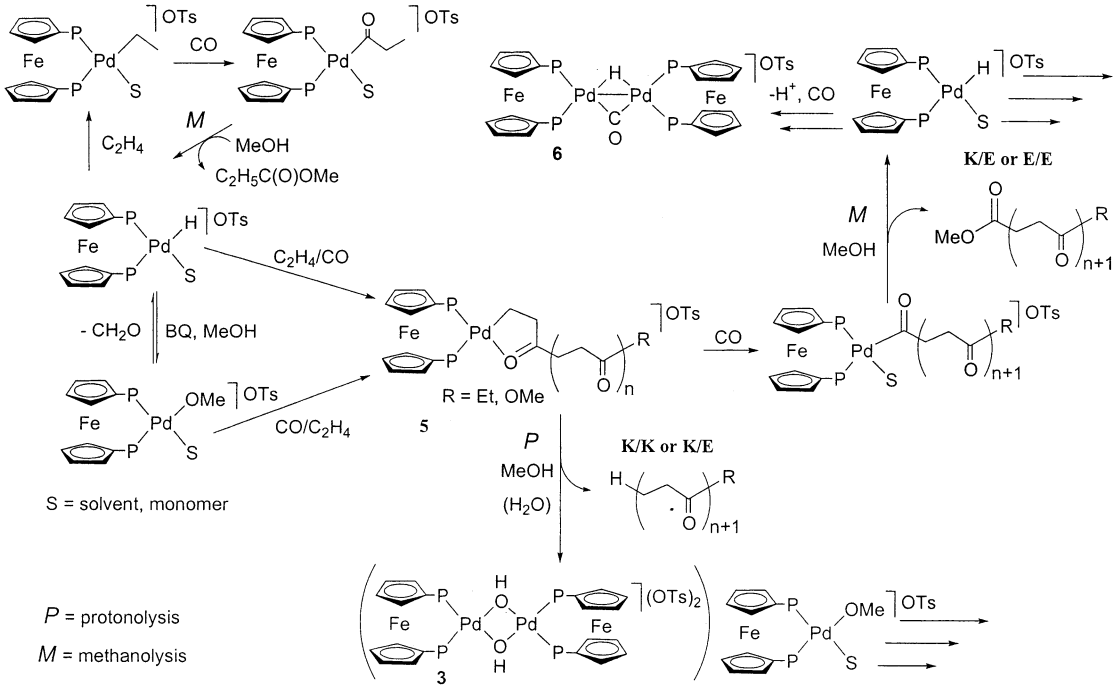
On the basis of the experimental results and model studies described in the section above, one may conclude that the behavior of the dppf precursor **1** in the methoxycarbonylation of ethene is quite similar to that of any other Pd^{II} catalyst modified with a chelating diphosphine.[2] In particular, the formation of β-chelate intermediates from either Pd−H or Pd−OMe has been experimentally determined (Figure 1), and their importance in controlling the perfect alternation of monomers has been demonstrated in the model studies illustrated in Schemes 2 and 3.

The formation of the μ-OH binuclear complex **3** during the catalysis together with that of diethyl ketone demonstrate that the chain transfer can proceed by protonolysis of Pd-alkyl, most likely through the enolate mechanism reported by van Leeuwen et al. (Scheme 6).[3f] The chain transfer by protonolysis seems to be much less important than that by methanolysis of Pd-acyl, however. In fact, the production of diethyl ketone occurred in very low yield and only in the presence of an excess of protic acid. Upon methanolysis of Pd-acyl, the Pd−H moiety is regenerated, which can initiate the next catalytic cycle; however, this species is unstable and can also degrade to the hydride(carbonyl) complex **6** through the mechanism reported in Scheme 5. The termination product **3** is not a dead-end for the catalytic reaction, as it may be considered a resting state for catalytically active Pd^{II} (Table 1, entries 10−13). The mechanism by which [Pd(μ-OH)(P−P)]$_2^{2+}$ complexes may re-enter the copolymerization cycle has been proposed to involve the cleavage of the binuclear structure by CO, followed by a water-gas-shift process to generate Pd-H moieties.[5c,7]

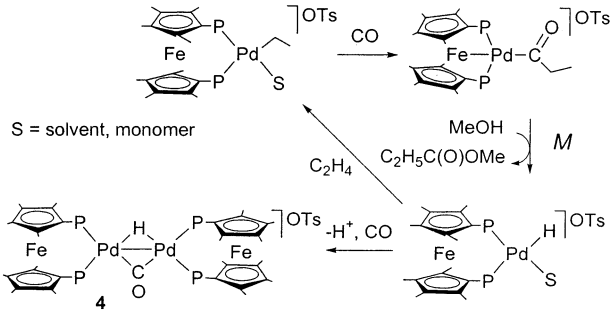
In contrast to **1**, the dppomf precursor **2** yields methyl propanoate exclusively, irrespective of the experimental conditions (Table 1), which means that the whole activity of the dppomf-modified catalyst is confined in the reaction sequence reported in Scheme 11. Indeed, the alternative path to generate methyl propanoate via protonolysis of a possible β-chelate complex of the formula [Pd(CH_2CH_2C(O)OMe)(dppomf)]$^+$ can be ruled out on the basis of both direct evidence and model studies.

The HPNMR studies did not reveal the formation of any β-chelate species with dppomf at any stage of the carbonylation reaction under a CO/C_2H_4 pressure of 40 bar, while methyl propanoate was selectively and efficiently produced under conditions that do not allow for the formation of Pd-C(O)OMe initiators (i.e., in the

Scheme 10



Scheme 11



presence of a large excess of acid, see Table 1, entry 18). The occurrence of the Pd-OMe mechanism is unlikely on the basis of the results of the model study with the acyl complex **15** that showed the methanolysis of **15**, yielding methyl acetate and **4**, to be much faster than the insertion of ethene into Pd-COMe to give a Pd-alkyl (Scheme 9). Studies underway in this laboratory confirm that the insertion of ethene into the Pd−COMe bond of **15** is a thermodynamically allowed process in CH_2Cl_2, yet kinetically disfavored over alcoholysis by MeOH even under a high pressure of ethene (20 bar).[28] In this respect, the behavior of the η^3-*P*,*P*,*Fe*-dppomf acyl complex **15** contrasts dramatically with that of the η^2-*P*,*P*-dppf analogues $[Pd(COR)(S)(dppf)]^+$ (S = MeOH, monomer), which convert to β-chelate species by reaction with C_2H_4 even in neat MeOH (Figure 1).[12,30]

The Pd-H initiator in Scheme 11 has been drawn as containing an η^2-chelating dppomf ligand. Although this representation is arbitrary, as no spectroscopic evidence whatsoever was obtained for a mononuclear Pd-H complex during the catalysis, the probability that such an intermediate contains a η^2-*P*,*P*-dppomf ligand is indeed very high. The hydride ligand lacks all important criteria, established in the course of previous studies,[3a,c,k] for the formation of a dative Fe−Pd bond in [PdL(ferrocenyldiphosphine)]$^+$ complexes; that is, L must be bulky or have an electron-withdrawing character to make the Pd center susceptible to accept e_{2g} electron density from iron. Consistent with this rule, the methyl derivative **14** exhibits a chelating dppomf ligand, while the acyl complex **15** contains a dative Fe−Pd bond and *trans* P atoms.

The overall TOFs obtained with **2** are by far lower than those obtained with **1** under comparable conditions (Table 1). The propensity of the precursor **2** to degrade spontaneously to the Pd^I-Pd^I binuclear complex **10** and, under CO/C_2H_4, to the Pd^0 μ-CO complex **11** may well account for the low productivity of the dppomf-modified catalyst. Another factor that can contribute to decrease the catalytic activity of **2** is the formation of a propionyl intermediate with a dative Fe−Pd bond and *trans* P atoms (Scheme 11). In fact, the methanolysis of the propionyl intermediate may be rate limiting in the catalysis cycle shown in Scheme 11, as it involves the reaction of MeOH with a coordinatively saturated square-planar Pd^{II} complex. To accomplish this reaction, a change in the hapticity of dppomf from η^3-*P*,*P*,*Fe* (*trans* P atoms) to η^2-*P*,*P* (*cis* P atoms) is required to provide a free coordination site for MeOH coordination and to allow for the nucleophilic attack by the oxygen atom to the acyl carbon atom. The energy barrier to this hapticity change is presumably high. Moreover, as recently shown by van Leeuwen et al.,[30] under acidic conditions methanol is a too weak a nucleophile to give direct attack from solution.

The stabilizing effect of the η^3-*P*,*P*,*Fe*-dppomf bonding mode seems to be particularly important in the methoxycarbonylation reactions carried out in the presence of an excess of BQ, yielding a TOF of 95 only (Table 1, entry 19). The organic oxidant, promoting the conversion of Pd-H into Pd-C(O)OMe (eq 1), increases the concentration of the η^3-*P*,*P*,*Fe*-dppomf carbomethoxy

(30) van Leeuwen, P. W. N. M.; Zuideveld, M. A.; Swennenhuis, B. H. G.; Freixa, Z.; Kamer, P. C. J.; Goubitz, K.; Fraanje, J.; Lutz, M.; Spek, A. L., submitted for publication.

complex **12** (Figure 4), which is not a good catalyst precursor to form Pd-H due to its reluctance to undergo methanolysis.

Conclusions

The square-planar palladium(II) complexes $[Pd(H_2O)_2(dppf)](OTf)_2$ and $[Pd(H_2O)_2(dppomf)](OTf)_2$ are effective catalysts for the methoxycarbonylation of ethene, yet they exhibit quite different selectivity: the dppf-modified catalyst produces several low molecular weight oxygenates, spanning from methyl propanoate to alternating oligoketones, while the dppomf catalyst yields exclusively methyl propanoate. Batch catalytic reactions, in situ high-pressure NMR experiments, and model studies with isolated compounds agree to indicate the greater propensity of dppomf versus dppf to form palladium(II) complexes with a dative Fe−Pd bond as the factor leading to the selective production of methyl propanoate. In fact, the presence of an Fe−Pd bond forces the P atoms to be *trans* to each other and ultimately results in Pd-acyl species that do not react with ethene in MeOH.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an atmosphere of nitrogen using Schlenk-type techniques. All reagents and solvents were used as purchased from commercial suppliers. The complexes PdCl(Me)(COD) (COD = cycloocta-1,5-diene),[31] $[Pd(H_2O)_2(dppf)](OTs)_2$,[1] $[Pd(H_2O)_2(dppomf)](OTs)_2$,[1] $[Pd(\mu\text{-}OH)(dppf)]_2(OTs)_2$,[3n] [Pd(Me)(NCMe)(dppf)]OTf,[3l] and [Pd(COMe)(NCMe)(dppf)]OTs[3l] were synthesized according to published procedures. All the isolated solid samples were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen. Elemental analyses were performed using a Carlo Erba Model 1106 elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrophotometer. Conductivities were measured with an ORION model 990101 conductance cell connected to a model 101 conductivity meter. The conductivity data[32] were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions. Carbonylation reactions were performed with a 250 mL stainless steel autoclave, constructed at the ICCOM-CNR (Firenze, Italy), equipped with a magnetic drive stirrer and a Parr 4842 temperature and pressure controller. The autoclave was connected to a gas reservoir to maintain a constant pressure over all the catalytic reactions. Deuterated solvents for routine NMR measurements were dried over molecular sieves. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were obtained a Bruker ACP 200 spectrometer (200.13, 50.32, and 81.01 MHz, respectively). Chemical shifts are reported in ppm (δ) with reference to either TMS as an internal standard (^{1}H and ^{13}C{^{1}H} NMR spectra) or 85% H_3PO_4 as an external standard (^{31}P{^{1}H} NMR spectra). The 10 mm sapphire NMR tube was purchased from Saphikon, Milford, NH, while the titanium high-pressure charging head was constructed at the ICCOM-CNR (Firenze, Italy).[33] *Caution*: Since high gas pressures are involved, safety precautions must be taken at all stages of studies involving high-pressure NMR tubes. GC analyses were performed on a Shimadzu GC-14 A gas chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μm film thickness) SPB-1 Supelco fused silica capillary column. The product composition of the catalytic reactions was determined by using dimethyl oxalate as the internal standard. GC/MS analyses were performed on a Shimadzu QP 5000 apparatus equipped with a column identical with that used for GC analysis.

Catalytic Carbonylation of Ethene in Methanol. Typically, MeOH (100 mL) was introduced by suction into a 250 mL autoclave, previously evacuated by a vacuum pump, containing 0.01 mmol of catalyst precursor along with the desired amounts of BQ and/or TsOH. The autoclave was then pressurized with 1:1 CO/C_2H_4 (600 psi) at room temperature and heated to 85 °C. As soon as the reaction mixture in the autoclave reached the desired temperature, stirring (1400 rpm) was applied for the desired time (1−3 h). A constant pressure was maintained over all the experiments by a continuous feeding of the same mixture of CO/C_2H_4 from a gas reservoir. The reaction was stopped by cooling the autoclave to room temperature by means of an ice bath. After the unreacted gases were released, the insoluble CO/C_2H_4 material, if any, was filtered off, washed with cold MeOH, and dried overnight under reduced pressure at 70 °C. The filtrate was analyzed by GC using dimethyl oxalate as the internal standard.

Characterization of the Co-oligomers. The elemental analysis values were in agreement with a CO/C_2H_4 ratio of 1. Spectroscopically (IR and NMR), the oligomers showed chemical−physical properties comparable to those reported in the literature for perfectly alternating copolymers obtained by CO/C_2H_4 copolymerization in methanol by Pd^{II}-diphosphine catalysis.[2] In general, all samples showed the presence of both ketonic and ester end groups; however, a different ratio of these groups was observed depending on the reaction conditions. Anal. Calcd for $(COCH_2CH_2)_n$: C, 64.27; H, 7.19. Found: C, 64.21; H, 7.16. IR (powder sample in KBr pellet): 3391 (w), 2912 (m), 1694 (vs), 1408 (s), 1333 (s), 1259 (m), 1056 (s), 811 (m), 592 (m) cm^{-1}. ^{1}H NMR (HFIP-d_2): δ 3.73 (s, $CH_2CO_2CH_3$), 2.83 (s, CH_2COCH_2), 2.55 (q, J(HH) = 7.4 Hz, $COCH_2CH_3$), 1.09 (t, J(HH) = 7.4 Hz, $COCH_2CH_3$). ^{13}C{^{1}H} NMR (HFIP/$CDCl_3$, 9:1, v/v): δ 217.2 ($COCH_2CH_3$), 213.0 (CH_2COCH_2), 176.6 ($CH_2CO_2CH_3$), 52.6 ($CH_2CO_2CH_3$), 36.1 (CH_2COCH_2), 27.9 ($CH_2CO_2CH_3$), 7.1 ($COCH_2CH_3$).

In Situ HPNMR Study of the Methoxycarbonylation of Ethene Catalyzed by 1. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **1** (13.5 mg, 0.013 mmol) in MeOH-d_4 (2 mL) and then pressurized with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature. The reaction was followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. A sequence of selected ^{31}P{^{1}H} NMR spectra is reported in Figure 1. NMR data for **1**: ^{31}P{^{1}H} NMR (MeOH-d_4, 20 °C): δ 47.9 (s). ^{1}H NMR (MeOH-d_4, 20 °C): δ 8.0−7.0 (m, 28H, Ar-PPh_2 + Ar-OTs), 4.69 (s, 4H, H-Cp), 4.55 (s, 4H, H-Cp), 2.23 (s, 6H, Me-OTs).

Synthesis of 6. A. A solution of **1** (130 mg, 0.13 mmol) in CH_2Cl_2 (20 mL) was introduced into a 100 mL autoclave and pressurized with CO to 20 bar at room temperature. After 2 h, the unreacted gas was released and the contents were transferred into a round-bottomed flask and concentrated to half the volume under vacuum. The solution was filtered on Celite to eliminate precipitated palladium, and a 3:1 mixture of *n*-hexane/diethyl ether (10 mL) was added to precipitate **6**, which was collected on a sintered-glass frit, washed with *n*-hexane, and dried under a stream of nitrogen. Yield: 70%. Anal. Calcd for $C_{76}H_{64}Fe_2O_4P_4Pd_2S$: C, 59.98; H, 4.24. Found: C, 59.89; H, 4.22. ^{31}P{^{1}H} NMR (20 °C): δ (MeOH-d_4) 19.6 (br s); (CD_2Cl_2): 18.5 (br s). ^{31}P NMR (CD_2Cl_2, 20 °C): δ 18.5 (d, ^2J(PH) = 42.1 Hz). ^{1}H NMR (20 °C): δ (CD_2Cl_2) 8.0−6.9 (m, 44H, Ar-PPh_2 + Ar-OTs), 4.38 (s, 8H, H-Cp), 4.11 (s, 8H, H-Cp), 2.32 (s, 3H, Me-OTs), −6.08 (quintet, ^2J(HP) = 41.9 Hz, 1H, μ-H); (MeOH-d_4) 8.0−7.0 (m, 44H, Ar-PPh_2 + Ar-OTs), 4.69 (s, 8H, H-Cp), 4.54 (s, 8H, H-Cp), 2.23 (s, 3H, Me-OTs), −6.01 (quintet, ^2J(HP) = 42.0 Hz, 1H, μ-H). ^{13}C{^{1}H} NMR (CD_2Cl_2,

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20 °C): δ 229.7 (quintet, ^2J(CP) = 34.1 Hz, μ-CO). IR (CH_2Cl_2, cm^{-1}): 1841 (CO).

B. Methanol (10 equiv) was syringed into a 5 mm NMR tube containing a 3.3×10^{-2} M solution of [Pd(COMe)(NCMe)(dppf)]OTs in CD_2Cl_2 (0.7 mL) under 1 bar of CO at room temperature. ^{1}H and ^{31}P{^{1}H} NMR spectra showed the quantitative formation of the dimer **5** (^{31}P{^{1}H} NMR singlet at δ 18.5; ^{1}H quintet for the hydride at −6.08 (^2J(HP) = 41.9 H)) and methyl acetate.[12] The use of ^{13}CO resulted in an additional P−C coupling in the ^{31}P{^{1}H} NMR spectrum (d, ^2J(PC) = 34.1 Hz) and an additional H−C coupling for the hydride signal (quintet of d, ^2J(CH) = 4.5 Hz) in the ^{1}H NMR spectrum. When MeOH-d_4 was added to the solution of the starting acyl complex, the deuterated analogue [Pd_2(dppf)$_2$(μ-D)(μ-CO)]OTs formed; three signals were observed in the ^{31}P{^{1}H} NMR spectrum in an intensity ratio of 1:1:1 due to the phosphorus−deuterium coupling (^2J(PD) = 6.1 Hz).

Synthesis of 7. A stream of CO was bubbled through a solution of [PdMe(NCMe)(dppf)]OTf (162 mg, 0.19 mmol) in CH_2Cl_2 (2 mL) at −60 °C for 10 min, then ethene was substituted for CO. After bubbling ethene for 1 min, the resulting solution was allowed to warm to −20 °C. After 20 min, evaporation of the solvent at −20 °C gave an orange solid residue that was washed with cold diethyl ether and *n*-pentane. Yield: 80%. Anal. Calcd for $C_{39}H_{35}F_3FeO_4P_2PdS$: C, 53.17; H, 4.00. Found: C, 52.65; H, 4.19. ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 38.7 (d, ^2J(PP) = 35.7 Hz), 15.8 (d). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 7.8−7.3 (m, 20H, Ar-PPh_2), 4.65 (m, 2H, Cp), 4.56 (m, 2H, Cp), 4.36 (m, 2H, Cp), 3.79 (m, 2H, Cp), 3.19 (dt, ^3J(HH) = 6.2 Hz, ^4J(HP) = 7.8 Hz, 2H, PdCH_2CH_2), 2.31 (s, 3H, C(O)CH_3), 1.39 (dtd, ^3J(HH) = 6.2 Hz, ^3J(HP) = 7.4, 3.2 Hz, 2H, PdC$H_2$$CH_2$). ^{13}C{^{1}H} NMR ($CD_2Cl_2$, −20 °C): δ 238.9 (d, ^4J(CP) = 12.6 Hz, *C*(O)CH_3), 136−130 (m, Ph), 76−69 (m, Cp), 52.5 (d, ^3J(CP) = 6.0 Hz, Pd$CH_2$$CH_2$), 39.0 (d, ^2J(CP) = 85.2 Hz, Pd$CH_2$$CH_2$), 28.9 (s, C(O)*C*$H_3$). IR (KBr pellet, cm^{-1}): 1630 (CO).

Single crystals of **7**·0.5CH_2Cl_2 suitable for an X-ray analysis were obtained by crystallization from CH_2Cl_2/Et_2O in a Schlenk tube stored at −20 °C. Anal. Calcd for $C_{39}H_{35}F_3FeO_4P_2PdS$·0.5$CH_2Cl_2$: C, 51.37; H, 3.93. Found: C, 51.02; H, 3.89.

Synthesis of 8. A solution of **7** (52.8 mg, 0.06 mmol) in CD_2Cl_2 (2 mL) was maintained under a stream of CO at −40 °C for 15 min and then transferred into a 5 mm NMR tube at −40 °C. The tube was inserted into a NMR probe-head precooled at −40 °C. ^{1}H and ^{31}P{^{1}H} NMR spectra showed the quantitative formation of the carbonyl acyl complex **8**. ^{31}P{^{1}H} NMR (CD_2Cl_2, −40 °C): δ 23.0 (d, ^2J(PP) = 62.1 Hz), 11.3 (d). ^{1}H NMR (CD_2Cl_2, −40 °C): δ 7.8−7.3 (m, 20H, Ar-PPh_2), 4.77 (m, 2H, Cp), 4.66 (m, 2H, Cp), 4.34 (m, 2H, Cp), 3.70 (m, 2H, Cp), 2.56 (br s, 2H, PdC(O)CH_2CH_2), 2.12 (br s, 2H, PdC(O)-C$H_2$$CH_2$), 1.97 (s, 3H, C(O)$CH_3$). ^{13}C{^{1}H} NMR ($CD_2Cl_2$, −40 °C): δ 229.3 (d, ^2J(CP) = 86.7 Hz, Pd*C*(O)CH_2), 208.1 (s, CH_2*C*(O)CH_3), 177.0 (br s, Pd(CO)), 136−130 (m, Ph), 78−69 (m, Cp), 49.9 (m, PdC(O)*C*H_2), 39.6 (s, *C*H_2C(O)CH_3), 30.2 (s, C(O)*C*H_3).

On using ^{13}CO, the resonance at δ 11.3 in the ^{31}P{^{1}H} NMR spectrum became a doublet of doublets with ^2J(PC) = 87.0 Hz.

Synthesis of 9. Ethene was bubbled for 10 min through a solution of **7** (54.5 mg, 0.06 mmol) obtained as above in CD_2Cl_2 (2 mL) at −60 °C. A sample of the resulting solution (1 mL) was transferred into a 5 mm NMR tube at −20 °C, and the tube was inserted into a NMR probe-head precooled at −20 °C. Another sample of the solution was transferred into a KBr cell for IR measurements. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and IR spectra showed the quantitative formation of **9**. ^{31}P{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 39.1 (d, ^2J(PP) = 35.9 Hz), 15.1 (d). ^{1}H NMR (CD_2Cl_2, −20 °C): δ 7.8−7.3 (m, 20H, Ar-PPh_2), 4.65 (m, 2H, Cp), 4.56 (m, 2H, Cp), 4.34 (m, 2H, Cp), 3.79 (m, 2H, Cp), 3.18 (dt, ^3J(HH) = 6.6 Hz, ^4J(HP) = 7.7 Hz, 2H, PdCH_2CH_2), 2.87 (t, ^3J(HH) = 5.6 Hz, 2H, C(O)CH_2CH_2), 2.31 (t, ^3J(HH) = 5.6 Hz, 2H, C(O)C$H_2$$CH_2$), 1.64 (s, 3H, C(O)$CH_3$), 1.56 (tdd, ^3J(HH) = 6.3 Hz, ^3J(HP) = 7.4, 2.7 Hz, 2H, PdCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, −20 °C): δ 239.4 (dd, ^3J(CP) = 12.8, 1.3 Hz, CH_2*C*(O)CH_2), 207.2 (s, CH_2*C*(O)CH_3), 135−123 (m, Ph), 78−71 (m, Cp), 51.6 (d, ^3J(CP) = 6.0 Hz, PdCH_2*C*H_2), 39.2 (d, ^2J(CP) = 86.0 Hz, Pd*C*$H_2$$CH_2$), 37.5 (s, *C*$H_2$$CH_2$C(O)$CH_3$), 34.7 (s, *C*$H_2$C(O)$CH_3$), 30.0 (s, C(O)*C*$H_3$). IR ($CD_2Cl_2$, cm^{-1}): ν(CO) 1629, 1710.

Stability Study of 2 in Methanol by NMR Spectroscopy. Synthesis and Characterization of 10. The starting solutions employed in this study were obtained by dissolving samples of **2** (8 mg, 0.007 mmol) in MeOH-d_4 (1 mL) at room temperature. A 5 mm NMR tube was charged under nitrogen with one of these solutions and then placed into the NMR probe at room temperature. The reaction was followed by ^{31}P-{^{1}H} and ^{1}H NMR spectroscopy. The results of this investigation are discussed in a previous section. NMR data for **2**: ^{31}P{^{1}H} NMR (MeOH-d_4, 20 °C): δ 71.6 (s). ^{1}H NMR (MeOH-d_4, 20 °C): δ 6.9−8.3 (m, 28H, Ar-PPh_2 + Ar-OTs), 2.23 (s, 6H, Me-OTs), 1.49 (s, 12H, Me-Cp*), 1.32 (s, 12H, Me-Cp*).

NMR data for **10**: ^{31}P{^{1}H} NMR (MeOH-d_4, 20 °C): δ −1.3 (s). ^{1}H NMR (MeOH-d_4, 20 °C): 8.3−6.9 (m, 48H, Ar-PPh_2 + Ar-OTs), 2.23 (s, 6H, Me-OTs), 1.86 (br s, 24H, Me-Cp*), 0.51 (br s, 24H, Me-Cp*). ^{31}P{^{1}H} NMR (MeOH-d_4, −40 °C): δ −1.4 (s). ^{1}H NMR (−40 °C, MeOH-d_4): 8.3−6.9 (m, 48H, Ar-PPh_2 + Ar-OTs), 2.22 (s, 6H, Me-OTs), 1.87 (s, 24H, Me-Cp*), 0.50 (s, 24H, Me-Cp*).

In Situ HPNMR Study of the Methoxycarbonylation of Ethene Catalyzed by 2. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **2** (15 mg, 0.013 mmol) in MeOH-d_4 (2 mL) and then pressurized with a 1:1 mixture of CO/C_2H_4 to 40 bar at room temperature. TsOH (10 mg, 0.052 mmol, 4 equiv) and/or BQ (23 mg, 0.208 mmol, 16 equiv), if any, were also added. The reactions were followed by variable-temperature ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. Selected ^{31}P{^{1}H} NMR spectra are reported in Figures 3 and 4.

Synthesis of 4. A. A solution of **2** (150 mg, 0.13 mmol) in CH_2Cl_2 (20 mL) was introduced into a 100 mL autoclave and pressurized with CO to 20 bar at room temperature. After 2 h, the unreacted gas was released and the contents were transferred into a round-bottomed flask and concentrated to half of the volume under vacuum. The solution was filtered over Celite to eliminate black palladium, and a 3:1 mixture of *n*-hexane/diethyl ether (10 mL) was added to precipitate the product, which was collected on a sintered-glass frit, washed with *n*-hexane, and dried under a stream of nitrogen. Yield: 75%.

B. A solution of **2** (150 mg, 0.13 mmol) and TsOH (100 mg, 0.52 mmol) in MeOH (20 mL) was introduced into a 100 mL autoclave and pressurized with 1:1 CO/C_2H_4 to 40 bar at room temperature. After 30 min, the unreacted gases were released and the contents was concentrated to dryness under vacuum. The solid residue was dissolved in THF and filtered over Celite to give an organic phase that was concentrated again to dryness. The solid residue was washed with *n*-pentane, filtered off, and dried under a stream of nitrogen. Yield: 60%. Anal. Calcd for $C_{92}H_{96}Fe_2O_4P_4Pd_2S$: C, 63.28; H, 5.54. Found: C, 63.14; H, 5.51. ^{31}P{^{1}H} NMR δ: (CD_2Cl_2, 20 °C) 23.7 (s); (THF-d_8, 20 °C) 22.2 (s); (THF-d_8, −70 °C) 27.3 (d, ^2J(PP) = 36.1 Hz), 19.4 (d, ^2J(PP) = 36.1 Hz). ^{31}P NMR δ: (THF-d_8, 20 °C) 22.2 (d, ^2J(PH) = 40.1 Hz); (THF-d_8, −70 °C) 27.3 (dd, ^2J(PP) = 36.1 Hz, ^2J(PH) = 82.1 Hz), 19.4 (d, ^2J(PP) = 36.1 Hz). ^{1}H NMR δ: (CD_2Cl_2, 20 °C) 8.1−6.8 (m, 44H, Ar-PPh_2 + Ar-OTs), 2.36 (s, 3H, Me-OTs), 1.62 (s, 24H, Me-Cp*), 1.25 (s, 24H, Me-Cp*), −6.18 (quintet, ^2J(HP) = 42.4 Hz, 1H, μ-H); (THF-d_8, 20 °C) −6.02 (quintet, ^2J(HP) = 42.6 Hz, 1H, μ-H); (THF-d_8, −70 °C) −5.72 (tt, ^2J(HP) = 80.8, 5.2 Hz, 1H, μ-H). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ (20 °C) 226.4 (quintet, ^2J(CP) = 34.1 Hz, μ-CO). IR (Nujol mull, KBr plates/CH_2Cl_2, cm^{-1}): ν(CO) 1848/1846.

NMR experiments in MeOH-d_4 showed **4** to decompose into **2** and several unknown species when treated with TsOH or BQ.

Synthesis of 11. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **2** (15 mg, 0.013 mmol) in MeOH-d_4 (2 mL) and pressurized to 40 bar with 1:1 CO/C_2H_4 at room temperature. The tube was introduced into a spectrometer and heated to 40 °C. The first spectrum acquired at this temperature showed the presence of the **11**. The tube was removed from the probe-head, frozen in liquid nitrogen, and subjected to high vacuum. To the frozen solution was added 1 equiv of TsOH. This mixture was allowed to thaw and reach room temperature. The formation of the μ-hydride, μ-CO complex **4** was determined by NMR spectroscopy. $^{31}P\{^1H\}$ NMR (MeOH-d_4, 20 °C): δ 5.6 (s). ^1H NMR (MeOH-d_4, 40 °C): δ 7.9−7.0 (m, 40H, Ar-PPh_2), 1.62 (s, 24H, Me-Cp*), 1.11 (s, 24H, Me-Cp*).

Synthesis of 12. A 10 mm sapphire HPNMR tube was charged under nitrogen with a solution of **2** (15 mg, 0.013 mmol) in MeOH-d_4 (2 mL) and pressurized to 10 bar with CO at room temperature. ^1H and $^{31}P\{^1H\}$ NMR spectra showed the quantitative formation of **12**. On standing at room temperature, this complex slowly undergoes methanolysis ($t_{1/2}$ = 12 h), decomposing to **4** and dimethyl carbonate-d_6 (GC/MS analysis). Attempts to isolate **12** failed due to its decomposition to **2** when the CO pressure was released and nitrogen was added. $^{31}P\{^1H\}$ NMR (MeOH-d_4, 20 °C): δ −19.1 (s). ^1H NMR (MeOH-d_4, 20 °C): δ 8.1−6.9 (m, 24H, Ar-PPh_2 + Ar-OTs), 2.28 (s, 3H, Me-OTs), 1.71 (s, 12H, Me-Cp*), 0.84 (s, 12H, Me-Cp*). $^{13}C\{^1H\}$ NMR (MeOH-d_4, 20 °C): δ 209.9 (br s, *C*(O)-OCD_3).

Synthesis of 13. To a solution of dppomf (292 mg, 0.438 mmol) in THF (30 mL) was added a solution of PdCl(Me)(COD) (116 mg, 0.439 mmol) under stirring. After 15 min, the solution was concentrated to half volume and *n*-hexane (15 mL) was added. The formed yellow solid was filtered off, washed with *n*-hexane, and dried in a stream of nitrogen. Yield: 86%. Anal. Calcd for $C_{43}H_{47}ClFeP_2Pd$: C, 62.72; H, 5.75. Found: C, 62.70; H, 5.69. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ 45.2 (d, ^2J(PP) = 24.5 Hz), 12.8 (d). ^1H NMR (CD_2Cl_2, 20 °C): δ 8.3−7.2 (m, 20H, Ar-PPh_2), 1.56 (s, 6H, Cp*), 1.52 (s, 6H, Cp*), 1.28 (s, 6H, Cp*), 1.10 (s, 6H, Cp*), 0.96 (dd, ^3J(HP) = 7.0, 3.8 Hz, 3H, Me).

Synthesis of 14. To a solution of **13** (150 mg, 0.182 mmol) in CH_2Cl_2 (10 mL) was added AgOTs (51 mg, 0.182 mmol). After the resulting mixture was stirred overnight, it was filtered over Celite and the filtrate was concentrated to 5 mL. Addition of Et_2O caused the precipitation of a yellow microcrystalline solid, which was filtered off, washed with Et_2O, and dried in a vacuum. Yield: 87%. Anal. Calcd for $C_{50}H_{56}FeO_4P_2PdS$: C, 61.45; H, 5.78. Found: C, 61.38; H, 5.79. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): (20 °C) δ 48.8 (br), 12.6 (d, ^2J(PP) = 20.5 Hz); (−80 °C) δ 50.8 (d, ^2J(PP) = 24.6 Hz), 12.7 (d). ^1H NMR (CD_2Cl_2, 20 °C): δ 8.2−6.7 (m, 24H, Ar-PPh_2 + Ar-OTs), 1.55 (s, 12H, Cp*), 1.28 (s, 6H, Cp*), 1.12 (s, 6H, Cp*), 0.88 (br t, ^3J(HP) = 6.4 Hz, 3H, Me). This complex behaves as a 1:1 electrolyte in both CH_2Cl_2 (Λ_M: 8 Ω^{-1} cm^2 mol^{-1}) and nitroethane (Λ_M: 38 Ω^{-1} cm^2 mol^{-1}).[32]

Reaction of 14 with CO: Synthesis of 15. Carbon monoxide was bubbled for 5 min through a solution of **14** (15 mg, 0.015 mmol) in CD_2Cl_2 (1.5 mL) at 0 °C. A 1 mL sample of the resultant solution was transferred by syringe into a 5 mm NMR tube at room temperature. ^1H and $^{31}P\{^1H\}$ NMR spectra showed the quantitative formation of **15**. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20 °C): δ −13.3 (s). ^1H NMR (CD_2Cl_2, 20 °C): δ 7.8−7.0 (m, 24H, Ar-PPh_2 + Ar-OTs), 3.09 (t, ^4J(HP) = 1.7 Hz, 3H, Me), 2.31 (s, 3H, Me-OTs), 1.74 (s, 12H, Me-Cp*), 1.21 (s, 12H, Me-Cp*).

Reaction of 15 with MeOH. A solution of **15** in CD_2Cl_2 was prepared as above and transferred into a 5 mm NMR tube equipped with a rubber cap. A 100 μL sample of MeOH was injected by syringe into the tube at room temperature. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy showed the formation of **4** and methyl acetate already in the first spectra.

Reaction of 15 with CO/C_2H_4. A 1:1 CO/C_2H_4 mixture was bubbled for 15 min at room temperature into a CD_2Cl_2 solution of **15** in a 5 mm NMR tube equipped with a rubber cap. Then, the tube was closed and allowed to stand for 15 min at room temperature. A 100 μL sample of MeOH was injected by syringe into the tube. ^1H and $^{31}P\{^1H\}$ NMR spectra showed the formation of **4** and methyl acetate. GC/MS confirmed the exclusive formation of methyl acetate.

X-ray Data Collection and Structure Determination of $[C_{38}H_{35}FeOP_2Pd^+][SO_3CF_3^-]\cdot 0.5(CH_2Cl_2)$. X-ray data were collected at 150 K on an Enraf-Nonius TurboCAD4 (Rotating Anode, Mo Kα, θ max = 26.5°). Reflection profiles turned out to be broad and highly structured. Pertinent data: monoclinic, space group $P2_1/c$ (No. 14), a = 11.057(2) Å, b = 23.767(4) Å, c = 16.203(3) Å, β = 116.78(1)°, Z = 4. The structure was solved by direct methods (SIR97)[34] and refined on F^2 with SHELXL96[35] to a final R = 0.0813 for 3287 reflections with $I > 2\sigma(I)$ [wR2 = 0.167 for 7763 reflections]. The main cation structure contains two solvent-accessible voids at 0,1/2,0 and 0,0,1/2 of 419 Å^3, each containing disordered OTf^- and CH_2Cl_2. Their contribution to the structure factors was taken into account by back-Fourier transformation using the PLATON/SQUEEZE[36] procedure. A total of 189 electrons/per void were accounted for (corresponding with two OTf^- and one CH_2Cl_2 per void). Data were corrected for absorption with the PLATON/DELABS[36] procedure. Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms.

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Supporting Information Available: Tables of crystal data and collection parameters, bond lengths and angles, and positional and thermal parameters for compound **7**·0.5CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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