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Alcoholysis of Acylpalladium(II) Complexes Relevant to the Alternating Copolymerization of Ethene and Carbon Monoxide and the Alkoxycarbonylation of Alkenes: the Importance of Cis-Coordinating Phosphines

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Abstract: The mechanism and kinetics of the solvolysis of complexes of the type $[(L-L)Pd(C(O)CH_3)(S)]^+[CF_3SO_3]^-$ (L−L = diphosphine ligand, S = solvent, CO, or donor atom in the ligand backbone) was studied by NMR and UV−vis spectroscopy with the use of the ligands **a**−**j**: SPANphos (**a**), dtbpf (**b**), Xantphos **(c**), dippf (**d**), DPEphos (**e**), dtbpx (**f**), dppf (**g**), dppp (**h**), calix-6-diphosphite (**j**). Acetyl palladium complexes containing trans-coordinating ligands that resist cis coordination (SPANphos, dtbpf) showed no methanolysis. Trans complexes that can undergo isomerization to the cis analogue (Xantphos, dippf, DPEphos) showed methanolyis of the acyl group at a moderate rate. The reaction of [*trans*-(DPEphos)-$Pd(C(O)CH_3)]^+[CF_3SO_3]^-$ (**2e**) with methanol shows a large negative entropy of activation. Cis complexes underwent competing decarbonylation and methanolysis with the exception of **2j**, [*cis*-(calix-diphosphite)-$Pd(C(O)CH_3)(CD_3OD)]^+[CF_3SO_3]^-$. The calix-6-diphosphite complex showed a large positive entropy of activation. It is concluded that ester elimination from acylpalladium complexes with alcohols requires cis geometry of the acyl group and coordinating alcohol. The reductive elimination of methyl acetate is described as a migratory elimination or a 1,2-shift of the alkoxy group from palladium to the acyl carbon atom. Cis complexes with bulky ligands such as dtbpx undergo an extremely fast methanolysis. An increasing steric bulk of the ligand favors the formation of methyl propanoate relative to the insertion of ethene leading to formation of oligomers or polymers in the catalytic reaction of ethene, carbon monoxide, and methanol.

Introduction

Since the introduction of well-defined and fast palladium catalysts for copolymerization of ethene and carbon monoxide, characteristically containing weakly coordinating anions and bidentate ligands,[1−3] chain initiation and termination reactions, as compared to insertion reactions, have received relatively little attention, although their importance is well recognized. Alcohols are suitable solvents for the copolymerization, and not only do they initiate the reaction, but they also function as chain transfer agents. As a result, the chain ends contain a hydrogen atom (as an ethyl group) and a methoxy group (as a methyl ester group). In alcohols, several routes are available to form the two initiating palladium species, hydrides, and carbomethoxy species, and the conditions applied determine which species will be formed and how.[2] Chain initiation does not have to be left at chance either, as methylpalladium complexes were found to be effective initiators for the polymerization reaction.[1,4] The common chain termination reactions comprise β-hydrogen elimination, nucleophilic attack at an acylpalladium complex, and protonation of an alkylpalladium complex (see Scheme 1).

In the simplest case, each route leads to polymer chains or oligomers containing one ester (E) and one ketone (K) end group, KE polymers. When reactions 2 and 3 occur at comparable rates, which accidentally seems to be the case in several catalyst systems, there is formation of EE and KK polymers in addition to KE polymers. This is so because the growing polymer chain does not "remember" whether it started from a hydride or a methoxy group, and thus, a statistical distribution of chain ends within one molecule will be obtained (EE:KE:KK = 1:2:1).[3] Deviations from an average K:E = 1:1 have been observed, because the intermediate palladium species Pd^{2+} or PdH^+ can be reduced or oxidized, respectively, to one

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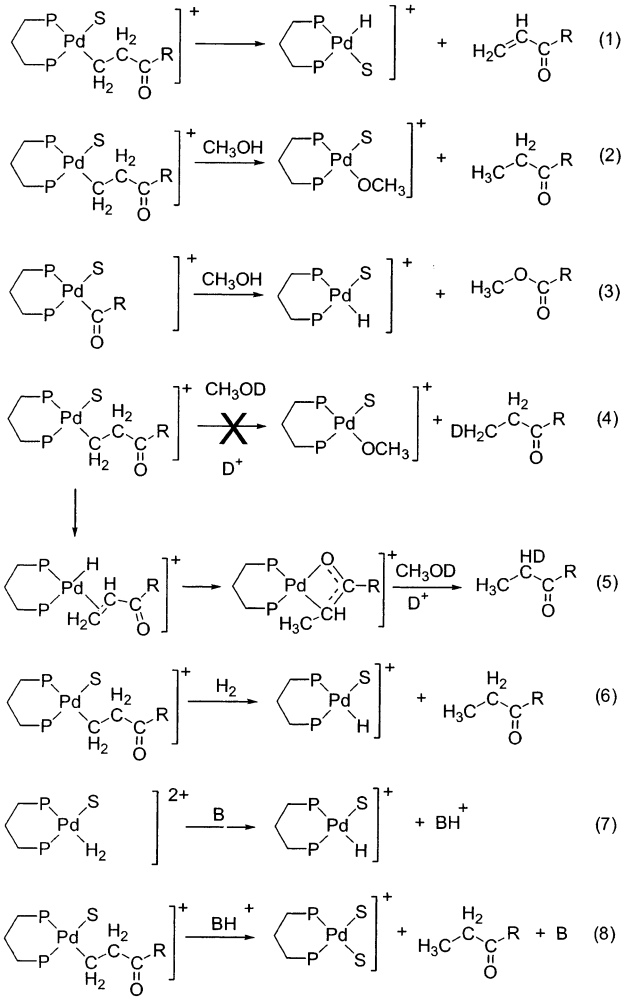
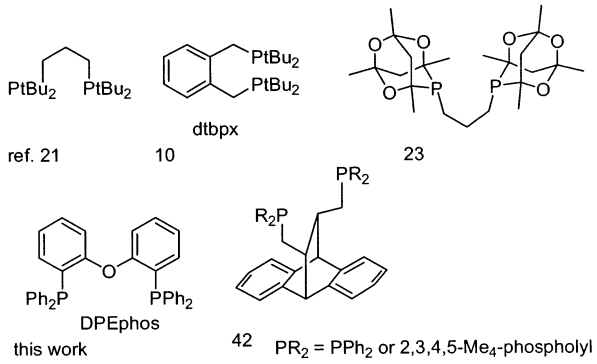
Scheme 1



another leading to an excess of K or E chain ends or even one type of chain end only.[2] Chain termination ratios also depend on the phase in which the chain end resides, liquid phase or solid phase, as higher oligomers precipitate.[3c] Formally, eq 2 involves a protonation of the alkyl chain, which is not a very fast reaction at the cationic palladium center, as is also apparent from the stability of methylpalladium cations.[5] At room temperature, the half-life time of $[(dppp)Pd(CH_2C(CH_3)_3)(CH_3CN)]^+[CF_3SO_3]^-$ in CD_3OD with a 10-fold excess of CF_3COOH is 1 h;[6a] and methyl platinum complexes containing electron-withdrawing diphosphines survive strong acids for several days.[6b,c] For a number of model compounds, it has been shown[4b,7] that reaction of compounds containing a γ-keto group such as shown in reactions 4 and 5 with CH_3OD or D_2O form a ketone having the deuterium atom in the β-position (relative to palladium) instead of the expected α-position (relative to palladium), which has been explained by an enolate mechanism (Scheme 1, eqs 4−5).

Scheme 2 [a]



[a] Numbers denote references.

As in alkene polymerizations, dihydrogen can also be used as a chain transfer agent in polyketone formation. The reaction is depicted as a hydrogenolysis (reaction 6 in Scheme 1), but it can also be described as a sequence involving heterolytic cleavage of dihydrogen (eqs 7, 8). As a result, only KK polymers (or oligomers) will be obtained.

Water and carbon monoxide can play the same role as hydrogen, as has been shown in the synthesis of diethyl ketone (pentan-3-one).[4b] Ether chain ends have been observed in polymerization reactions,[8] and low molecular weight products can also contain an ether moiety at one end and an ester group at the other end. Most likely, ether chain ends are formed by a palladium-catalyzed attack of alcohols at enones resulting from β-hydride elimination; the catalyzed Michael reaction has been observed in separate experiments.[9]

When chain transfer is very fast, the reaction observed is the alkoxycarbonylation of ethene, which is nothing but a perfect chain transfer after the insertion of just two monomers. In recent years, several very fast catalysts for this reaction have been reported (Scheme 2, showing some of the ligands).[10−24,41] Catalyst systems and conditions for the two reactions are very

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similar. The initial observations led to a rule of thumb that fast polymerization catalysts required bidentate ligands with a 1,3-propanediyl bridge and that carbomethoxylation was favored using monodentate ligands.[2] Results of recent years have shown that substituents on phosphorus that are more bulky than phenyl groups lead to a high molecular weight polymer even when the bridge comprises one carbon atom or one nitrogen atom only.[25,26] However, the most active catalyst for methyl propanoate formation known to date contains bidentate cis ligands,[10,21,23] although one of these bulky ligands easily leads to the formation of trans-coordinated, oligomeric diphosphine complexes.[10c] Formation of dimeric trans complexes had been observed before for diphosphines containing a four-membered carbon bridge.[27] Since monophosphines also form trans complexes[2,10b−c,28,29] the latter were held responsible for the alkoxycarbonylation reaction. For the bidentate ligand systems mentioned, the possibility remains that one phosphine moiety dissociates from the palladium center.

The mechanism of the alkoxycarbonylation reaction catalyzed by palladium has been the topic of research for many years, and it seemed fairly well understood at the end of the eighties.[30] Stepwise reactions had shown the feasibility of mechanistic pathways, but kinetic studies and in situ observations on catalytic systems were lacking. Besides, since the development of the fast catalysts for polyketone formation, it became evident that a lot of improvement could be made in alkoxycarbonylation. The first publications on fast catalysts for methoxycarbonylation originate from Drent.[21] The resting state of the new catalysts may well be an acyl complex,[28−31] while the attack of alcohol at the acylpalladium complex is considered to be the rate-determining step. It is probably more precise to say that fast preequilibria exist between the acyl complex and other complexes en route to it and that the highest barrier is formed by the reaction of alcohol and acylpalladium complex. There is general agreement that the catalytic cycle starts with palladium hydride species, except for methyl methacrylate catalysis.[32]

Sen et al have shown that changing the reaction medium of the copolymerization reaction from methanol to higher alcohols (ethanol, *tert*-butyl alcohol) increased the molecular weight of the copolymer produced.[1b] Milani has shown that the molecular weight in styrene−CO copolymerization increases when 2,2,2-trifluoroethanol is used instead of methanol.[33] Thus, the alcohol has a distinct effect on the rate of the termination reaction, at least relative to the rate of propagation.

Tóth and Elsevier showed that the reaction of an acetylpalladium complex and sodium methoxide/methanol is very fast and occurs already at low temperature[34] to give methyl acetate and a palladium(I) hydride dimer.[30a,35,36] The reactivity of cationic acylpalladium complexes toward alcohols under neutral and acidic conditions has not been studied in great detail so far.

In the present study, we have looked at the stoichiometric reaction of several acetylpalladium species containing a variety of cis and trans diphosphines with alcohols. We have studied a series of ligands ranging from ones that exclusively form trans complexes, via those that form both trans and cis complexes, to those that form cis complexes only, having different electronic properties. From previous literature, the impression[2,28,29] had grown that trans bis-phosphine complexes are responsible for methoxycarbonylation, while cis coordination of bidentate ligands leads to polymer formation via multiple insertions. The pivotal questions to be answered are what are the steric and electronic ligand requirements for the control of alkene/CO insertion versus termination of the cycle by alcoholysis of the palladium acyl species.

Results

Ligands Used in this Study. Scheme 3 depicts the ligands **a**−**j** that have been used in this study arranged in the order of their propensity to form trans complexes. It represents only a small selection of the many ligands that have been used for the catalytic studies in the literature, but they are representative, as we will show. Their methylpalladium triflate complexes are numbered **1**, and their acetylpalladium complexes are designated **2**.

Synthesis, Structure, and Reactivity of *trans*-Coordinated Acetylpalladium Complexes. Acetylpalladium complexes were synthesized by bubbling carbon monoxide through a dichloromethane solution of the corresponding methylpalladium precursor at room temperature. Ligands that coordinate in a purely trans fashion are rare, and the "trans" coordinating ligands reported often also form cis complexes as a result of their flexibility.[37] We have recently reported on a new trans-spanning ligand, SPANphos (**a**),[38] characterized by a large phosphorus-to-phosphorus distance and forming trans complexes with platinum and palladium. When [*trans*-(SPANphos)PdCH_3(CH_3CN)]$^+$[CF_3SO_3]$^-$ (**1a**-CH_3CN) was dissolved in CD_2Cl_2 and CO was bubbled through for 15 min at room temperature, the acetyl complex, **2a**, was formed.

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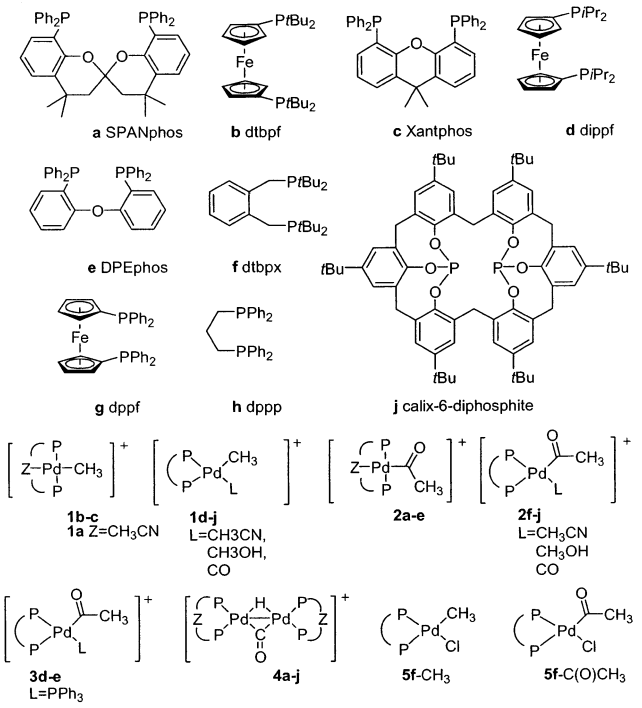
Scheme 3



Complex [*trans*-η^3-(dtbpf)PdC(O)CH_3]$^+$[CF_3SO_3]$^-$ (**2b**) was synthesized from [*trans*-η^3-(dtbpf)PdCH_3]$^+$[CF_3SO_3]$^+$ (**1b**).[39] The insertion of CO was slow ($t_{1/2} \approx 15$ min) at room temperature compared to the time for CO insertion into the ionic methylpalladium complexes containing Xantphos **c** and DPEphos **e** ($t_{1/2} < 1$ min). The dtbpf ligand remained an η^3 terdentate P,Fe,P ligand in complex **2b** as shown by the large chemical shift difference of the α and β-hydrogen atoms of the Cp-rings ($\Delta\delta = 0.82$ ppm).[40]

[*trans*-η^3-(Xantphos)PdC(O)CH_3]$^+$[CF_3SO_3]$^-$ (**2c**) was synthesized from [*trans*-η^3-(Xantphos)PdCH_3]$^+$[CF_3SO_3]$^-$ (**1c**), and its structure is trans, η^3-P,O,P according to NMR spectroscopy.

Complex [*trans*-η^3-(dippf)PdC(O)CH_3]$^+$[CF_3SO_3]$^-$ (**2d**) was synthesized from [*cis*-(dippf)PdCH_3(CH_3CN)]$^+$[CF_3SO_3]$^-$ (**1d**-CH_3CN). The CO insertion for **2d** is faster than that for **2b**, the dtbpf complex ($t_{1/2} \approx 5$ min). In the methylpalladium complex **1d**-CH_3CN, dippf acts as a cis bidentate ligand, but, in the acetylpalladium complex, it coordinates as an η^3-terdentate P,Fe,P ligand as indicated by the ^{31}P and ^{13}C NMR spectra (Table 1) and by the large chemical shift difference of the α- and β-hydrogen atoms of the Cp-rings ($\Delta\delta = 0.72$ ppm). The addition of an excess of triphenylphosphine to a solution of **2d** in CD_2Cl_2 led to the formation of **3d** (Scheme 3). This demonstrates that the dippf ligand can coordinate in both a trans fashion and a cis fashion and that the Pd−Fe dative bond can be broken by the addition of a strongly coordinating ligand.

When [*cis*-(DPEphos)PdCH_3(CH_3CN)]$^+$[CF_3SO_3]$^-$ (**1e**-CH_3CN) was dissolved in CD_2Cl_2 and CO was bubbled through, the acetyl complex, *trans*-**2e**, was formed (Scheme 4). The addition of silver triflate to a solution of *cis*-(DPEphos)Pd(C(O)CH_3)Cl in CD_2Cl_2 also yielded *trans*-**2e**. The complex was isolated by the addition of diethyl ether to a solution of **2e** in CH_2Cl_2. Conductivity measurements in CH_2Cl_2 showed that **2e** was ionic ($\Lambda_m = 56$ S mol^{-1} L^{-1}). The use of ^{13}CO did not result in additional P−C couplings in the ^{31}P{^{1}H} NMR spectrum. These data suggest that the phosphorus atoms are coordinated in a trans fashion and both cis to the acetyl group. At room temperature, the compound was unstable toward decarbonylation, even in the solid state. The acetylpalladium complex (**2e′**) was synthesized using complex **1e′** containing the BARF anion ([B(*p*-$C_6H_3(CF_3)_2)_4$]$^-$, which proved to be thermally more stable (i.e., less prone to deinsertion of CO).

Table 1. Selected NMR Data of Complexes **1a**−**e**, **2a**−**e**, **2g**, **3d**, and **3e**[a]

complex	^{1}H NMR	^{31}P NMR
	Pd−C*H*$_3$	
1a-CH_3CN	0.14 t $^3J_{PH} = 6.3$	22.0 s
1b	1.70 t $^3J_{PH} = 4.8$	29.3 s
1c	1.50 t $^3J_{PH} = 5.7$	20.4 s
1d-CH_3CN	0.73 br.d $^3J_{PH} = 4.8$	54.1 d $^2J_{PP} = 21.3$ 32.7 d $^2J_{PP} = 21.3$
1e-CH_3CN	0.88 dd $^3J_{PH} = 6.6, 2.9$	31.8 d $^2J_{PP} = 31.7$ 7.7 d $^2J_{PP} = 31.7$
	Pd−C(O)C*H*$_3$	
2a	1.75 s	9.0 s
2b	2.91 t $^4J_{PH} = 1.5$	30.2 s
2c	2.20 t $^4J_{PH} = 1.5$	10.2 s
2d	2.83 s	18.7 s
2e[b]	2.38 t $^4J_{PH} = 1.5$	7.0 s
2g-CO[c]	1.87 s	24.1 d $^2J_{PP} = 62$ 12.1 d $^2J_{PP} = 62$
3d[d]	2.35 s	31.6 dd $^2J_{PP} = 43.8, 228$ 10.8 dd $^2J_{PP} = 43.8, 228$ 17.2 t $^2J_{PP} = 43.8$
3e[e]	1.79 s	26.5 dd $^2J_{PP} = 46.0, 241$ 10.6 dd $^2J_{PP} = 46.0, 241$ −0.9 t $^2J_{PP} = 46.0$

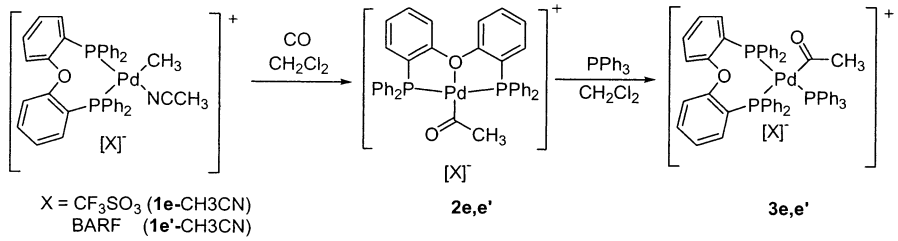
[a] CD_2Cl_2, 25 °C, δ (ppm), J (Hz). [b] $T = -90$ °C. [c] ^{13}C{^{1}H} NMR: *C*(O)CH_3, d, 229.5 ppm, $^2J_{PC} = 82$ Hz; Pd(*C*O), dd 175.7 ppm, $^2J_{PC} = 82$ Hz and $^2J_{PC} = 19$ Hz. [d] $T = -30$ °C. ^{13}CO ^{31}P{^{1}H} NMR: 10.8 ppm, d$^2J_{PC} = 81.3$ Hz. ^{13}C{^{1}H} NMR: 230.0 ppm, d $^2J_{PC} = 81.3$ ppm. [e] $T = -90$ °C. ^{13}CO ^{31}P{^{1}H} NMR: −0.9 ppm, d $^2J_{PC} = 82.3$ Hz. ^{13}C{^{1}H} NMR: 228.7 ppm, d $^2J_{PC} = 82.3$ ppm.

The DPEphos ligand was found to coordinate in an η^3 (planar P,O,P) fashion in complex **2e** even in the presence of additional ligands such as CO and acetonitrile. The capacity of the DPEphos ligand to coordinate in an η^2 P,P fashion to palladium was demonstrated by the addition of triphenylphosphine to a solution of **2e** in CD_2Cl_2 (Scheme 4). The NMR data (Table 1) are in accordance with the structure [*cis*-(DPEphos)Pd(C(O)-CH_3)(PPh_3)]$^+$[CF_3SO_3]$^-$ (**3e**, Scheme 4).The reaction of **2e** and methanol in a CH_2Cl_2 solution under 1 bar of CO resulted in the formation of a palladium(I) hydride dimer, [Pd$_2$(μ-H)-(μ-CO){(DPEphos)}$_2$]$^+$[CF_3SO_3]$^-$ (**4e**), and methyl acetate (Scheme 5). The IR spectrum in CH_2Cl_2 showed a CO stretching frequency at 1847 cm^{-1}.

X-ray Crystal Structure Analysis of 2e′. The anion in **2e′** was highly disordered due to the rotation of the trifluoromethyl groups, but the structure of the cation could be determined accurately. The metal center has a square planar geometry with all donor atoms and the metal center in one plane. The phosphorus atoms are coordinated in a trans fashion with a P1−Pd−P2 angle of 154.70(8)° (Table 3). The oxygen atom of the ligand backbone is coordinated to palladium (2.261(6) Å, Figure 1), and there are no close contacts between the anion and the palladium atom.

(39) Zuideveld, M. A.; Swennenhuis, B. H. G.; Kamer, P. C. J.; van Leeuwen, P. W. N. M. *J. Organomet. Chem.* **2001**, *637*, 805.
(40) Sato, M.; Shigeta, H.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1993**, *458*, 199.

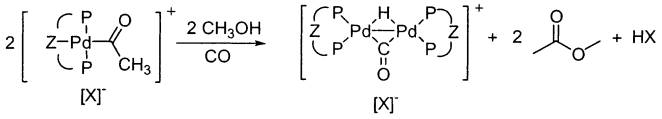
Scheme 4



X = CF_3SO_3 (**1e**-CH3CN)
BARF (**1e'**-CH3CN)

2e,e' **3e,e'**

Scheme 5



P-Z-P = SPANphos (**2a**) no reaction
dtbpf (**2b**) no reaction
Xantphos (**2c**)
dippf (**2d**)
DPEphos (**2e**)

4c,d,e

Table 3. Selected Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms of **2e′**

Pd−P1	2.315(2)	Pd−P2	2.313(2)
Pd−O1	2.261(6)	Pd−C1	1.936(10)
C1−C2	1.521(19)	C1−O2	1.176(13)
P1−Pd−P2	154.70(8)	P2−Pd−O1	78.77(15)
P1−Pd−O1	80.05(18)	P2−Pd−C1	99.6(3)
P1−Pd−C1	100.9(3)	Pd−C1−O2	123.6(8)
Pd−C1−C2	113.2(9)		

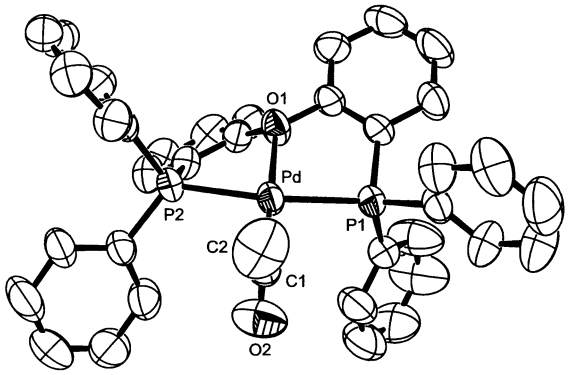


Figure 1. X-ray crystal structure of **2e′**. The ellipsoids are drawn at the 50% probability level. Hydrogen atoms and anion ((3,5-$(CF_3)_2$−C_6H_3)$_4$B) have been omitted for clarity.

Synthesis, Structure, and Reactivity of Cis-Coordinated Acetylpalladium Complexes. Three methods were used to generate ionic cis-coordinated acetylpalladium complexes (methods A, B, and C; Scheme 6). In method A, carbon monoxide is bubbled through a solution of an ionic methylpalladium complex. The product is the ionic, solvent-coordinated acetylpalladium complex.[27a] Alternatively, the ionic methylpalladium complex is synthesized in situ through the reaction of an acid with a dimethylpalladium complex[5] and bubbling CO into the solution (method B). In method C, the complex is synthesized from the neutral methylpalladium compound by abstraction of the chloride anion with silver triflate in a coordinating solvent (method C).[5c,27a]

The reactivity and stability of *cis*-chelated acetylpalladium dppf complexes were studied. Cis-chelated acetylpalladium complexes have already been shown to decarbonylate very easily in the absence of CO.[27a] Therefore, the cis-chelated acetyl-

Scheme 6

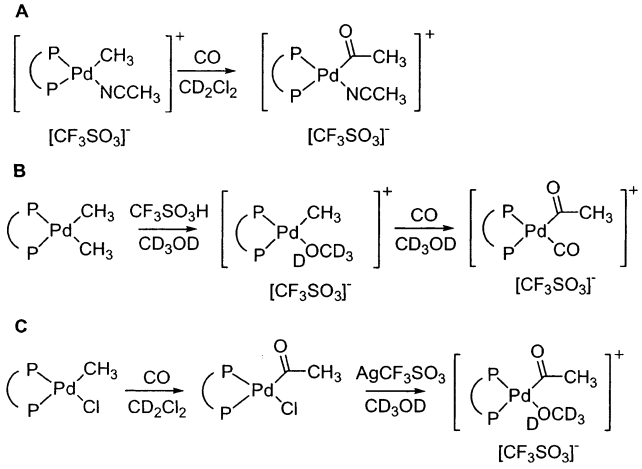


Table 2. Selected NMR Data of Complexes **4c**−**g**

complex	^{1}H NMR μ-H	^{31}P NMR	^{13}C NMR μ-CO
4c	−8.58 q $^2J_{PH}$ = 42	5.5 s	217.7 q $^2J_{PC}$ = 36
4c[a]	−8.58 q $^2J_{PH}$ = 42,	5.5 d $^2J_{PC}$ = 36	217.7 q $^2J_{PC}$ = 36
4d	−7.12 q $^2J_{PH}$ = 39	35.3 s	233.7 q $^2J_{PC}$ = 33
4e	−6.90 q $^2J_{PH}$ = 42	10.8 s	225.1 q $^2J_{PC}$ = 33
4e[b]	−6.90 qd $^2J_{PH}$ = 42, $^2J_{CH}$ = 2.7	10.8 d $^2J_{PC}$ = 33	225.1 q $^2J_{PC}$ = 33
4g	−6.10 q $^2J_{PH}$ = 42	20.3 s	232.0 q $^2J_{PC}$ = 34
4g[b]	−6.10 qd $^2J_{PH}$ = 42, $^2J_{CH}$ = 4.5	20.3 d $^2J_{PC}$ = 34	232.0 q $^2J_{PC}$ = 34

[a] CD_2Cl_2, 25 °C, δ (ppm), J (Hz). [b] ^{13}CO.

palladium complexes were studied in methanol in the presence and in the absence of CO. When 10 equiv of methanol were added to [(dppf)PdC(O)CH_3(CH_3CN)]$^+$[CF_3SO_3]$^-$ (**2g**-CH_3CN) in CH_2Cl_2 in the presence of 1 bar of CO at room temperature,[27a] the palladium(I) hydride dimer, [Pd_2(μ-H)(μ-CO){(dppf)}$_2$]$^+$-[CF_3SO_3]$^-$ (**4g**), and methyl acetate were formed (for NMR data, see Table 2). The acetonitrile-free acetylpalladium complex was synthesized in situ. When (dppf)Pd$(CH_3)_2$ was reacted with 1 equiv of triflic acid in CD_3OD at room temperature, [(dppf)PdCH_3(CD_3OD)]$^+$[CF_3SO_3]$^-$ (**1g**-CD_3OD) was formed. When CO was bubbled through this solution at −90 °C, this resulted in the formation of a mixture of [(dppf)Pd-(C(O)CH_3)(CO)]$^+$[CF_3SO_3]$^-$ (**2g**-CO) and [(dppf)Pd(C(O)CH_3)-(CD_3OD)]$^+$[CF_3SO_3]$^-$ (**2g**-CD_3OD) in a 1:2.5 ratio. When CO was led through a solution of **1g**-CD_3OD at −70 °C, **2g**-CO was formed in high yield (>85%, according to the ^{31}P{^{1}H} NMR spectrum). The structure of the complex was evidenced by ^{13}CO labeling. The acetylpalladium complex **2g**-CD_3OD containing CD_3OD as the fourth ligand was the minor product (<15%). When the temperature was raised to room temperature, an instantaneous reaction of **2g**-CO and **2g**-CD_3OD with CD_3-OD was observed. The color changed from orange to dark-red to give [Pd_2(μ-D)(μ-CO){(dppf)}$_2$]$^+$[CF_3SO_3]$^-$ and methyl

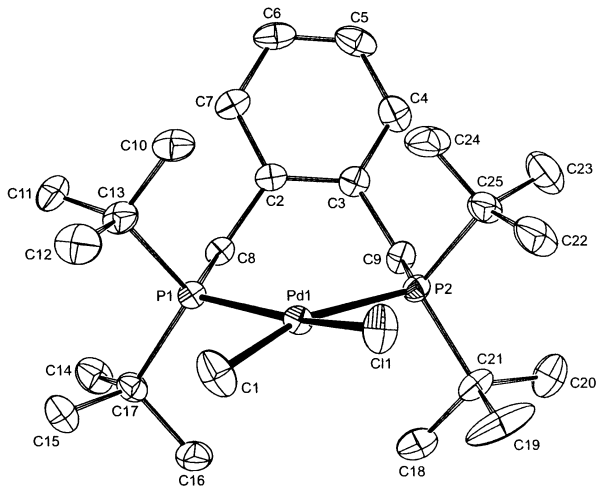


Figure 2. X-ray crystal structure of **5f-Me**. The ellipsoids are drawn at the 50% probability level. The chlorine ligand is disordered over two positions. Only the major disorder component is shown. Hydrogen atoms have been omitted for clarity.

acetate. The $^{31}P\{^1H\}$ NMR spectrum showed a 1:1:1 triplet at 20.3 ppm ($^2J_{PD} = 6$ Hz).

$[(dppp)Pd(C(O)CH_3)(CD_3OD)]^+[CF_3SO_3]^-$ (**2h**-CD_3OD) was synthesized in situ from $(dppp)Pd(C(O)CH_3)Cl$ and 1 equiv of $AgCF_3SO_3$ in CD_2Cl_2/CD_3OD (1:1.33, v/v, [Pd] = 3.3×10^{-2} M) at −75 °C.[5c] Complex **2h**-CD_3OD is stable at this temperature. Raising the temperature to room temperature led to decarbonylation of complex **2h**-CD_3OD and deposition of metallic palladium. Complex $[(dppp)Pd(C(O)CH_3)(CO)]^+[CF_3SO_3]^-$ (**2h**-CO) was synthesized in situ in CD_3OD when $(dppp)Pd(CH_3)_2$ was reacted with 1 equiv of triflic acid and subsequent bubbling through of CO at −60 °C ([Pd] = 3.3×10^{-2} M).[5c] Complex **2h**-CO gives deposition of palladium metal instead of **4h** upon methanolysis at room temperature.

$(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(CH_3)Cl$ (**5f**-Me) was synthesized from $(COD)Pd(CH_3)Cl$ and $o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2$, **f**, in toluene. Bubbling of CO through a solution of **5f**-Me in CD_2Cl_2 resulted in the formation of $(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(C(O)CH_3)Cl$ (**5f**-C(O)Me). Minor quantities of water resulted in the formation of $(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(H)Cl$ (**5f**-H) instead of $(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(C(O)CH_3)Cl$ (**5f**-C(O)Me). For the methanolysis studies, $(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(C(O)CH_3)(O_2CCF_3)$ was synthesized in situ from $(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(C(O)CH_3)Cl$ (**5f**-C(O)Me) and silver trifluoroacetate.

X-ray Structure Determination of 5f-Me. Single crystals were grown from CH_2Cl_2/Et_2O, and an X-ray crystal structure analysis was performed. The complex is severely distorted from a square planar geometry, due to the very large P−Pd−P angle (104.14(1)°), which is one of the largest observed for a cis-chelating ligand in palladium(II) complexes (Figure 2).[10a,41] Two positions were found for the chloride atom in the crystal structure. Characteristic data are shown in Table 4.

The crystal structure of the corresponding propionyl palladium complex has been reported.[10a] The bite angle in the latter complex is almost the same (103°), and the palladium−carbon distance is somewhat smaller at 2.01 Å, as might be expected. The difference in the Pd−P distances is large in both complexes and is due to the difference in trans influences.

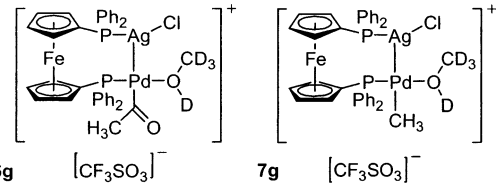
(41) Doherty, S.; Robins, E. G.; Knight, J. G.; Newman, C. R.; Rhodes, B.; Champkin, P. A.; Clegg, W. *J. Organomet. Chem.* **2001**, *640*, 182.

Table 4. Selected Bond Distances (Å) and Angles (deg) for Non-Hydrogen Atoms of **5f-Me**

Pd1−P1	2.2717(5)	Pd1−P2	2.4535(5)
Pd1−Cl1[a]	2.4003(7)	Pd1−Cl1A[b]	2.431(5)
Pd1−C1	2.069(2)	P1−Pd1−P2	104.140(17)
P1−Pd1−C1	87.03(7)	C1−Pd1−Cl1[a]	80.53(7)
C1−Pd1−Cl1A[b]	78.19(16)	Cl1[a]−Pd1−P2	90.84(2)
Cl1A[b]−Pd1−P2	89.74(15)		

[a] Major disorder component. [b] Minor disorder component.

Scheme 7



In Situ Synthesis of Silver−Palladium Complexes. The in situ syntheses of ionic complexes **2** from chloro compounds **5g** and **5j** at low temperatures gave rise to the formation of intermediates **6** and **7** (Scheme 7). See Supporting Information for details.

Kinetics

Kinetics of the Solvolysis Reaction of Acetylpalladium Complexes Containing Trans-Coordinating Ligands. The reaction rate of the methanolysis of acetylpalladium complexes **2a**−**2e** was determined in the absence and presence of CO. The presence of CO had an effect neither on the rate of the methanolysis reaction nor on the course of the reaction.

Complex **2a** containing SPANphos did not react at all with a 10-fold excess of methanol at room temperature during 20 h according to ^1H NMR in the presence of 1 bar of CO.

$[(dtbpf)PdC(O)CH_3]^+[CF_3SO_3]^-$ (**2b**) did not react with methanol in CD_2Cl_2 at room temperature. When $[(Xantphos)Pd\text{-}C(O)CH_3]^+[CF_3SO_3]^-$ (**2c**) was dissolved in CD_3OD containing 3.3 M CF_3COOD ([Pd] = 3.3×10^{-2} M) in the presence of CO, the formation of the palladium(I) dimer and methyl acetate-d_3 was observed. A reaction rate of 7.3×10^{-5} L mol^{-1} s^{-1} was found at 12 °C. Complex **2c** reacted very slowly with 10 equiv of methanol in CH_2Cl_2 at 25 °C ($t_{1/2} \approx 3$ h) to yield in part the palladium(I) hydride dimer, $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(Xantphos)\}_2]^+[CF_3SO_3]^-$ (**4c**), and methyl acetate, but the reaction was accompanied by deinsertion of CO to afford complex **1c**.

A solution of $[(dippf)PdC(O)CH_3]^+[CF_3SO_3]^-$ (**2d**) reacted slowly with 10 equiv of methanol in dichloromethane (3.3×10^{-2} M) at 25 °C ($t_{1/2} = 20$ min), but the reaction was much faster than that of **2a,b** (no reaction) and **2c**. The ^1H NMR and the $^{13}C\{^1H\}$ NMR spectrum indicate the formation of the palladium(I) hydride dimer, $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)\{(dippf)\}_2]^+[CF_3SO_3]^-$ (**4d**).

The isolated compound **2e** was used to perform kinetics with the use of ^1H NMR spectroscopy. CO was bubbled through a 3.3×10^{-2} M solution of **2e** and 3.3×10^{-1} M methanol (10 equiv) in CD_2Cl_2 at −90 °C. The rate constants were determined over a 30° temperature range (−30 through 0 °C). Five data points were used to produce an Eyring plot (Figure 3) giving the activation enthalpy ($\Delta H^{\ddagger} = 33.8$ (±3.5) kJ mol^{-1}) and the activation entropy ($\Delta S^{\ddagger} = {}^{-1}79$ (±32) J K^{-1} mol^{-1}). The use of different amounts of methanol (10−23 equiv) at −20 °C

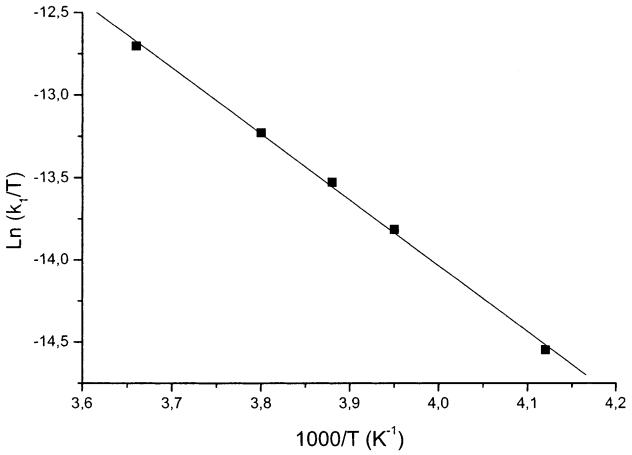


Figure 3. Eyring plot of the methanolysis of [(DPEphos)PdC(O)-CH_3]$^+$[CF_3SO_3]$^-$ (**2e**) from −30.0 to 0 °C. *T* is in K.

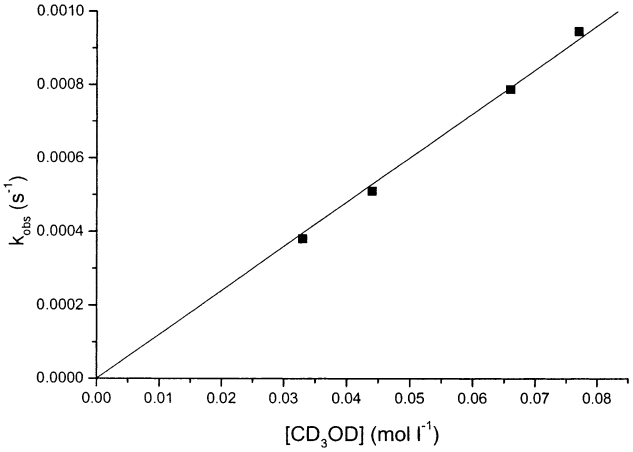


Figure 4. The methanol concentration dependency on the rate of methanolysis of **2e** ([Pd] = 3.3×10^{-2} M, [CD_3OD] = 3.3×10^{-1} to 7.6×10^{-1} M, $T = -20$ °C).

showed a first-order dependency of the methanolysis reaction on the methanol concentration (Figure 4). The plot of the observed rate constants k_{obs} versus the concentration of methanol resulted in a straight line with an intercept with the *y* axis at zero indicating that the kinetics obey the typical rate law $k_{obs} = k_2[CH_3OH]$.

The rate of insertion of ethene into the acetylpalladium bond of [(DPEphos)PdC(O)CH_3]$^+$[CF_3SO_3]$^-$ (**2e**) was determined over a 20° temperature range (−60 through −40 °C). Ethene (10.5 equiv) was injected via a gastight syringe into a 2.21×10^{-2} M solution of **2e** in CD_2Cl_2 at −78 °C. Five data points were used to produce an Eyring plot (Figure 5). From the Eyring plot, we calculated the activation enthalpy ($\Delta H^{\ddagger} = +36.1$ (±2.5) kJ mol^{-1}) and the activation entropy ($\Delta S^{\ddagger} = -149.1$ (±22) K^{-1} mol^{-1}).

Methanol, ethanol, 2-propanol, CF_3CH_2OH, and *tert*-butyl alcohol were used to determine the dependency of the rate of solvolysis on the alcohol (Figure 6). The alcohol (10 equiv) was added to a 3.3×10^{-2} M solution of **2e** in CD_2Cl_2. Neither CF_3CH_2OH nor *tert*-butyl alcohol reacted with **2e** at 25 °C and 40 °C. Methanol reacted too fast to determine the reaction rate by ^{1}H NMR spectroscopy at 25 °C. An extrapolation of the Eyring plot in Figure 3 was used to estimate the rate of solvolysis at 25 °C. ^{31}P{^{1}H} NMR spectroscopy was used to measure the rate of solvolysis using 2-propanol, since the O*H*

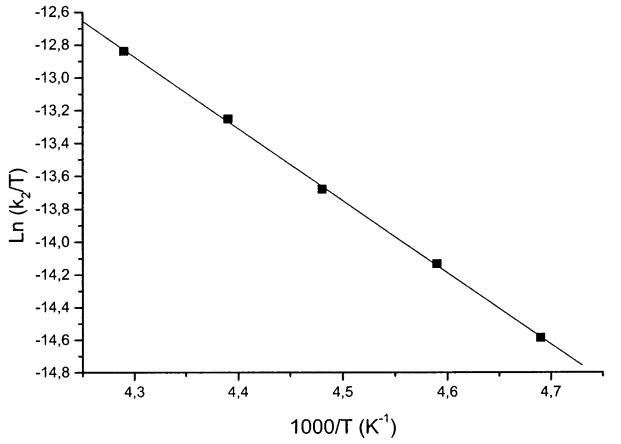


Figure 5. Eyring plot of the ethene insertion of [(DPEphos)PdC(O)-CH_3]$^+$[CF_3SO_3]$^-$ (**2e**) from 213.0 to 233.0 K ([Pd] = 2.21×10^{-2} M, [ethene] = 2.32×10^{-1} M).

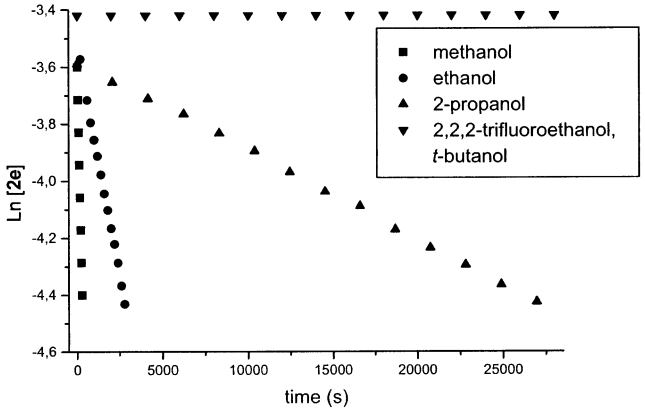
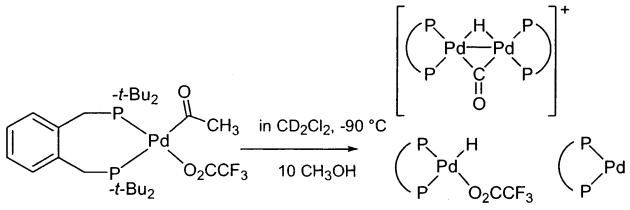


Figure 6. The rates of alcoholysis of **2e** at 25 °C for various alcohols. The rate of methanolysis was calculated from the Eyring plot in Figure 3. [Pd] = 3.26×10^{-2} M. [Alcohol] = 3.26×10^{-1} M. The data points of 2,2,2-trifluoroethanol and *tert*-butyl alcohol overlap one another (no decrease of the integrals of **2e** is observed).

Scheme 8



signal of the 2-propanol reagent overlapped with the C(O)C*H*$_3$ signal of the acetylpalladium complex in the ^{1}H NMR spectrum. The solvolysis using 2-propanol was very slow and therefore could be monitored by ^{31}P{^{1}H} NMR spectroscopy.

Kinetics of the Solvolysis Reaction of Acetylpalladium Complexes Containing Cis-Coordinating Diphosphine Ligands. Monitoring of the alcoholysis of (*o*-C_6H_4(CH_2P(*t*-Bu)$_2$)$_2$)Pd(C(O)CH_3)(O_2CCF_3) (**2f**-O_2CCF_3) was attempted by NMR spectroscopy at −90 °C in CD_2Cl_2 with the use of 10 equiv of MeOH. The reaction was instantaneous giving methyl acetate and the tentatively assigned palladium products shown in Scheme 8. The half-life time is well below 3 min.

The in situ synthesized compound [(dppf)Pd(C(O)CH_3)-(CO)]$^+$[CF_3SO_3]$^-$ (**2g**-CO) in CD_3OD was used to study the kinetics of the reaction ([Pd] = 3.3×10^{-2} M). The reaction was monitored by ^{1}H NMR spectroscopy between −40 and 0

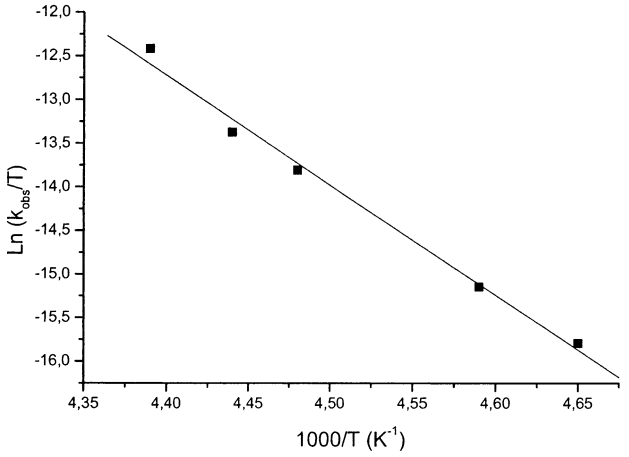


Figure 7. Eyring plot of the methanolysis of in situ synthesized [(*syn*-(calix[6]arene)diphosphite)Pd(C(O)CH_3)(CD_3OD)]$^+$[CF_3SO_3]$^-$ (**2j**) from 215.0 to 228.0 K (−58 to −45 °C).

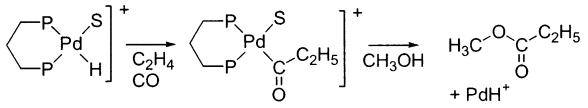
°C. A pseudo first-order behavior in [**2g**] was not observed. At −30 °C, the observed half-life time of the reaction was 83 min. The absence of CO in the reaction mixture of the in situ generated cationic acetylpalladium complex [(dppf)Pd(C(O)CH_3)(CD_3OD)]$^+$[CF_3SO_3]$^-$ (CD_2Cl_2:CD_3OD = 1:1.33, v/v; [Pd] = 3.3×10^{-2} M; [CD_3OD] = ∼14 M) avoids the interference of CO during kinetics. The methanolysis reaction is faster in the absence of CO. Unfortunately, decarbonylation occurs at the temperature at which methanolysis is observed ($T > -40$ °C), and the kinetics remained complex.

The solvolysis of complexes containing the dppp ligand **h** could not be studied by NMR spectroscopy due to a fast decomposition of the acetylpalladium complex to yield metallic palladium. Instead, the solvolysis reaction of in situ synthesized [(dppp)Pd(C(O)CH_3)(CO)]$^+$[CF_3SO_3]$^-$ (**2h**-CO) in methanol could be studied by UV−vis spectroscopy at 30 °C, although lower palladium concentrations ([Pd] = 2×10^{-4} M) had to be applied. The absorption at 456 nm (palladium(I) hydride dimer **4h**) was monitored during the reaction. The amount of acid added to the reaction mixture had a large influence on the reaction rate. Under neutral reaction conditions (0 equiv of CF_3SO_3H), methanolysis was not observed. The addition of excess triflic acid resulted in methanolysis of [(dppp)Pd(C(O)CH_3)(CO)]$^+$[CF_3SO_3]$^-$. The highest reaction rate was observed when 9 equiv of triflic acid were added to the reaction mixture. The rate of reaction decreased again when more equivalents of triflic acid were added to the solution.

[(*syn*-(Calix[6]arene)diphosphite)Pd(C(O)CH_3)(CD_3OD)]$^+$[CF_3SO_3]$^-$ (**2j**-CD_3OD) decarbonylates above −40 °C in CD_2Cl_2 in the presence of 10 equiv of methanol, but its methanolysis could be studied by ^{1}H NMR spectroscopy in the temperature range −58 through −45 °C (CD_2Cl_2:CD_3OD = 1:1.33, v/v). In this case, the rate of methanolysis is pseudo first order. The reaction is extremely temperature dependent. From the data in Figure 7, we calculated the activation enthalpy ($\Delta H^{\ddagger}$ = 101.7 (±10) kJ mol^{-1}) and the activation entropy ($\Delta S^{\ddagger}$ = 151 (±37) J K^{-1} mol^{-1}).

Catalytic CO and Ethene Copolymerization Reactions. The methylpalladium complexes were tested in the catalytic CO and ethene copolymerization reaction. The ionic methylpalladium complexes were tested in methanol containing 5 equiv of *p*-toluenesulfonic acid at 20 bar of CO and ethene (1:1, v/v)

Scheme 9



at 80 °C. The ionic methylpalladium complexes containing SPANphos (**a**),[38] dtbpf (**b**), and Xantphos (**c**) were inactive. [(DPEphos)Pd $CH_3(CF_3CO_2)$] showed an activity of 2500 mol mol^{-1} h^{-1}. The only products observed were methyl propanoate and the low molecular weight oligomers $H_3COC(O)CH_2CH_2C(O)C_2H_5$ and $H_3COC(O)CH_2CH_2C(O)OCH_3$ (in a 40:4:1 ratio). In dichloromethane solution, a copolymer was formed at low reaction rates, probably due to catalyst decomposition. Catalysis with the use of **f**−**j** has been published previously (vide infra, Table 5).

Discussion

Although the ligands of this study form a limited set, they were selected on the basis of steric and electronic properties, and we will show that it provides us with new and crucial information. Our present findings will lead to an interpretation of many old facts and adjustments of previous interpretations. The histories of copolymerization of alkenes and carbon monoxide and oxycarbonylation of alkenes are long, and it is impossible to do justice to all contributions to chain transfer in this one paper. In due time, an overview on the topic will be published[42] also describing chain transfer.[43]

The key questions to be answered in alkoxycarbonylation and alkene/CO copolymerization are what factors govern the chain transfer versus chain growth, what is the mechanism of alkoxycarbonylation, and how can we explain the low rate for a number of palladium-catalyzed reactions. The focus of this work is on the formation of an ester or acid as the chain end (reaction 3, Scheme 1), but it should be borne in mind that in polymerization systems the other chain transfer mechanisms play a role as well or may even dominate. Alkoxycarbonylation of alkenes using palladium complexes has been the subject of many reviews and research papers.[44] For convenience, we show in a short-hand notation the two mechanisms, Scheme 9, the "hydride" mechanism, and Scheme 10, the "carbomethoxy" mechanism.

All individual steps for each mechanism have been observed in model compounds, and it is conceivable that both mechanisms occur, depending on catalyst and conditions. Even kinetic studies or in situ observations of catalyst resting states may not give a definite answer to this question.[45] There is consensus in the literature that the fast catalysts reported in the past decade operate via the "hydride" mechanism, Scheme 9.[10,29,45,46] Circumstantial evidence for a hydride mechanism is the absence of acrylate (or its methanol adduct formed via a palladium-

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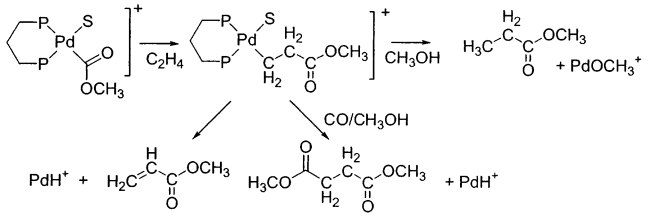
Table 5. Overview of Ligand Properties **a**−**j**, Structures and Reactivities of Compounds **1** and **2**, and Catalysis Results[a]

ligand	$\theta_{1/2}$[b]	χ	X-ray angle (deg) P–M–P	**1a**–**j**	**1**, CO insertion	**2a**–**j**	methanolysis *T* (K), [MeOH] (M)	reaction of **2** with CH_3OH[c] $t_{1/2}$, $\Delta G^{\ddagger}$ (*T* in K)[c]	estimated $t_{1/2}$ at 243 K and 0.33 M MeOH	catalysis results[a]
a, SPANphos	162[d]	10.3	172[e]	trans	slow	trans	298, 0.33	no reaction, 20 h	$>5 \times 10^6$	no reaction
b, dtbpf	167	4.3	158[60], 104[f]	trans	slow	trans	298, 0.33	no reaction, 24 h	$>5 \times 10^6$	no reaction
c, Xantphos	162	10.3	150−165[60], 104, 108[g]	trans	slow	trans	285, 24.7, 3.3 M CF_3COOD	158′, 92 (285)	2.7×10^5	no reaction
d, dippf	155	6.7	99[h], 103[i]	cis	moderate	trans	298, 0.33	20′, 91 (298)	800′	oligomers
e, DPEphos	162	10.3	101, 165[60]	cis	fast	trans	243−273, 0.33	15′, 83 (273)	102′	methyl propanoate 10% oligomers
f, dtbpx	174	3.7	104[10,this work]	cis	very fast	cis	183, 0.33	<3′, <52 (183)	$<5 \times 10^{-6}$	methyl propanoate[10]
g, dppf	145	13.0	99[58]	cis	fast[27a]	cis	243, 24.7	83′, 77 (243)	83′	oligomers[96]
h, dppp	140	10.9	91[58]	cis	very fast[4a]	cis	303, 24.7	5′, 90 (303) acid added 374′	3.5×10^6, 2.6×10^8	polymer[2]
j, calix-6-diphosphite	145	30.2	90[87]	cis	fast	cis	215−228, 14	4′, 66 (228)	0.14′	no reaction MeOH polymer in CH_2Cl[87]

[a] Catalysis results were obtained typically in methanol, 20−60 bar ethene/CO (1:1), 60−90 °C. [b] Tolman's parameters θ and χ were estimated for half ($\theta_{1/2}$) the bidentate ligands using published methods.[101a,b] [c] Not corrected for [MeOH]. $\Delta G^{\ddagger}$ is in kJ mol^{-1}. [d] Value for Ph_2P(*o*-anisyl).[104a] [e] Value for *trans*-(**a**)$PtCl_2$.[38] [f] Value for *cis*-(nor)(**b**)Rh^+ complex[104b] [g] Value for *cis*-(**c**)Pd(allyl)$^+$ 108°.[104c] Value for *cis*-(**c**)Pd(TCNE) 104°.[104d] [h] Value for (cod)(**d**)Ir^+ complex.[104e] [i] Value for (**d**)$PdCl_2$.[104f]

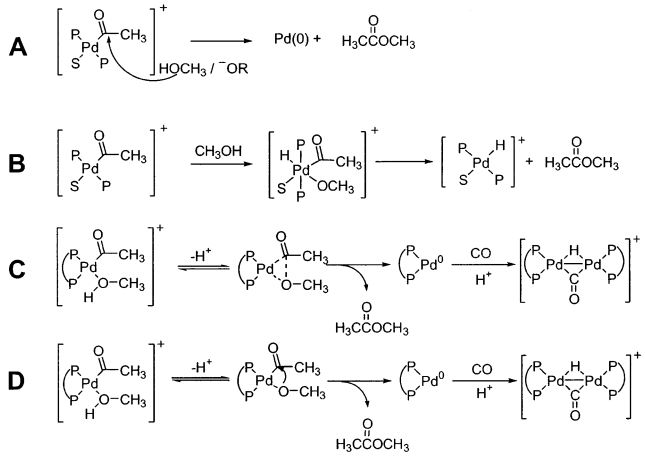
Scheme 10



catalyzed Michael addition)[9] and succinate in the product, the putative byproducts of a carbomethoxy route, Scheme 10. Note that after formation of these side products the catalysis *continues as a hydride cycle* and oxidation is needed to turn the catalyst back into the carbomethoxy cycle. Thus, in the absence of oxidizing agents, any catalyst is bound to end up in the hydride cycle. A best guess about rates will also point to the hydride cycle as being the fastest one: (a) insertion of ethene into a palladium hydride is much faster than insertion of ethene in a palladium−carbomethoxy bond,[47] (b) insertion of CO is fast in any case, (c) protonation of alkylpalladium bonds is slow. In the hydride mechanism, the highest barrier occurs at the alcoholysis of the acyl species, the topic we will discuss in the following. Under oxidative conditions, palladium-catalyzed methoxycarbonylation of ethene does lead to dimethyl succinate, but the reaction is much slower than methyl propanoate formation.[48]

Synthesis of Acetylpalladium Complexes. The new acetylpalladium complexes we synthesized can be divided in trans complexes and cis complexes. Part of the ligands coordinating in a trans fashion can be forced to form cis complexes by adding a strongly coordinating ligand, such as triphenylphosphine. The *trans*-acetylpalladium(diphosphine) complexes are relatively stable in the absence of CO at room temperature, which enabled us to study the alcoholysis reaction. The acetylpalladium complexes **2a** and **2b** containing SPANphos and dtbpf as the ligand do not show methanolysis at all, but the other complexes are reactive toward methanol. Carbonylation of *cis*-**1d**-CH_3CN resulted in a trans complex *trans*-**2d**, due to the sp^2 character and the larger trans influence of the acetyl carbon-to-palladium bond. In the presence of CO, the *cis*-acetylpalladium complexes contain coordinated CO,[4a,49] but, in the absence of CO at room temperature, they lose the coordinated CO and the acetyl groups decarbonylate instantaneously (Scheme 10). This limits the conditions at which the methanolysis of *cis*-acetylpalladium complexes can be studied.

Scheme 11



The palladium−silver complexes **6** and **7** seem to have no precedent. Presumably, they are intermediates in the common anion exchange reactions. Similar platinum complexes have been reported by Usón et al.[50]

Mechanism of the Alcoholysis of Acetylpalladium Complexes. The ionic acetylpalladium complexes **2a**−**j** were used to study the mechanism and kinetics of the alcoholysis reaction, because they are involved in the common catalysts. We will discuss several mechanistic proposals of the solvolysis of acylpalladium bonds (Scheme 11).

Mechanisms A and B allow coordination of the two phosphines in trans positions and we have drawn them as such, but

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a cis coordination is not excluded for this type of mechanism. The trans coordination has often been said to play a role in creating a preference for chain termination rather than growth reactions,[2,4b,14,51] which by nature of the migratory insertion reaction requires cis positions for the substrate and growing chain and, hence, for the two phosphine ligands.[3b] Trans acyl complexes containing two monophosphines have been identified by $^{31}P\{^{1}H\}$ NMR spectroscopy in several instances[4b,14,51] albeit at temperatures lower than those at which the reaction takes place, because at the reaction conditions exchange of triphenylphosphine takes place on the NMR time scale leading to one broad signal for the excess and coordinated phosphine.[29] Thus, we must assume that cis−trans isomerization is very fast in monophosphine based catalysts and so is dissociation of a ligand. Dissociation of one phosphine has also been suggested as a possible step involved in hydroxycarbonylation of styrene.[29] Mechanism C is a classic reductive elimination reaction, and mechanism D is a reductive elimination preceded by a migratory step of the alkoxy moiety; both reactions require cis positioning of the two groups.

Outer-Sphere Attack. Mechanism A is an outer-sphere attack of the alcohol or alkoxyde nucleophile at the acetyl-carbon atom, similar to alcoholysis of acyl chlorides, and this mechanism was assumed to be the most likely one.[30] In the absence of base, one molecule of alcohol attacks the acyl-carbon atom, while a second molecule of alcohol may serve as a general base, abstracting the proton. Therefore, acyl chloride alcoholysis often gives a higher order in alcohol concentration than one.[52] In our experiments, only first-order dependency on the methanol concentration was observed, but, in general alcoholysis, is a too complex a reaction to draw firm conclusions. As in ester hydrolysis under acidic conditions, protonation of the acyl oxygen may also occur. The reactivity order found MeOH > EtOH > *i*-PrOH > *t*-BuOH > CF_3CH_2OH is not the order of nucleophilicity, except for the nonreactivity of trifluoroethanol, but this order is usually encountered in alcoholysis reactions of acyl chlorides, organyl halides, and the alcoholysis of chlorosilanes.[53] The order is ascribed to the predominance of steric effects when the reaction is of an S_N2 type and also to inductive and entropic effects.[54] Capture of bulky vinylic cations by alcohols is also dominated by steric effects of the alcohols.[55] In the following, we will discard the mechanism of direct attack.[56]

Since for trans diphosphine complexes direct attack is the only available mechanism (after having excluded oxidative addition mechanisms, vide infra), we studied complexes with an enforced trans configuration, that is, a P−Pd−P angle close to 180°. Ligands that coordinate in a purely trans fashion are rare, and it is often observed that trans-coordinating ligands form cis complexes as well, like some of the ligands in this work.[37,57−59]

We have recently reported on a new trans-spanning ligand, SPANphos (**a**), which forms trans complexes with platinum and palladium and does not form cis complexes. In the crystal structure of the free ligand, the P−P distance is 4.99 Å, and in the platinum dichloride trans-adduct, the P−P distance is 4.59 Å, which shows that even for the formation of a trans complex some distortion of the ligand is needed and a cis coordination cannot be achieved.[38] Interestingly, this bis-triarylphosphine ligand was *completely inactive* in the methoxycarbonylation reaction of ethene (or copolymerization) under the standard conditions with the use of several ways of initiation. After the reaction, the palladium complexes were still intact and no palladium metal was formed.

Ligand **a** forms trans complexes **1**−**2a**. For ligands **b** (dtbpf) and **c** (Xantphos), it was known that they form ionic *trans*-methylpalladium complexes,[60] but the *i*-propyl derivative of ferrocene diphosphine **d** formed a cis complex under the same conditions. The trans configuration of **1c** was explained by the wide bite angle and the stabilizing coordination of the ether oxygen atom, while the trans configuration of **1b** was ascribed to the steric repulsion of the *tert*-butyl groups. Trans-acetyl complexes **2a** and **2b** showed no methanolysis with a 10-fold excess of methanol at room temperature, while the methanolysis of **2c** had a half-life time of almost 3 h at 12 °C. Since the acyl carbon atoms in the cationic acetyl complexes **2a**−**c** all have weak donor atoms in trans positions, we assume that they are highly electrophilic, and yet they do not (or very slowly) react with methanol. From this we conclude that alcoholysis of acylpalladium complexes in neutral to acidic media does not involve a direct attack by alcohol at the acyl carbon atom.

An outer-sphere attack of alkoxide ions has been discussed as a possible mechanism for the related methoxycarbonylation reaction of organic halides, which typically occurs in highly basic media and where the nucleophile is the alkoxide anion.[30,61,62] Yamamoto et al. reported in their study of the reductive elimination of aryl acetates from (aryloxy)(acetyl)-palladium complexes that addition of free alkoxides as the base had no effect on the rate.[61] Buchwald also excluded an outer-

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sphere attack of alkoxide at the ipso-carbon of an aryl−palladium bond as the mechanism for palladium-catalyzed aryl ether formation.[63]

Thus, trans-acyl complexes resist alcoholysis, and apparently *cis complexes are required for alcoholysis*. The question then arises why did the trans complexes **1a**−**c** undergo insertion of carbon monoxide, which definitely requires cis coordination of the methyl group and carbon monoxide and, hence, also of the two phosphine donors, assuming they remain bonded to the metal. There are several solutions to this, but there are no experimental data in support of any mechanism. CO is a relatively strong ligand, and it may replace one of the phosphines in **1a**−**c**. Monocoordination of **a** has been observed in rhodium complexes under CO.[38] For ligand **c**, we know it can also function as a cis ligand. Complex **2b** could under the influence of CO break the palladium−iron interaction and act as a short-lived cis bidentate. A second general possibility is the formation of 5-coordinate 18-electron species, iso-electronic with the rhodium species involved in rhodium hydroformylation, which could perform an insertion reaction as has been proposed for platinum and nickel complexes.[64] Thus, carbon monoxide can enter the coordination sphere more easily than methanol, and routes to its insertion are accessible.

Oxidative Addition of Alcohols to Palladium(II). Mechanism B (Scheme 11) involves an oxidative addition of methanol, which results in a cationic Pd(IV) complex that undergoes a reductive elimination to form methyl acetate. This mechanism seems unlikely for cationic palladium(II) complexes containing phosphine ligands, although palladium(IV) intermediates have also been proposed for Heck reactions[65] and, in compounds containing nitrogen donor atoms, their occurrence is abundant.[66] Palladium(IV) formation does not comply with the low reactivity of CF_3CH_2OH, as it is known that especially the acidic alcohols such as phenols and fluoro-substituted alkanols will oxidatively add to palladium(0)[67] and methanol will add when the palladium(0) center is very electron-rich,[35] but oxidative addition to palladium(II) has not been observed. The low reactivity of some of the alkyl-substituted phosphines argues against oxidative addition as the mechanism. An oxidative addition mechanism has been proven as the pathway for the protonolysis of the Pt−C bond in neutral Pt(II) complexes using strong acids,[68] but the reactivity of cationic complexes toward oxidative addition is much lower, while strong acids are much stronger oxidizing species in such reactions than alcohols. Thus, most likely alcoholysis of acylpalladium species does not proceed via an oxidative addition pathway.

Reductive Elimination in Cis Complexes. In mechanisms C and D, the methoxy group (or molecule of methanol) and the acetyl group should occupy cis positions relative to one another and therefore the diphosphine ligand coordinates also in a cis fashion. Mechanism C is a concerted reductive elimination in which the new carbon−oxygen bond is formed while the palladium−carbon and palladium−oxygen bonds are being broken. Three pathways have been proposed and experimentally verified for this reaction when both groups are hydrocarbyls: elimination from a reactive, 14-electron, three-coordinate species after dissociation of one of the ligands,[69,70] elimination from four-coordinate species,[61a,71] and elimination from five-coordinate species.[61a] Dissociation of a monophosphine prior to reductive elimination has been established experimentally, and it was found to occur also for cis complexes.[61a] The intermediacy of three-coordinate species in hydroxycarbonylation of alkenes has been invoked to explain[29] the differences between monophosphines and diphosphines in these reactions, in terms of rates and selectivities.[17,72] As they show similar behavior as monophosphines, the selectivities for low molecular weight products of bulky diphosphines have been assigned to the assumed propensity to dissociate one arm of the bidentate ligand.[2,10b,16] A direct elimination of esters from a four-coordinate palladium species has been observed,[61a] and also in related C−X bond forming reactions, it has been demonstrated that this is the most likely pathway.[71] Reductive elimination from a five-coordinate intermediate often involves a π-acceptor ligand (such as benzoquinone or acrylonitrile) as the fifth ligand, which accelerates the reductive elimination, especially for dialkyl nickel complexes and also, if only slightly, for palladium complexes.[61a,69a,73] Addition of benzoquinone to a copolymerization system of palladium sometimes leads to a reduction of the molecular weight of the polymer, which might indicate that benzoquinone induces chain termination by reductive elimination.[74]

Mechanism D is a reductive elimination that due to the unlikeness of the two groups starts off as a migratory reaction, in which one of the reactants acts as a nucleophile migrating to the electrophilic neighbor. In recent years, a lot of evidence has been presented for this reaction mode in the palladium-catalyzed C−X bond formation by the groups of Buchwald and Hartwig.[63,75] An early theoretical study about migratory hydrocarbyl 1,2-shifts between transition metals and coordinated main group atoms was published by Hoffmann and co-workers.[76]

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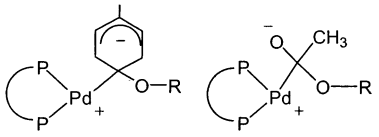
Scheme 12



They studied reductive elimination/oxidative addition of P−C fragments to various transition metals including the Pd(II)−(IV) couple in relation to P−C bond cleavage.[77] The migration barrier of a phenyl group turned out to be lower than that of a methyl group due to the π-stabilization.

The cross-coupling reaction is particularly effective when one of the partners of the reductive elimination has an sp^2-hybridized carbon atom bonded to the metal, and usually this is the (former) electrophile stemming from the organic halide. The reductive elimination of ethene from a vinyliridium hydride complex was best described as a migration of the hydride anion to the vinyl group.[78] Calhorda et al. analyzed the reductive elimination of propene from *cis*-$(PH_3)_2Pd(CH_3)(CH{=}CH_2)$ and they found that the best description for this reaction is a migration of the methyl group to the sp^2 carbon of the vinyl unit.[79]

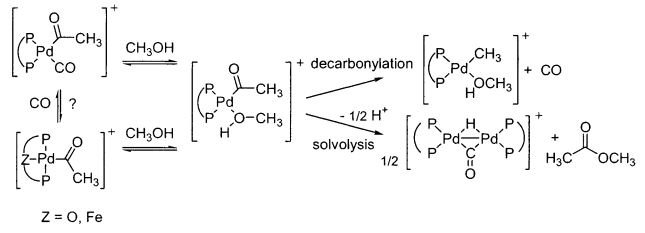
The formation of the C−X bond in hetero-cross-coupling reactions studied in the past decade is thought to proceed via a migration of the heteroatom to the aryl group, which develops a negative charge, which is π-stabilized by mesomeric interaction with acceptor substituents. π-Stabilization of 1,2-phenyl carbanion shifts has been analyzed many years ago.[80] The resonance-stabilized Meisenheimer complex proposed by Buchwald for the reductive elimination of aryl ethers is depicted in Scheme 12.

For the reverse reaction, oxidative addition of substituted chlorobenzenes to zerovalent palladium, Portnoy and Milstein proposed that the Hammett correlation obtained could be best explained by the assumption of an intermediary Meisenheimer (or similar) complex having a late transition state.[81] As early as 1971, Fitton and Rick described the oxidative addition of aryl halides in a similar fashion.[82]

We are strongly in favor of a migratory elimination to form esters from acyl-alkoxy palladium complexes for reasons given in the following. First, the acyl carbon atom is sp^2 hybridized, much more electrophilic than an aryl carbon atom, and highly stabilized by the structure where the negative charge is on the oxygen atom (Scheme 12). The acyl oxygen atom may, as in acid-catalyzed alcoholysis of esters, be protonated, before or after the formation of the new carbon−oxygen bond. Second, for the reverse reaction, the oxidative addition of esters to palladium(0), the atom at which the nucleophilic palladium center will attack the ester clearly is the electrophilic ester carbon atom, rather than the oxygen atom.

Cationic acetylpalladium complexes *cis*-$(L{-}L)PdC(O)CH_3(S)^+$ have been reported (S = nitrile, thf, CO, PPh_3),

Scheme 13



Z = O, Fe

[3a,10,27a,49b,83−85] but their reactivity toward methanol has received little attention. When S is replaced in *cis*-$(L{-}L)PdC(O)CH_3(S)^+$ by methanol, one of the fast reactions observed is formation of methyl acetate, even in the absence of a base. When less nucleophilic alcohols were used, such as phenols, both the cis and trans complexes $L_2PdC(O)CH_3(OAr)$ could be isolated containing even the aryloxide anions instead of the alcohols, and the reactivity of these aryloxide-palladium complexes has been studied.[61a] For Ar = *p*-NCC_6H_4, a slow formation of aryl acetate was observed ($t_{1/2}$ = 24 h, 35 °C), while, after addition of *p*-$CH_3C_6H_4OH$ to this complex, rapid formation of *p*-tolyl acetate was found ($t_{1/2}$ = 1 h, 25 °C) indicating a rapid exchange of aryl oxides and a much faster elimination reaction for the stronger nucleophile. The same reduction in $t_{1/2}$ was observed when dppe was added to a solution of *trans*-$(PEt_3)_2PdC(O)CH_3(OAr)$, which also led to the suggestion that cis complexes are required for ester formation. The low reactivity of the acetylpalladium(aryloxide) complexes is in accord with the nonreactivity of CF_3CH_2OH toward ionic acetylpalladium, and it illustrates the enormous range of reactivities.

Complexes *cis*-$(L{-}L)PdC(O)CH_3(CH_3OH)^+$ (L−L is a diphosphine) react extremely fast to give methyl acetate, but we hardly succeeded in collecting any data on this process. The kinetics turned out to be very complex, and the cationic species are highly prone to decarbonylation. Thus, ironically, one can only study the elimination reaction for the most reactive alcohol, that is, methanol! Part of the complexity of the kinetics becomes evident from Scheme 13. In the cis complexes, a competition exists between the coordination of CO and methanol, and the rate of methyl acetate formation depends on the concentration of CO. In the absence of CO, decarbonylation occurs, and this reaction is fast.[3a,27a,49b] Second, like esterification reactions, there may be a general acid and base catalysis, as probably the coordinated methanol is deprotonated before it migrates to the acyl carbon. Water, alcohol, the anion, and also palladium(0) may serve as a general base. During the reaction, acid is released because only one out of two protons ends up in the palladium dimer product. Since the rate of methyl acetate formation is dependent on the acid concentration, this rate will change during the alcoholysis process. It is expected that hydrogen bond formation, protonation and deprotonation, and methanol exchange may constitute an important step in the process, but since they are all occurring at a very high rate, they can be dealt with as fast preequilibria (Curtin−Hammett conditions).

For the study of ligand **f**, complex $(o\text{-}C_6H_4(CH_2P(t\text{-}Bu)_2)_2)Pd(C(O)CH_3)(O_2CCF_3)$ was synthesized with the aim to slow

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slightly the rate of alcoholyisis by the use of a coordinating anion, but the reaction was too fast, even at −90 °C. While this manuscript was in preparation, Clegg et al. reported the same result for the related complex (o-$C_6H_4(CH_2P(t\text{-}Bu)_2)_2$)-$Pd(C(O)C_2H_5)(THF)^+$.[10a]

The in situ synthesized compound $[(dppf)Pd(C(O)CH_3)(S)]^+[CF_3SO_3]^-$ (**2g**; S = MeOD, CO) did not yield a pseudo first-order behavior. At −30 °C, the observed half-life time of the reaction was 83 min when CO was present, while, in the absence of CO, decarbonylation took place simultaneously with methanolysis (>−40° C).

$[(dppp)Pd(C(O)CH_3)(CO)]^+[CF_3SO_3]^-$, **2h**-CO, gave only little solvolysis at room temperature under neutral reaction conditions in pure methanol. The reaction was accelerated by the addition of triflic acid. The role of the acid might be to activate the acetyl group and enhance the electrophilicity of the carbonyl carbon. The experiments showed that the reaction is slower when a large excess of acid is used. Because of the complexity of this system, no conclusions can be drawn, although it seems justified to say that half-life times are in the order of tens of minutes at 30 °C, which is fairly slow compared to those of other cis ligands, and are even in the range of several "trans" ligands.

The only cis complex that neither decarbonylated nor solvolyzed too fast was [(*syn*-(calix[6]arene)diphosphite)Pd-$(C(O)CH_3)(CD_3OD)]^+[CF_3SO_3]^-$, **2j**. The extremely large positive entropy of activation ($\Delta S^{\ddagger}$ = 151 (±37) J K^{-1} mol^{-1}) can be explained by the loss of the proton and/or the reaction of ions with opposite charges. The conversion of the ionic complex into a neutral complex, which is less solvated and less highly structured, can give rise to a high positive entropy of activation. Similar effects have been reported in proton transfer studies.[86] The value found for $\Delta S^{\ddagger}$ remains relatively high for such phenomena, and perhaps more preequilibrium steps are involved in the overall expression of the rate. At −45 °C, $[CD_3OD]$ = ~14 M, the value for $t_{1/2}$ amounts to 13′. In view of the fast termination reaction, it would have been interesting to test the activity of catalyst **2j** in methanol, but unfortunately, it is inactive in methanol/dichloromethane. Presumably, it is inactive because after the fast termination reaction, a stable, zerovalent palladium complex is formed, which cannot be reprotonated by acid. In dichoromethane, **2j** gave a polymer containing in part acid groups as chain ends indicating the presence of traces of water.[87] Proton release from water coordinated to an electron-poor palladium center should be facile compared to the other ligand systems discussed here, and a reductive elimination step should be fast in view of the electron-withdrawing character of a triaryl phosphite. The P−Pd−P angle is small at 90°, which is not attractive for reductive elimination, but we propose that the dominant factor is not a steric one in this instance but an electronic one. This results in a fast reductive elimination irrespective whether it proceeds via mechanism C or D.

The rate of methanolysis decreases in the series of cis ligands reported here as follows: dppp < dppf < calix-6, **j** < dtbpx, **f**. The series dppp < dppf < dtbpx represents a series of steric bulk and bite angles, but the former is more important. Initially, it was thought that bite angle effects were dominant in many palladium-, nickel-, and rhodium-catalyzed reactions,[58,88−91] but evidence is growing that the steric bulk, measured as cone angle, solid angle, or pocket angle, determines the relative rates of insertion reactions and reductive elimination reactions.[26] If the substituents at phosphorus are all phenyl groups for the ligands we are comparing, clearly the backbone induced bite angles run parallel with the steric properties of the (bidentate) ligands. High rates for reductive elimination, be it a symmetric type (C, Scheme 11) or a migratory type of reaction (D, Scheme 11), are well documented for a large number of palladium-catalyzed reactions.[63,78,79,81] Thus, when complexes are used containing ligands having a high steric bulk, a fast elimination takes place, and for ligands that are less bulky, the insertion reactions become dominant (e.g., dppp). For still smaller ligands, the overall productivity decreases, but the rate of the elimination reaction is affected more than the insertion reactions. The first insertion taking place in methyl propanoate formation is insertion of ethene in a palladium hydride bond, and clearly this is little affected by the steric bulk of the cis diphosphine as is the insertion of CO. Insertion of ethene into acyl-palladium bonds is slowed drastically by sterically encumbered ligands such as **f**.

The critical bite angle seems to be 103−104°; the bite angle found in (o-$C_6H_4(CH_2P(t\text{-}Bu)_2)_2$)$Pd(CH_3)Cl$ (**11**) amounted to 104°, and Clegg[10] found 103° for the $-C(O)C_2H_5$ analogue. Ligands having similar bite angles but carrying the smaller phenyl groups instead of the *tert*-butyl groups at phosphorus, or a phosphole group, give polymerization catalysts rather than methyl propanoate catalysts, although sometimes a bimodal product distribution has been observed.[92]

Reductive Elimination in Trans Complexes. Previously, we concluded that the trans complexes should rearrange to the cis complexes, during which the Z atom (Fe, O) decoordinates and methanol enters the coordination sphere (Scheme 13). The large negative entropy of activation ($\Delta S^{\ddagger}$ = −179 (±32) J K^{-1} mol^{-1}), which has been observed for the methanolysis of [*trans*-$(DPEphos)PdC(O)CH_3]^+[CF_3SO_3]^-$, can be accounted for by the associative nature of the reaction involving the coordination of methanol. The kinetic data for ethene insertion in this complex are almost the same (Figures 4 and 5). The present tridentate ligands are indeed capable of rearranging to cis-chelating bidentate ligands, as can be inferred from the addition of ligands, such as triphenylphosphine, to a solution of acetylpalladium complexes **2e** and **2d** giving complexes **3e** and **3d**, respectively. Furthermore, the related methyl derivative *cis*-(DPEphos)-$PdCH_3(CH_3CN)]^+[CF_3SO_3]^-$ (**1d**-CH_3CN) has a cis structure with a P−Pd−P bite angle of 103°.[60] A similarly large negative entropy of activation was reported for the association/insertion reactions in N,N,N tridentate acetylpalladium complexes.[93] The large negative value is in contrast to the large positive value

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found for **2j**, and this raises the question if the same steps are involved in the rate equation. Since the bite angle of DPEphos is rather wide, we expect (vide infra) that the methanolysis reaction will be extremely fast, once the cis complex has been formed. It might well be therefore that the rate-determining step for the methanolysis of **2e** is the formation of the cis complex via association of methanol. This would also explain the neat first-order dependency in methanol we have found for this reaction, which one would not expect for a complex process such as acyl-palladium bond rupture and ester formation, similar to alcoholysis of reactive acyl halides. The first-order dependency is also in accord with the noninterference of carbon monoxide with the alcoholysis process, because the rate of alcohol complexation does not change when no substantial amount of *trans*-**2e** is converted in a CO adduct.

Extrapolation of the present kinetic data of DPEphos complexes shows that the expected rate of methanolysis is 35 mol mol^{-1} h^{-1} at 80 °C in 0.33 M methanol. Since the reaction rate is first order in methanol concentration, this corresponds to 3200 mol mol^{-1} h^{-1} in pure methanol, which is the maximum rate to be expected for the catalytic process. This is considerably lower than the value for the most effective catalysts (40 000 mol mol^{-1} h^{-1} at 80−100 °C for "fast" ligands such as **f**),[10] because the DPEphos (**e**) system resides in the inactive trans configuration for a great deal of the time. The observed reaction rate in the CO and ethene co-oligomerizations reaction (2500 mol mol^{-1} h^{-1}) corresponds very well with this number. Extrapolation of the data for the insertion rates of ethene in the acetylpalladium complex shows a rate of 45 mol mol^{-1} h^{-1} at 80 °C at an ethene concentration of 0.23 M. Assuming a first-order dependency in ethene concentration, we would correspond this to 900 mol mol^{-1} h^{-1} at 20 bar of ethene pressure, which is the correct order of magnitude. On the basis of the Flory−Schulz constant found (0.1), one would expect 270 mol mol^{-1} h^{-1}, but we did not and cannot take into account the competing coordination of CO at higher pressures, which will lead to a lower rate than the one calculated (900 mol mol^{-1} h^{-1}). Furthermore 20% of the oligomer is a diester (EE) product; this proves that for this catalyst part of the reaction occurs via the carbomethoxy cycle, which may lead to a lower productivity, as part of the palladium content is tied up as a less reactive carbomethoxy complex.

It is interesting to compare the product distributions obtained with DPEphos and PPh_3 under similar conditions in methanol. The Flory−Schulz constant (growth factor) for DPEphos is ~0.1, and that for PPh_3 was reported to be ~0.33.[1] The resting state for PPh_3 is also the trans complex, which has to rearrange to the cis complex before it can undergo insertion reactions of substrates or undergo a chain termination. The respective bite angles of the two complexes are 103° (DPEphos) and 100.5° (*cis*-$(PPh_3)_2$),[94] and since the aryl substituents are almost the same, the pocket angle for the DPEphos complex will be smaller. In line with our reasoning, this will result in a lower Flory−Schulz constant for the DPEphos-based catalyst.

As mentioned previously, the order of the rate of alcoholysis for the several alcohols is methanol > ethanol > *i*-propanol > *tert*-butyl alcohol, CF_3CH_2OH. This is the order of nucleophilicity toward the acyl-palladium center, but also toward the palladium cation, or the order of stability of the alcohol solvate complexes to palladium. CF_3CH_2OH is much less reactive toward the acetylpalladium complex than ethanol, due to its reduced nucleophilicity. The very low rate of alcoholysis observed for CF_3CH_2OH is in agreement with the results of the copolymerization of CO and styrene reported by Milani et al.[33] who observed that the molecular weight of the copolymer obtained in CF_3CH_2OH was higher than that in methanol. This result and ours seems to be in contrast to the findings of Yamamoto et al. who compared the selectivity of acylpalladium chloride complexes in a competition experiment between diethylamine and various alcohols. They found that the more acidic alcohols resulted in a higher selectivity for ester instead of acid amide.[15] In these competition experiments, the more acidic alcohols such as CF_3CH_2OH may react via the alkoxide, because a replacement of the chloride ion by alkoxide may be required and thus the position of CF_3CH_2OH in the series is different from that in our series. Another factor we did not mention so far is the strong ionizing power of CF_3CH_2OH, but also that of methanol, compared to those the other alcohols. These solvents cause a relative stabilization of the ionic species, which are the catalytically active ones, compared to the neutral palladium zero resting states of the catalyst. Even though we presume that especially the anions will be stabilized by the alcohols with a high ionizing power[95] rather than the large cations constant, these effects can be very large.

The order of the rate of methanolysis of complexes containing the trans-coordinating diphosphine ligands is SPANphos ≈ dtbpf (no reaction) < Xantphos ≪ dippf < DPEphos. The slow reaction of $[(Xantphos)PdC(O)CH_3]^+[CF_3SO_3]^-$ with methanol can be explained by the rigidity of Xantphos compared to DPEphos. The DPEphos ligand can rearrange to a cis ligand more easily than the rigid Xantphos ligand. The complex containing the dtbpf ligand, **2b**, does not react at all with methanol. The cationic acetylpalladium complex is too sterically crowded to form a cis complex that can undergo methanolysis. The less crowded dippf complex, **2d**, does react with methanol faster than the Xantphos complex, **2c**, but more slowly than the DPEphos complex, **2e**. A comparison of the steric properties between ferrocene based ligands and the other three ligands is not straightforward, but the order within each group {(SPANphos, Xantphos, DPEphos) versus (dtbpf, dippf)} is as expected. The ferrocene range can be extended with two examples from recent literature, dppf and octamethyl-dppf, carrying eight methyl substituents at the ferrocene rings.[96] It is known that dppf occasionally forms trans complexes,[97] but the acetylpalladium(dppf) complex has a cis structure in the presence of acetonitrile.[27a] The product of the co-oligomerization with the use of dppf is indeed a mixture of oligomers (rate 5000 mol mol^{-1} h^{-1}, at 85 °C). Octamethyl-dppf is sterically more crowded, although not via substitution directly at the phosphorus atoms, as appears from the P−Pd−P angle, which is 101° as

(94) A search in the CSD gave 39 structures of monometallic, square-planar, divalent palladium complexes containing two triphenylphophine ligands in cis positions with an average P−Pd−P angle of 100.46°. Typically the ones with angles > 100° contain small groups such as allylic or cyclopropenyl groups trans to the triphenylphosphine ligands. See Supporting Information for a listing.

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compared to 96° for dppf in the dicationic palladium diaqua adducts.[96] Indeed, octamethyl-dppf gives methyl propanoate in the palladium-catalyzed reaction with ethene, CO, and MeOH, albeit at a modest rate (600 mol mol^{-1} h^{-1}, at 85 °C). It should be noted that the dppf system is also highly susceptible to the "enolate" chain termination reaction, which contributes to the formation of short chains.[96,98]

When the *tert*-butyl groups are replaced by the smaller *i*-propyl groups in $(t\text{-Bu})_2P(CH_2)_3P(t\text{-Bu})$[21a] or ligand **f**,[10c] both systems give oligomers as the product instead of methyl propanoate at high rates. When the 1,3-propanediyl bridge in $(t\text{-Bu})_2P(CH_2)_3P(t\text{-Bu})_2$ is replaced by a 1,2-ethanediyl bridge, the accessiblity of the catalyst for ethene increases such that, in the reaction of ethene, CO, MeOH, and H_2, pentan-3-one was formed at extremely high rates (showing the fast insertion of ethene) instead of methyl propanoate, the product of the more bulky ligand.[21b]

Qualitative Overview. Previously, we have reported on the bidentate ligand effect on the rates of migration reactions, and we found that, in accord with the overall rates in the catalytic experiments of Drent et al.,[3] the rates of the stoichiometric insertion reactions followed the sequence dppe < dppp < dppb, which we explained using the model developed by Thorn and Hoffmann.[99] According to their EH calculations, the ligand sitting next to the migrating group will "follow" the migrating group, thus enlarging the bite angle of the bidentate ligand. This led Thorn and Hoffmann to the statement that dppe would be a bad choice as a ligand in catalysts for migration reactions. Ab initio results for platinum confirmed this picture.[99b] In the sequence tested, both the bite angle and the flexibility increase, and until recently, there was little reason to abandon this model.[100] In IMOMM calculations on alkene insertion in rhodium hydride bonds, it was found that the bite angle of the diphosphine hardly changes during the migration process.[89] In recent years, however, several small bite angle catalysts lacking flexibility have been reported that gave fast copolymerization catalysts.[25,26,34,60] Thus, the picture emerging from current literature is that the steric bulk of the complex enhances the migratory insertion reactions and that the effect is not one of flexibility or bite angle, although bite angle and steric properties are related within certain series of substituted ligands. The steric properties of bidentate ligands have been described in a number of ways in the literature, but we will not go into detail of that here (cone angle,[101a,b] AMS,[101c] solid angle,[101d] pocket angle[4c]). Destabilization of the starting hydrocarbyl−metal complex with the alkene by steric hindrance causes a higher reaction rate of migration. At a certain point though while the steric bulk of the complex increases, the complex can no longer fulfill the steric demands for alkene coordination and only CO coordination or alcohol coordination remains. Insertion of a CO in a metal−acyl bond does not take place, as it is thermodynamically unfavorable (note that in the overall thermodynamics even the insertion of isolated CO molecules in a polyethylene chain is thermodynamically uphill and, hence, kinetically determined!). The increased steric bulk also destabilizes the alcohol complex, facilitating the "migratory elimination" and thus causing chain transfer. The importance of steric bulk in this type of elimination reactions has been reported many times in recent years.[63,71c,102]

Quantitative Overview. Before we set out to try to present a quantitative comparison of the ligands, a comment on the rate-determining step seems in place. Several authors have suggested[10,11,29,31,51] that the solvolysis of the acylpalladium species is the rate-determining step of the reaction sequence. In a system like the present one, this often leads to confusion, because the barrier for the alcoholysis for the fast catalyst does not seem very high at all when one looks at the stoichiometric reaction. Indeed, neither we nor Clegg et al.[10] succeeded in measuring the rate of the methanolysis of acylpalladium complexes containing ligand **f**, not even when the fourth site was occupied by a coordinating trifluoroacetic acid anion. The half-life time for the reaction of the latter complex with methanol is below 180 s at −90 °C. When we extrapolated to the reaction conditions of the catalysis (80−90 °C), the rate could be 5−10 orders of magnitude higher, depending on the value we assign to the entropy of activation. At both low and high temperatures, it seems to be the fastest step of all steps considered! Perhaps the statement should be reconsidered or modified. Under the actual conditions, there is competition between the coordination of methanol and CO for the cis complexes. Furthermore, all species involved are very close in energy, and an equilibration between all species occurs as is shown in a shorthand notation, with omission of dimeric species and the various coordination states that the complexes may assume.

$$Pd(0) \rightleftharpoons PdH^+ \rightleftharpoons PdC_2H_5^+ \rightleftharpoons PdD(O)C_2H_5^+ \rightleftharpoons (CH_3OH)PdC(O)C_2H_5^+ \rightarrow C_2H_5CO_2CH_3$$

Only the last step is irreversible (the overall reaction has a free energy gain of ∼92 kJ mol^{-1}, and this seems to be gained mainly in the last step), and oxidative addition of nonactivated esters to palladium(0) cannot occur.[103] The equilibrium concentration of the acyl species can be low as the acyl species need not be the "resting" state of the catalyst. Even "dormant" states may be involved that require reactivation to form palladium(0). Improvement of catalyst systems are related not only to changing the rates of individual steps but also perhaps more so to the optimization of the positions of the equilibria involved.

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Since the rates of methanolysis differ by many orders of magnitude for the complexes studied, a comparison of ligand properties and the performance of their acetylpalladium complexes in the methanolysis reaction is a risky enterprise. For one trans complex, we have found a highly negative entropy of activation and for one cis complex, a highly positive entropy of activation has been measured. This makes that extrapolation of all data to the same temperature may lead to large errors, if one uses a wrong number for the entropy. Besides, at the temperature of extrapolation, another reaction might have become the dominant one. Nevertheless, to avoid vague descriptors, we have calculated the estimated half-life times for complexes **2a**−**j** in the reaction with methanol at 243 K. For the trans complexes **2c**−**e**, we have assumed that the reaction is first order in methanol and $\Delta S^{\ddagger}$ is taken as -179 J mol^{-1} K^{-1} (as found for **2e**). For the cis complexes, it was assumed that the reaction is zero order in methanol, the effects of CO and acid were not taken into account, and $\Delta S^{\ddagger}$ is taken as $+151$ J mol^{-1} K^{-1} (as found for **2j**). Table 5 gives the results of these estimates together with a few properties such as the Tolman values $\theta_{1/2}$ and χ, P−M−P angles taken from X-ray studies as a measure for the bite angle.[58] It can be seen that, for the fastest and the slowest systems (**2a** vs **2f**), the rates may differ by as much as 12 orders of magnitude, and even if one would assume a highly negative entropy of activiation for **2f**, a difference of still 8 orders of magnitude would remain. Ligand **h**, dppp, is the best ligand for making polymers in this list. Using the assumptions mentioned previously, we find a half-life times for methanolysis at 353 K of milliseconds and tenths of seconds in the presence of acid. These values seem too low because the time for the growth of one polymer chain is in the order of minutes, but the presence of CO will lead to much higher values. Clearly, more data are needed, but the present set of ligands containing many extreme cases can probably serve as a good starting point for further research.

Conclusions

The alcoholysis of a variety of acetylpalladium complexes has been studied, and it was found that cis coordination of alcohol and acetyl is needed to form an ester. Trans complexes containing SPANphos, **a**, or dtbpf, **b**, do not react at all. Complexes that have a trans structure but can temporarily adopt a cis structure do react with methanol to form methyl acetate. This proves that an outer-sphere attack of alkoxides/alocohols is not a viable mechanism for alcoholysis. The reaction of [(DPEphos)Pd(C(O)CH$_3$)]$^+$[CF$_3$SO$_3$]$^-$ with methanol shows a large negative entropy of activation as the association with methanol is rate determining; the kinetics of this reaction are similar to that of the insertion reaction of this complex with ethene. The pressure of carbon monoxide has no effect on the rate of the methanolysis reaction. The mechanism is thought to be an intramolecular, migratory, nucleophilic attack of alcohol/alkoxide at the acyl group, which is in accord with the rates of reaction found for the series of alcohols (methanol > ethanol > *i*-propanol > *tert*-butyl alcohol, CF$_3$CH$_2$OH), the less sterically hindered alcohols reacting faster as is commonly observed in solvolysis reactions.

Cis acetyl complexes underwent competing decarbonylation and methanolysis, and for these complexes, the rate depends strongly on acid and carbon monoxide concentration. The calix-6-diphosphite complex showed a large positive entropy of activation, which was ascribed to the loss of solvation in the transition state. On the basis of electronic properties of the ligand, one expects a high rate of reductive elimination (methyl acetate formation), and indeed the reductive elimination is relatively fast. For the phosphine series, the steric effects dominate. In a series of increasing steric bulk of bidentate ligands, initially the rates of insertions increase giving more productive polymerization catalysts due to destabilization of the alkene complexes formed prior to insertion; at one point, this breaks down as ethene coordination becomes unfavorable and only carbon monoxide or alcohol can coordinate cis to an acyl group. In its turn, elimination is also accelerated by an increasing steric bulk, and thus, the bulkiest ligands such as dtbpx, **f**, give the fastest catalysts for making methyl propanoate. The two insertion reactions involved in this process can remain fast because neither ethene insertion into a palladium hydride bond nor CO insertion into an ethylpalladium bond requires much space.

Experimental Section

Kinetics of the Protonolysis Reaction of [(dppf)PdCH$_3$(CH$_3$CN)]$^+$[CF$_3$SO$_3$]$^-$ (1g-CH$_3$CN). An NMR tube was charged with **1g-CH$_3$CN** and 0.700 mL of CD$_3$OD. CF$_3$COOH (10 equiv) was added to this solution at −78 °C. The tube was shaken and immediately transferred to the NMR probe, which was set to the required temperature, and the spectra were acquired after the temperature of the probe was stabilized. The integrals of [PdC*H*$_3$]$^+$ were measured to follow the decay of **1g** to give [Pd]$^{2+}$.

Kinetics of the Alcoholysis Reaction of [(DPEphos)PdC(O)CH$_3$]$^+$[CF$_3$SO$_3$]$^-$ (2e). The reaction was followed by ^{1}H NMR spectroscopy (methanol, ethanol, 1,1,1-trifluoroethanol, and *tert*-butyl alcohol) or ^{31}P NMR spectroscopy (*i*-propanol). NMR probe temperatures were calibrated using an anhydrous methanol sample.[105] An NMR tube with a Young valve was charged with 0.700 mL of a 3.3×10^{-2} M CD$_2$Cl$_2$ solution of [(DPEphos)PdC(O)CH$_3$]$^+$[CF$_3$SO$_3$]$^-$. Alcohol (ROH, 10 equiv) was added to this solution at −78 °C. The tube was shaken and immediately transferred to the NMR probe, which was set to the required temperature, and the spectra were acquired after the temperature of the probe was stabilized. The integrals of PdC(O)C*H*$_3$ and ROC(O)C*H*$_3$ were measured to follow the decay of [(DPEphos)PdC(O)CH$_3$]$^+$[CF$_3$SO$_3$]$^-$. The mass balance was checked using the C*H*DCl$_2$ peak.

Kinetics of the Alcoholysis Reaction of [(*syn*-Calix[6]arene diphosphite)PdC(O)CH$_3$(CH$_3$OD)]$^+$[CF$_3$SO$_3$]$^-$, 2j-CH$_3$OD. The reaction was followed by ^{1}H NMR spectroscopy. NMR probe temperatures were calibrated using an anhydrous methanol sample. An NMR tube with a Young valve was charged with 0.3 mL of a 5.13×10^{-2} M solution of (*syn*-calix[6]arene diphosphite)Pd(C(O)CH$_3$)Cl in CD$_2$Cl$_2$. A solution of CD$_3$OD (0.4 mL) containing 1 equiv of TlCF$_3$SO$_3$ was added to the solution at −90 °C. The NMR tube was shaken and immediately transferred to the NMR probe, which was set to the

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required temperature, and the spectra were acquired after the temperature of the probe was stabilized. The integrals of $PdC(O)CH_3$ and $CH_3C(O)OCD_3$ were measured to follow the decay of [(*syn*-calix[6]-arene diphosphite)$Pd(C(O)CH_3)(CD_3OD)]^+[CF_3SO_3]^-$. The mass balance was checked using the $CHDCl_2$ peak.

Catalytic CO/Ethene Copolymerization Reactions. The experiments were carried out in a 180 mL stainless steel autoclave. The autoclave was charged with 20 mL of methanol and 0.100 mmol of *p*-toluenesulfonic acid and was pressurized with 10 bar of ethene. The autoclave was then heated to 80 °C. A dichloromethane solution (1 mL) containing 0.20 mmol $(L-L)Pd(CH_3)(CF_3CO_2)$ or $[(L-L)-PdCH_3]^+[CF_3SO_3]^-$ was introduced into the autoclave, and the autoclave was further pressurized to 20 bar of CO and ethene (1:1 ratio). The autoclave was depressurized after 1 h. The methanol soluble fractions were analyzed by GC, GC-MS, and ^1H and ^{13}C NMR spectroscopy ($CDCl_3$). The products with higher boiling points than that of methyl propanoate were analyzed by ^1H and ^{13}C NMR spectroscopy in CD_2Cl_2/CF_3CO_2D (90:10, v/v).

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Supporting Information Available: Experimental details, Synthesis and NMR spectra of all compounds, UV spectra of compounds **2e**, the list of complexes containing *cis*-$(PPh_3)_2PdX_2$, and CIF files for the two crystal structures (compounds **2e′** and **5f-Me**). This material is available free of charge via the Internet at http://pubs.acs.org.

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