DOI: 10.1002/chem.200501398

The Mechanism of the Hydroalkoxycarbonylation of Ethene and Alkene–CO Copolymerization Catalyzed by Pd^{II}–Diphosphine Cations

Jianke Liu, Brian T. Heaton, Jonathan A. Iggo,* Robin Whyman, Jamie F. Bickley, and Alexander Steiner[a]

Abstract: All the intermediates in the "carboalkoxy" pathway, and their interconversions giving complete catalytic cycles, for palladium–diphosphine-catalyzed hydroalkoxycarbonylation of alkenes, and for alkene–CO copolymerization, have been demonstrated using $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy. The propagation and termination steps of the "hydride" cycles and the crossover between the hydride and carboalkoxy cycles have also been demonstrated, providing the first examples of both cycles, and of chain crossover, being delineated for the same catalyst. Comparison of the propagation and termination steps in the pathways affords new insight into the selectivity-determining steps. Thus, reaction of [Pd(dibpp)$(CH_3CN)_2$](OTf)$_2$ (dibpp = 1,3-(iBu$_2$P)$_2$C$_3$H$_6$) with Et_3N and CH_3OH affords [Pd(dibpp)(OCH_3)-(CH_3CN)]OTf, which, on exposure to CO, gives [Pd(dibpp){C(O)OCH_3}-(CH_3CN)]OTf immediately. Labeling studies show the reaction to be readily reversible. However, the back reaction is strongly inhibited by PPh_3, indicating an insertion/deinsertion pathway. Ethene reacts with [Pd(dibpp)-{C(O)OCH_3}(CH_3CN)]OTf at 243 K to give [Pd(dibpp){$CH_2CH_2C(O)OCH_3$}]-OTf, that is, there is no intrinsic barrier to alkene insertion into the Pd–C(O)OMe bond, as had been proposed. Instead, termination is proposed to be selectivity determining. Methanolysis of the acyl intermediate [Pd-(dibpp){C(O)CH_3}L]X (L = CO, CH_3OH; X = $CF_3SO_3^-$ (OTf^-), $CH_3C_6H_4SO_3^-$ (OTs^-)) is required in the hydride cycle to give an ester and occurs at 243 K on the timescale of minutes, whereas methanolysis of the β chelate, required to give an ester from the carbomethoxy cycle, is slow on a timescale of days, at 298 K. These results suggest that slow methanolysis of the β chelate, rather than slow insertion of an alkene into the Pd–carboalkoxy bond, as had previously been proposed, is responsible for the dominance of the hydride mechanism in hydroalkoxycarbonylation.

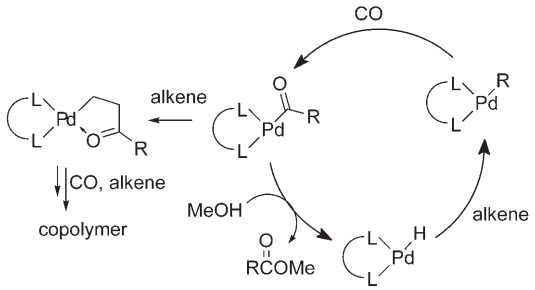
Keywords: carbonylation · copolymerization · NMR spectroscopy · palladium · reaction mechanisms

Introduction

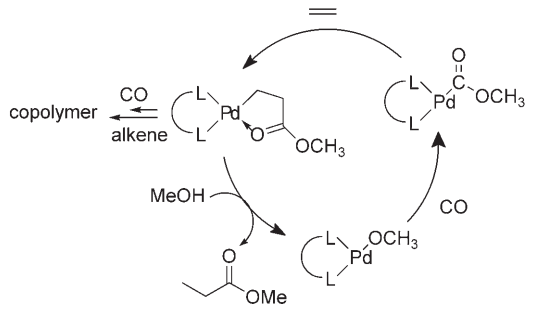
The hydroalkoxycarbonylation of alkenes and the alkene–CO copolymerization[1] catalyzed by Pd–diphosphine complexes are mechanistically related reactions.[2] Commercial interest in hydromethoxycarbonylation of ethene is strong; Lucite International currently operates pilot plants and has announced construction of a commercial unit as part of an environmentally preferred route to methyl methacrylate, namely, the Lucite ALPHA process.[3] Two mechanisms are believed to operate in the catalysis; initiation can occur by insertion of an alkene into a Pd–hydride bond or by insertion of CO into a Pd–methoxy bond, hence the two mechanisms are usually referred to as the "hydride" (Scheme 1) and "carboalkoxy" (Scheme 2) cycles, respectively. Termination after insertion of one unit each of CO and alkene corresponds to hydroalkoxycarbonylation, whereas propagation by multiple alternating insertions of CO and alkene yields a perfectly alternating copolymer. Termination can occur by one of a number of routes, of which methanolysis of the acyl, to give an ester end group and regenerate a Pd–H initiator, and methanolysis of the so-called β-chelate species to give a ketone end group and regenerate a Pd–OCH_3 species, appear to dominate the reaction. The relative effectiveness

[a] Dr. J. Liu, Prof. Dr. B. T. Heaton, Dr. J. A. Iggo, Dr. R. Whyman, J. F. Bickley, Dr. A. Steiner
Department of Chemistry
Donnan and Robert Robinson Laboratories
University of Liverpool
P.O. Box 147, Liverpool, L69 7ZD (UK)
Fax: (+44) 151-794-3588
E-mail: iggo@liv.ac.uk

Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. It contains experimental details and all NMR spectra used in characterizing the complexes (81 pages).



Scheme 1. The "hydride" cycle for the hydroalkoxycarbonylation of alkenes/CO–alkene copolymerization catalyzed by Pd^{II} cations.



Scheme 2. The "carboalkoxy" cycle for the hydroalkoxycarbonylation of alkenes/CO–alkene copolymerization catalyzed by Pd^{II} cations.

of the propagation versus termination steps dictates whether the copolymerization or hydroalkoxycarbonylation product is formed.

Somewhat surprisingly, given the close relationship between the hydroalkoxycarbonylation and copolymerization reactions, polymer-end-group analysis[4,5] shows that both the hydride and carboalkoxy mechanisms operate in copolymerization yet a consensus has emerged that only the hydride catalytic cycle operates in hydroalkoxycarbonylation.[6–12] The explanation advanced for the latter conclusion is that alkene insertion into the Pd–carbomethoxy bond is extremely slow.[13,14] This seems somewhat remarkable given that such insertion must be fast in the case of alkene–CO copolymerization catalysis.

In order to shed some light on this apparent paradox we have extended our mechanistic studies of these reactions and demonstrated, by using NMR spectroscopy, complete carboalkoxy and hydride cycles for a single catalyst system. Despite the intense interest in recent years in the mechanism of these, and of similar reactions employing nitrogen or mixed nitrogen–phosphorus donor ligands,[1,2,14–20] the complete carboalkoxy cycle for either hydroalkoxycarbonylation or CO–alkene copolymerization has not previously been demonstrated. Thus, it has not been possible, prior to our work reported here, to make a direct comparison of analogous steps in the two cycles for a catalytically active system. As we will show, previous work relying on isolable, model complexes has led to an erroneous conclusion, whereas the direct, spectroscopic observation of the reactivity of catalytically relevant intermediates reported here has afforded new insight into the selectivity-determining steps in this chemistry. Thus, we find that alkenes insert rapidly into the Pd–carboalkoxy bond at low temperature, in contrast to all previous reports,[13,14,20–22] and that there are significant differences in methanolysis rates leading to an ester product in the hydride and carbomethoxy pathways. These results indicate that the consensus that "slow" insertion of alkenes into the Pd–carboalkoxy bond in hydroalkoxycarbonylation is the pathway/selectivity-determining step must be reassessed. Parts of this work have appeared in a preliminary form.[23,24]

Results and Discussion

The initial focus of this study was the complete delineation of both catalytic pathways leading to both ester and copolymer products for the same catalyst system and the demonstration of chain crossover with initiation of the "other" catalytic cycle, none of which has previously been reported. This would allow a comparison of analogous steps in the two pathways to be made, in the absence of artifacts due to changes in the diphosphine and ancillary ligands, or of the counterion. It was hoped that this would provide new insight into the factors governing the reaction outcome.

The hydride cycle: The complete hydride cycle has been demonstrated only once; namely, by us for the Lucite hydromethoxycarbonylation catalyst, [Pd(dtbpx)H(CH_3OH)]OTf (dtbpx = 1,2-(CH_2PtBu_2)$_2C_6H_4$),[25,26] whereas Nozaki et al. demonstrated the propagation steps of the Pd–BINAPHOS-catalyzed enantioselective copolymerization of CO with alkenes starting from [Pd(BINAPHOS)(CH_3)(CH_3CN)]$^+$ (BINAPHOS = (*R*)-2-(diphenylphosphino)-1,1′-binaphthalene-2′-yl-{(*S*)-1,1′-binaphthalene-2,2′-diyl}phosphite).[27]

Initiation: In our earlier work on the Lucite ALPHA process, we were successful in observing the hydride complex [Pd(dtbpx)H(solvent)]OTf and studied its insertion reaction with ethene.[25,26] Attempts to cleanly synthesize the Pd-(dibpp)–hydride complex analogous to the Lucite catalyst were unsuccessful. However, we have been able to access the propagation steps of the hydride cycle through the Pd–methyl cations [Pd(dibpp)CH_3(L)]$^+$ (dibpp = 1,3-(iBu$_2$P)$_2C_3H_6$); L = see Table 1) (**1-L**),[28–31] and infer the insertion of ethene into the Pd–H bond by analogy with our earlier work.[25,26] Complexes **1-L** were prepared by protonation of [Pd(dibpp)(CH_3)$_2$] with the appropriate acid,[32] in the appropriate solvent. Although we have not been able to isolate analytically pure samples of **1**, ample literature precedent for these complexes exists.[28–30,33,34] Thus, for example, Brookhart et al. prepared a series of complexes [Pd($\widehat{LL}$)-Me(Et_2O)][B(3,5-(CF_3)$_2C_6H_3$)$_4$] ($\widehat{LL}$ = various diphosphine ligands) by using an analogous procedure.[29]

The NMR spectra (Table 1) are consistent with the proposed formulation of **1**. Thus a doublet resonance at approximately δ = 0.34 ppm (^3J(P,H) = 7 Hz) in the ^{1}H NMR spectrum confirms the presence of a Pd–Me fragment in **1-**

Table 1. NMR spectroscopic data recorded at 193 K for the Pd–methyl complexes **1**.

Compound	$^{31}P\{^1H\}$ δ [ppm] mult.[b] ^2J(P,P) [Hz] P *cis* to Me	$^{31}P\{^1H\}$ δ [ppm] mult.[b] ^2J(P,P) [Hz] P *trans* to Me	$^{13}C\{^1H\}$[a] δ [ppm] mult.[b] ^2J(P,C) [Hz]
1-OTf	18.8 d 41	−16.6 d 41	
1-PPh$_3$	32.0 dd 356, 34	−3.7 dd 356, 49; −14.8[c] dd 49, 34	
1-Cl	11.4 d 41	−12.9 d 41	
[**1-CH$_3$CN**]OTf	11.0 d 41	−15.6 d 41	
[**1-CO**]OTf	−0.5 d 47	−12.3 d 47	181.6 dd 114, 16
[**1-CH$_3$OH**]OTf	18.8 d 41	−14.2 d 41	
[**1-H$_2$O**]OTf[32]	16.9 d 42	−15.4 d 42	
1-TFA	12.7 d 41	−11.4 d 41	
[**1-CH$_3$CN**]TFA	10.8 d 41	−15.6 d 41	
[**1-CO**]TFA	−0.8 d 48	−13.5 d 48	181.6 dd 114, 16
1-OTs	17.2 d 42	−12.2 d 42	
[**1-CH$_3$CN**]OTs	11.1 d 42	−15.7 d 42	
[**1-CO**]OTs	−0.6 d 47	−13.4 d 47	181.7 dd 114, 16
[**1-CH$_3$OH**]OTs	18.9 d 42	−14.3 d 42	

[a] Recorded using ^{13}CO. $^2J(P_{trans},C)$ given first. [b] Multiplicity. [c] $\delta(PPh_3)$ given last.

CH$_3$CN. The $^{31}P\{^1H\}$ NMR resonances of **1-L** recorded at 193 K appear as two doublets; the Pd–methyl compounds all show ^2J(P,P) in the range of 41 to 48 Hz, suggesting that the complexes **1-L** all adopt a similar square-planar structure in solution, irrespective of L. The chemical shift of the low-field resonance varies markedly with L, from $\delta_P = -0.5$ (**1-CO**) to 18.9 ppm (**1-CH$_3$OH**) (Figure 1a,b and Table 1), which confirms the *trans* disposition of these groups, and can be used to confirm the identity of L.[35] The resonance occurring at high field, $\delta_P = -11$ to -16 ppm, is then assigned to the phosphorus atom oriented *trans* to the methyl group.

These reactions occur cleanly at 193 K giving solutions of **1** suitable for an NMR study of the hydride cycle for ethene–CO copolymerization using the highly active Pd/dibpp/acid catalyst system.[36] Previous studies of related catalyst systems, such as those by Nozaki et al.[27] and Brookhart et al.,[28,29] validate this approach. Nozaki et al. have also shown that [Pd(BINAPHOS)Me(CH$_3$CN)]$^+$ is a good catalyst precursor in the copolymerization chemistry.[27,30] Thus, starting from **1** we have been able to demonstrate, by using multinuclear NMR studies (Figure 1), the propagation and termination steps of the hydride catalytic cycles leading to ester and to copolymer product (Scheme 3).

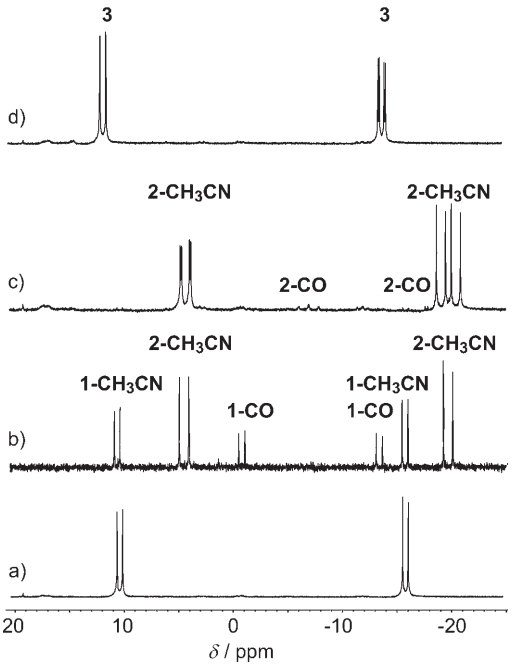
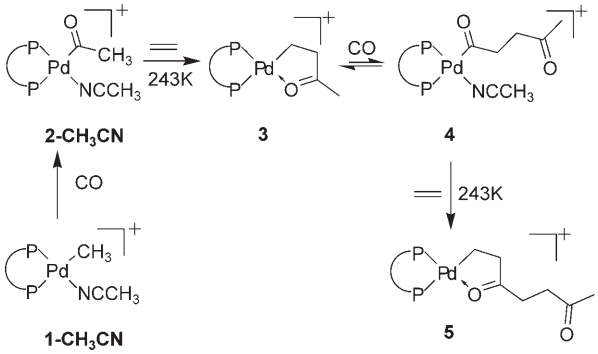


Figure 1. $^{31}P\{^1H\}$ NMR spectra recorded in dichloromethane/CH$_3$CN (9:1) at 193 K of key stages in the hydride cycle: a) [Pd(dibpp)(CH$_3$)(CH$_3$CN)]OTf **(1-CH$_3$CN)**; b) after bubbling CO through the sample, at 213 K, for 1 min; c) after bubbling ^{13}CO through a new sample, at 213 K, for 5 min, then purging with N_2 at 213 K; d) after bubbling C_2H_4 through the sample, at 213 K, for 5 min, then purging with N_2 at 213 K (see Scheme 3 for labeling scheme).



Scheme 3. Chain propagation in the hydride cycle.

Propagation: A survey of the relevant literature from the groups of Bianchini,[15] Brookhart,[28,29] Elsevier,[35] Nozaki,[38] and van Leeuwen[14] reveals that, for *cis*-Pd^{II}(diphosphine) complexes of the type encountered in this chemistry, ^{13}C NMR spectroscopic shifts and P,C coupling constants allow unambiguous assignment of the carbonyl groups in Pd−CO complexes (in Pd−Me complexes: $\delta_C \approx 180$–183 ppm; in Pd–acyl complexes $\delta_C \approx 175$–177 ppm, $^2J(P_{trans},C) \approx 80$ Hz, $^2J(P_{cis},C) \approx 20$ Hz), in Pd−C(O)R complexes ($\delta_C \approx 222$–239 ppm, $^2J(P_{trans},C) \approx 90$ Hz, $^2J(P_{cis},C) \approx 10$ Hz), and in Pd–(β chelate) complexes ($\delta_C \approx 237$–242 ppm, $^2J(P_{trans},C) \approx 0$ Hz, $^2J(P_{cis},C) \approx 12$ Hz).

*Insertion of CO into the first generation Pd–alkyl complex **1***: In contrast to Toth and Elsevier's report,[35] but in agree-

ment with that of Brookhart et al.,[29] we find that bubbling CO briefly (a few seconds) through a solution of **1-OTf** in CH_2Cl_2 at low temperature affords a short-lived intermediate that can be assigned as the cation [Pd(dibpp)-$(CH_3)(CO)]^+$ ([**1-CO**]OTf). Thus, the $^{13}C\{^1H\}$ NMR spectrum of [**1-^{13}CO**]OTf (Table 1) consists of a doublet of doublets at $\delta_C = 181.6$ ppm with $^2J(P_{trans},CO) = 114$ Hz and $^2J(P_{cis},CO) = 16$ Hz; values of δ_C and ^2J(P,C) similar to those reported for other Pd–methyl carbonyl complexes containing diphosphine ligands.[29,35] The $^{31}P\{^1H\}$ NMR spectrum of [**1-^{13}CO**]OTf shows two doublets of doublets at $\delta_P = -0.5$ (^2J(P,P) = 47 Hz) and −12.3 ppm ($^2J(P,CO) = 114$, 16 Hz). When excess CO[37] is bubbled through a solution of **1** in dichloromethane, migratory insertion of CO proceeds to completion. Thus, the resonances of **1-CO** disappear from the $^{31}P\{^1H\}$ NMR spectrum to be replaced by those of the acyl cation [Pd(dibpp){C(O)CH_3}(CO)]$^+$ ([**2-CO**]) at $\delta_P = -19.2$ ($^2J(P_{trans},C(O)CH_3) = 88$ Hz, $^2J(P_{cis},CO) = 5$ Hz) and −6.7 ppm ($^2J(P_{trans},CO) = 80$ Hz, $^2J(P_{cis},C(O)CH_3) = 20$ Hz), as shown in Table 2. The $^{13}C\{^1H\}$ NMR spectrum of [**2-CO**]OTf (Table 2) consists of two doublets of doublets at $\delta_C = 235.2$ and 176.9 ppm that can be assigned to the acyl and CO ligands, respectively; $^{13}C,^{13}C$ coupling between the acyl and carbonyl carbon atoms is not observed, as has previously been reported.[35] The large P,P coupling constant in **2** (ca. 70 Hz) compared with ^2J(P,P) (ca. 41 Hz) for the Pd–methyl complexes **1** is diagnostic for the formation of Pd–acyl complexes in this system. Both coordination of CO to the palladium center, and the migratory insertion reaction are readily reversible. For example, CO is displaced from [**2-CO**]OTs on being purged briefly with nitrogen at 193 K. Similarly, the acyl complex [**2-CO**]OTf exists in equilibrium with the corresponding methyl complex [**1-CO**]OTf in the absence of excess CO.

Insertion of alkene into Pd–acyl complexes: The second propagation step, alkene insertion into Pd–acyl complexes analogous to **2**, has been much studied and gives a "second-generation" alkyl complex in which the ketonic oxygen coordinates to the metal to form a five-membered ring.[39–42] The chelate ring is quite stable, even in the presence of strongly coordinating solvents and anions.[41] Similar complexes were obtained in this work by insertion of ethene into the Pd–acyl complexes **2** (Figure 1d, Scheme 3, Table 3). Thus, bubbling ethene through a solution of [Pd(dibpp){C(O)CH_3}(CH_3CN)]OTf ([**2-CH_3CN**]OTf) in CH_2Cl_2/CH_3CN (9:1) gives [Pd(dibpp)-$(CH_2CH_2C(O)CH_3)$]OTf ([**3**]OTf), the chelating Pd–alkyl complex, immediately. The $^{13}C\{^1H\}$ NMR spectrum of **3** (Table 3) shows a doublet at $\delta_C = 236.0$ ppm; the chemical shift and P,C coupling constant of 10 Hz are characteristic of an intramolecular chelating β-ketone structure.[42] The chelate ring is not opened in the presence of strongly coordinating ligands, such as CH_3CN or CF_3COO^- (TFA^-), at 243 K, consistent with the general assumption that such chelates are the resting state of the catalyst in the copolymerization reaction.[1,33]

It is noteworthy that the ethene-insertion reaction is not inhibited by the presence of CH_3CN or TFA^-, which are relatively strong donors to the Pd(dibpp) center (see below). For example, when ethene was passed through a solution of [Pd(dibpp){C(O)CH_3}(TFA)] (**2-TFA**) in CH_2Cl_2/CH_3CN (9:1), the palladium chelate analogous to **3** above was formed.

Insertion of CO into the second-generation alkyl complex, and of ethene into the second-generation acyl complex: Subsequent insertions of CO and alkene giving second- and

Table 2. NMR spectroscopic data recorded at 193 K for the Pd–acyl complexes **2**.

Compound	$^{31}P\{^1H\}$ δ [ppm] mult.[b] ^2J(P,P) [Hz] P *cis* to Ac	P *trans* to Ac	$^{13}C\{^1H\}$[a] δ [ppm] mult.[b] ^2J(P,C) [Hz]
[**2-CH_3CN**]OTf	5.4 d 70	−19.6 d 70	242.6 dd 112, 10
[**2-CO**]OTf	−6.7 d 73	−19.2 d 73	235.2 dd 88, 5; 176.9 dd 80, 20
[**2-CH_3OH**]OTf	13.4 d 66	−19.1 d 66	243.0 dd 116, 12
[**2-H_2O**]OTf[64]	4.9 d 70	−19.7 d 70	243.9 dd 113, 10
2-TFA	10.0 d 67	−15.8 d 67	247.8 dd 125, 10
[**2-CH_3CN**]TFA	4.9 d 70	−19.7 d 70	242.8 dd 112, 10
[**2-CO**]TFA	−6.1 d 73	−18.5 d 73	234.7 dd 88, 6; 176.9 dd 79, 20
2-OTs	12.5 d 70	−16.6 d 70	244.6 dd 122, 12
[**2-CH_3CN**]OTs	4.9 d 70	−19.7 d 70	242.6 dd 113, 10
[**2-CO**]OTs	−6.8 d 73	−18.6 d 73	235.5 dd 88, 5; 176.9 dd 80, 20
[**2-CH_3OH**]OTs	13.4 d 66	−19.2 d 66	245.5 dd 117, 12

[a] Recorded using ^{13}CO. $^2J(P_{trans},C)$ given first, ^2J(C,C) not resolved. [b] Multiplicity.

Table 3. NMR spectroscopic data recorded at 193 K for the complexes shown in Scheme 3.

Compound	$^{31}P\{^1H\}$ δ [ppm] mult.[b] ^2J(P,P) [Hz] P *cis* to C_{org}[d]	P *trans* to C_{org}[d]	$^{13}C\{^1H\}$[a] δ [ppm] mult.[b] ^2J(P,C) [Hz][c]	
[**3**]OTf	12.7 d 46	−13.5 d 46	236.0 d 10	
[**4-CH_3CN**]OTf[e]	3.9 d 69	−19.1 d 69	240.3 dd 115, 10	208.0 s
[**4-CO**]OTf	−7.3 d 72	−18.9 d 72	235.6 dd 90, 4; 177.8 dd 80, 20	207.7 s
[**5**]OTf	14.7 d 47	−13.6 d 47	237.4 d 10	206.4 s

[a] Recorded using ^{13}CO. Pd–*C*(O)R given first. [b] Multiplicity. [c] $^2J(P_{trans},C)$ given first. [d] C_{org} refers to the directly bonded carbon of the organic ligand. [e] ^2J(C,C) not resolved.

third-generation acyl and alkyl complexes have been less studied but are of importance here because we are interested in the factors that might determine whether an ester or copolymer product is produced.

In agreement with Drent,[33] we find that in contrast to the insertion into the Pd–CH_3 bond described above, insertion of CO into the second-generation alkyl complex does not go to completion at low pressures (<1 bar). Thus, on passing CO at 243 K through the solution of **3** in dichloromethane/CH_3CN (9:1) prepared above, a 1:1 mixture of **3** and the second-generation Pd–acyl complex [Pd(dibpp)-{C(O)CH_2CH_2C(O)CH_3}L]OTf **4-L** (L = CH_3CN, CO) was obtained. **4-CH_3CN** shows resonances in the $^{13}C\{^1H\}$ NMR spectrum at δ_C = 240.3 ($^2J(P_{trans},C)$ = 115 Hz, $^2J(P_{cis},C)$ = 10 Hz) and δ_C = 208.0 ppm as expected for the carbonyl carbon atoms in the Pd–*C*(O)CH_2CH_2*C*(O)Me group. An additional resonance is seen in the $^{13}C\{^1H\}$ NMR spectrum of **4-CO** at δ_C = 177.8 ppm ($^2J(P_{trans},C)$ = 80 Hz, $^2J(P_{cis},C)$ = 20 Hz), which confirms the presence of the Pd–*C*O group (Scheme 3, Table 3, Supporting Information Figure S5). Both "open" and chelating forms of complexes such as **4** can exist, with the position of the equilibrium being dependent on the ligand, alkene, and conditions of the reaction. Thus, Drent reports the exclusive formation of a six-membered chelate on reaction of [Pd(dppp)(CH_3)(OTf)] (dppp = bis(diphenylphosphino)propane) with CO/ethene in the solid state,[33] whereas Nozaki et al. report an equilibrium mixture of chelating and open forms for the γ ketone on exposing solutions of the Pd/(*R,S*)-BINAPHOS system to 1 bar of CO.[42] We find no resolvable P,C coupling between the γ-ketonic carbonyl and the phosphine ligand in our system, that is, no evidence for the formation of a chelating structure, which we attribute to the presence of residual acetonitrile from the starting material. Nozaki et al. also report opening of the six-membered ring by CH_3CN.[42] This contrasts with the chelation of the carbonyl oxygen of the β ketone in **3** and presumably reflects the intrinsic lower stability of six- versus five-membered rings. As required by the catalysis, **4** is unreactive toward CO insertion into the Pd–C(O)R bond. Thus, a Pd–acyl carbonyl species **4-CO** is formed in the presence of excess CO (see the Supporting Information for the experimental details).

The insertion of ethene into **4** occurs readily (Scheme 3, Table 3, Supporting Information Figure S5). A mixture of the second- and third-generation Pd–alkyl complexes, **3** and **5**, respectively, which can be distinguished in the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra, is formed. The additional resonance at δ_C = 206.4 ppm due to -CH_2CH_2*C*(O)Me in the $^{13}C\{^1H\}$ NMR spectrum of **5** confirms the increase in generation (see the Supporting Information, Figures S5 and S6). Complex **3** is present in the initial solution (see above); additional amounts of **3** may also be generated by deinsertion of CO from **4**. Drent has previously suggested that free CO catalyzes the insertion of ethene into the γ chelate by destabilizing the ring but did not observe the open γ-chelate intermediate analogous to **4-CO**.[33] Our observations are in accord with such a ring-opening mechanism and suggest that ethene is able to displace CH_3CN or CO from the Pd center even though these ligands seem to be more strongly coordinated to Pd than the oxygen atom of the γ chelate considered by Drent.

The carboalkoxy cycle: In the section above, we have demonstrated the propagation steps of the hydride cycles leading to ester and copolymer products by using Pd–dibpp catalysts. Rather than next discussing the termination steps of the hydride cycles mentioned above, we now present the initiation and propagation steps of the carbomethoxy cycles leading to ester and copolymer products. As we shall show, the most significant differences between the cycles occur in the termination rather than in the propagation steps as had previously been proposed. We therefore hold over discussion of termination in the hydride cycles until it can be discussed in conjunction with termination in the carbomethoxy pathway.

Synthesis of a Pd–methoxy complex: Although Pd–methoxy species have been proposed on many occasions as important intermediates in palladium-catalyzed reactions, there are few well-characterized examples of such complexes in the literature.[35]

Reaction of [Pd(dibpp)($CH_3CN)_2$](OTf)$_2$ with one equivalent of Et_3N in dichloromethane/CH_3OH/CH_3CN (9:1:trace) at 193 K gives a transient complex **6** (Figure 2, Scheme 4). Complex **6** can also be prepared, but less cleanly, by reaction of [Pd(dibpp)($CH_3CN)_2$](OTf)$_2$ with one equivalent of NaOMe (Supporting Information, Figure S8). Consistent

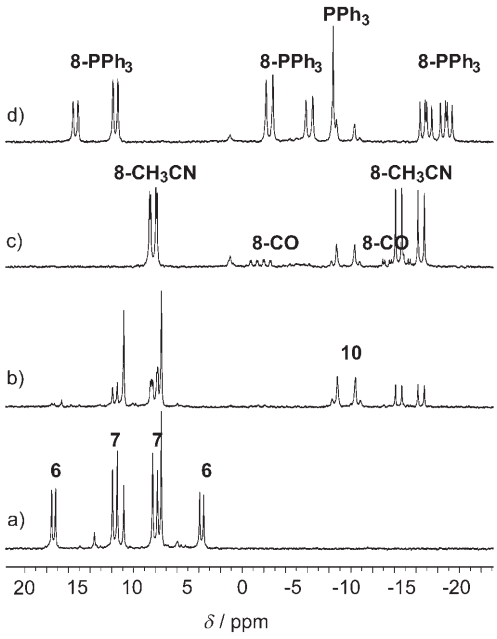
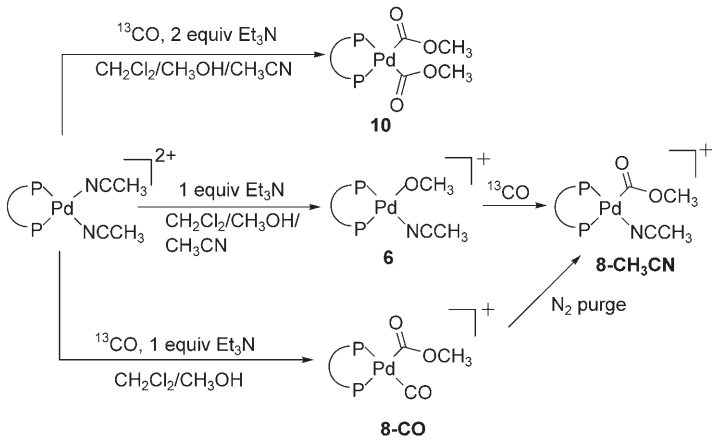


Figure 2. The formation of **8** via **6**: a) Et_3N (1 equiv) added to [Pd(dibpp)($CH_3CN)_2$](OTf)$_2$ in a mixture of CH_2Cl_2/CH_3OH (9:1) in the presence of CH_3CN (5 equiv) at 193 K; b) after ^{13}CO had been bubbled through the solution in (a) at 213 K; c) after 1 h at 243 K; d) after a slight excess amount of PPh_3 had been added to the solution in (c).



Scheme 4. Synthesis of palladium–carboalkoxy compounds as precursors for the carboalkoxy pathway.

with its synthesis, chemistry, and NMR spectra (Table 4), **6** is formulated as [Pd(dibpp)(OCH_3)(CH_3CN)]OTf. Elsevier and Toth have previously reported the preparation of [Pd{(*S*,*S*)-dbpp}(CH_3)(OCH_3)], ((*S*,*S*)-dbpp = (2*S*,4*S*)-2,4-bis-(diphenylphosphino)pentane) by metathesis reaction of [Pd{(*S*,*S*)-dbpp}(CH_3)Cl] with NaOMe[35] and was similarly unable to isolate the complex analytically pure. The $^{31}P\{^1H\}$ NMR spectrum of **6** shows two doublets at $\delta_P = 3.7$ and 17.0 ppm ($^2J(P,P) = 28$ Hz; Figure 2a) indicating inequivalent phosphorus donor sites. We favor a mononuclear, rather than a bridged dimeric structure for **6** because 1) a simple AB pattern is observed in the $^{31}P\{^1H\}$ NMR spectrum; Bianchini et al. report A_4 spectra in their related studies in which hydroxy-bridged complexes are observed[34,44] and, similarly, we observe a singlet at $\delta_P = 21.1$ ppm for [{Pd(dibpp)(μ-OH)}$_2$](OTf)$_2$; 2) bridged complexes seem to be the exception rather than the rule in this chemistry; and 3) there are no examples of [Pd_2(μ-OMe)(phosphine)] complexes in the Cambridge Crystallographic Database. The $^{13}C\{^1H\}$ NMR spectrum of **6** is, unfortunately, less informative, even when $^{13}CH_3OH$ is used in the preparation of **6**, due to fast exchange of Pd–OMe with the excess $^{13}CH_3OH$ present—excess methanol is essential to the preparation and stability of **6**, even at 193 K. Similarly, the ^1H NMR spectrum is not informative due to the severe overlap of the resonances of the Pd–OCH_3 group with those of the dibpp ligand and the excess methanol present. These observations are in accord with the report by Toth and Elsevier[35] in which it was noted that rapid exchange of the Pd–OCH_3 group with MeOH solvent prevents observation of the ^{13}C and ^1H NMR resonances of [Pd{(*S*,*S*)-dbpp}(CH_3)(OCH_3)]. Although the use of triethylamine as an acid scavenger is routine, we believe this is the first time it has been used in the synthesis of Pd–methoxy complexes.

Complex **6** does not undergo detectable β elimination at the low temperatures used in this study; formaldehyde, the organic product of such a decomposition, is not observed, even when using ^{13}C-labeled MeOH. We have not studied the decomposition pathways at higher temperature.

The remaining resonances in the $^{31}P\{^1H\}$ NMR spectrum of preparations of **6** (Figure 2a, Table 4) can be assigned tentatively as follows. The singlet at $\delta_P = 11$ ppm is also observed on addition of Et_3N to a solution of [Pd(dibpp)(CH_3CN)$_2$](OTf)$_2$ in CH_2Cl_2 (Supporting Information, page S80), that is, when -OCH_3 and CH_3OH are not present. This might be the bis-amine complex. The singlet at $\delta_P = 7$ ppm is observed when CH_3OH and CH_3CN are present and might be due to a bis-solvento complex. The pair of doublets at $\delta_P = 8.0$ and 11.7 ppm ($^2J(P,P) = 35$ Hz) is not observed in the reaction of [Pd(dibpp)(CH_3CN)$_2$](OTf)$_2$ with NaOMe to give **6**, that is, Et_3N is required to form **7** and is also not observed in the absence of CH_3CN or CH_3OH (compare Figure 2 with Figure S8 and page S80 in the Supporting Information). The chemical shift, δ_P, is sensitive to the *trans* ligand in these complexes; the close similarity in shifts observed between the resonances of **7** and those of the singlets leads us to propose that **7** is possibly [Pd(dibpp)(Et_3N)(L)](OTf)$_2$ (L = CH_3CN or CH_3OH or possibly OCH_3). The species responsible for these resonances appear to be in dynamic equilibrium with **6**, see below. Although **6** is only stable in the presence of excess methanol and at 193 K, the preparation of solutions of **6** allows access to the carbomethoxy chemistry and has enabled us to demonstrate, for the

Table 4. NMR spectroscopic data recorded at 193 K for the complexes shown in Schemes 4 and 5.

Compound	$^{31}P\{^1H\}$ δ [ppm] mult.[b] $^2J(P,P)$ [Hz]		$^{13}C\{^1H\}$[a] δ [ppm] mult.[b] $^2J(P,C)$ [Hz]
	P *cis* to C	P *trans* to C	
6	3.7 d 28	17.0 d 28	
7	8.0 d 35	11.7 d 35	
8-CH_3CN	8.3 d 47	−15.5 d 47	191.7 dd 167, 9, 4[c]
8-CO	−1.4 d 49	−14.1 d 49	185.5 dd 141, 9; 177.3 dd 98, 12
8-PPh_3	13.3 dd 298, 36; −4.3[d] dd 298, 50	−17.8 dd 50, 36	192.8 ddd 153, 5, 3
9	11.8 d 57	−3.8 d 57	190.3 dd 174, 18
10[e]	−8.2 d 45		203.0,[e] 152, 12, 6[f]
11	13.3 d 46	−12.0 d 46	193.3 d 10
12	29.2 d 57	−3.9 d 57	192.4 d 12
13	12.7 d 46	−12.6 d 46	179.0 dd 4, 2
14-CH_3CN	4.1 d 68	−18.6 d 68	241.5 dd 116, 9; 173.0 s
14-CO	−7.1 d 71	−18.6 d 71	234.9 dd 91, 5; 176.7 dd 81, 20; 172.7 s
15	13.2 d 46	−13.7 d 46	237.5 d 10; 174.0 s

[a] Recorded using ^{13}CO. Pd–*C*(O)X (X = OR or $CH_3CH_2C(O)OCH_3$) given first, Pd–CO last (if present); $^2J(P_{trans},C)$ given first, $^2J(C,C)$ not resolved. [b] Multiplicity. [c] ^{13}C NMR data obtained by using $^{13}CH_3OH$ as reactant. [d] $\delta(PPh_3)$. [e] AA′XX′ spin system. [f] $^2J(P_{trans},C)$, $^2J(P_{cis},C)$, then $^2J(C,C)$.

first time, complete carbomethoxy cycles leading to both ester and copolymer products.

Propagation

Insertion of CO into the Pd–methoxy complex: Pd–carboalkoxy complexes are usually prepared by transmetallation,[20,21] rather than by CO insertion reactions.[35,44,45] Indeed, although some reports of the synthesis of such complexes exist, for example, with phosphine,[10,13,20,22,35,44,46–49] bipyridine,[50] 2-pyridyldiphenylphosphine,[51] and PNP tridentate ligands such as 2-diphenylphosphinomethylenide-6-diphenylphosphinomethene pyridine,[52] and the syntheses of Pd–bis-carboalkoxy complexes containing phosphine or nitrogen[50] ligands have been reported, a general synthesis of Pd–mono-carboalkoxy complexes containing diphosphine ligands, by an insertion route, is absent from the literature.

On bubbling CO at 193–203 K through solutions containing **6**, the resonances of **6** disappear immediately to be replaced by those of a new complex **8-CH_3CN**, which can be formulated as [Pd(dibpp){C(O)OCH_3}(CH_3CN)]OTf on the basis of its $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra (Figure 2b, Table 4). On leaving **6** standing at 243 K, the additional species evident in Figure 2a are also converted to **8** (Figure 2b,c); we attribute this to rapid reaction of **6** with CO to give **8**, followed by slow re-equilibration of the solution generating additional amounts of **6** that then react immediately with CO. The operation of Le Chatelier's principle then results in nearly all material being converted into **8**. Traces of a Pd–bis-carboalkoxy complex **10** (see below) can also be seen in the spectrum at $\delta_P \approx -8$ ppm (Figure 2b).

Use of ^{13}CO and $^{13}CH_3OH$ in the reaction affords the doubly labeled analogue of **8-CH_3CN**, [Pd(dibpp)-{^{13}C(O)O$^{13}CH_3$}(CH_3CN)]OTf, the $^{31}P\{^1H\}$ NMR spectrum of which shows two doublets of doublets at $\delta_P = 8.3$ and -15.5 ppm with $^2J(P,P) = 47$ Hz, $^2J(P_{trans},C(O)OCH_3) = 167$ Hz, and $^2J(P_{cis},C(O)OCH_3) = 9$ Hz. The $^{13}C\{^1H\}$ NMR spectrum shows a doublet of doublets of doublets at $\delta_C = 191.7$ ppm with coupling constants of $^2J(P_{trans},C) = 167$ Hz, $^2J(P_{cis},C) = 9$ Hz, and $^2J(C,(O)OCH_3) = 4$ Hz. In this chemistry, Pd–acyl complexes have a carbon chemical shift in the range of $\delta_C \approx 222$–239 ppm, and show P,C coupling constants of $^2J(P_{trans},C) \approx 90$ Hz and $^2J(P_{cis},C) \approx 10$ Hz, whereas δ_C for Pd–carbonyl complexes is $< \approx 181$ ppm. There are fewer reports of ^{13}C NMR data for Pd–carbomethoxy compounds, for which shifts are typically in the range of 184–214 ppm.[35] Organic ester carbonyl carbon atoms typically resonate in the range 160–175 ppm, with the resonances of saturated esters being concentrated at the upfield end of this range. The observed phosphorus–carbon coupling constants ($^2J(P_{trans},C) = 167$ Hz, $^2J(P_{cis},C)$ 9 Hz) are inappropriate for either Pd–CO or Pd–acyl groups but are consistent with those reported by Elsevier and Toth[35] for a Pd–carbomethoxy group. We therefore assign the ^{13}C resonance at 191.7 ppm to the carbomethoxy carbonyl group of **8-CH_3CN**. Although the resonance of the methoxy carbon atom is overlapped by the strong resonance from $^{13}CH_3OH$, the presence of the methoxy group in **8-CH_3CN** is confirmed by an additional doublet splitting of the Pd–*C*OOMe carbon atom. The Pd–carboalkoxy carbonyl complex [Pd(dibpp){C(O)OCH_3}(CO)]OTf (**8-CO**) can be obtained in dichloromethane/CH_3OH (1:1), and shows resonances at $\delta_{C(O)OMe} = 185.5$ ppm ($^2J(P_{trans},C) = 141$ Hz, $^2J(P_{cis},C)$ 9 Hz) and $\delta_{CO} = 177.3$ ppm ($^2J(P_{trans},C) = 98$ Hz, $^2J(P_{cis},C) = 12$ Hz). The carbon chemical shifts, in conjunction with the J(P,C) values, clearly distinguish the carboalkoxy and carbonyl ligands (Table 4). Addition of a small excess of PPh_3 to a solution of **8-CH_3CN** gives **8-PPh_3**, the $^{31}P\{^1H\}$ NMR spectrum of which shows three doublet of doublets of doublets due to coupling between the phosphorus nuclei and the $^{13}C(O)OCH_3$ of the carbomethoxy ligand (Figure 2d, Table 4, see the Supporting Information for the spectral simulation). The $^{13}C\{^1H\}$ NMR spectroscopic data for **8-PPh_3** are given in Table 4 and are in complete accord with the proposed formulation. The magnitudes of ^2J(P,C) confirm that PPh_3 is oriented *cis* to the carbomethoxy ligand.

Variation of the procedure above allows the preparation of related complexes; thus, the bis(diphenylphosphino)propane (dppp) analogue of **8**, [Pd(dppp){C(O)OCH_3}-(CH_3CN)]OTf **9**, can be prepared from [Pd(dppp)-(CH_3CN)$_2$](OTf)$_2$ by an analogous procedure (Table 4). Complexes **8** and **9** are quite stable in a CH_3OH/CH_2Cl_2 mixture at low temperatures and solutions of **8-CH_3CN** may be taken to dryness and the oil redissolved in dichloromethane without change in the NMR spectra.

Use of two or more equivalents of triethylamine in the reaction affords the bis-carbomethoxy complex [Pd(dibpp){C(O)OCH_3}$_2$] **10**. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of **10** show AA′XX′ second-order patterns due to the magnetic non-equivalence of the phosphorus and of the carbonyl carbon nuclei as a result of the use of ^{13}CO. The chemical shifts and coupling constants ^2J(P,P), $^2J(P_{trans},C)$, and $^2J(P_{cis},C)$ (Table 4) were obtained by means of simulation by using gNMR (see the Supporting Information) and confirmed experimentally by using ^{12}CO. The carbon chemical shifts and P,C coupling constants of **8** and **10** support their formulation as the mono- and bis-carboalkoxy complexes, respectively. Complex **10** appears to be a thermodynamic sink for the reaction, thus, we find no evidence for deinsertion of CO from **10** or for conversion of **10** into **8**.

Mechanism of formation of 8: Complex **8** could be formed either by insertion of CO into the Pd–OMe bond of **6** or through attack of the external methoxide on a Pd–CO moiety. Insertion of CO into Pt–OCH_3 bonds has been reported,[53–55] but there is only one previous report of insertion of CO into a (diphosphine)Pd–OCH_3 bond.[35,56] On the other hand, a recent theoretical study found that CO insertion into the Pd–OCH_3 bond is thermodynamically favorable compared with insertion into a Pd–CH_3 bond; the former being driven by the stronger C–O bond that is formed in the carboalkoxy complex compared with the C–C bond of the acyl species.[57]

The concomitant disappearance of the resonances of **6** and the appearance of the resonances of **8** on reaction of **6** with CO, suggests an insertion pathway. However, the absence of an observable Pd–methoxy carbonyl intermediate, in contrast to the observation of the Pd–methyl carbonyl intermediate **1-CO** in the hydride cycle, means it is possible that rapid reaction of methoxide ions with traces of an unobserved Pd–CO species could be occurring, that is, differentiating CO insertion and attack of external methoxide is not straightforward.

The reaction of CO with the Pd–OMe complex is reversible, as previously shown by Toth and Elsevier,[35] and is confirmed in our system by an isotope-exchange experiment between $[Pd(dibpp)\{^{13}C(O)OCH_3\}L]^+$ (**8**) and ^{12}CO, Figure 3a–c. Exchange in **8-CH_3CN** requires approximately 60 h to approach completion at 243 K. The exchange is strongly suppressed on addition of PPh_3 to the solution, indeed **8-PPh_3** is essentially inert with respect to deinsertion over a period of 60 h at 243 K, Figure 3d–f. It is difficult to see how a spectator ligand at palladium might block direct dissociation of methoxide from the $C(O)OCH_3$ ligand, thus, the most likely explanation for the difference in reactivity of **8-CH_3CN** and **8-PPh_3** is that a deinsertion pathway operates. The "good" ligand PPh_3 (see below) blocks the fourth coordination site in the square plane at Pd in **8-PPh_3** preventing the deinsertion reaction,[58] whereas less-good ligands, that is, CO or CH_3CN, can be displaced from the square plane into the apical site allowing the deinsertion reaction to proceed in **8-CH_3CN** and **8-CO**. Operation of the Law of Microscopic Reversibility then requires that the forward reaction follows an insertion pathway rather than direct intermolecular attack of methoxide on a carbonyl ligand. Thus, we conclude that a direct insertion mechanism is probable.

Insertion of C_2H_4 into Pd–carbomethoxy complexes: In the section above, the CO insertion step of the carbomethoxy cycle was demonstrated. Alkene insertion into the Pd–carbomethoxy bond is also problematic because it has been reported that simple alkenes do not insert into the Pd–carboalkoxy bond. For example, Dekker et al.[22] reported that "Complexes $[(\widehat{PP})Pd\{C(O)OCH_3\}(PPh_3)]OTf$ ($\widehat{PP}$ = dppe, dppp, or dppb) underwent no reaction with styrene or methyl acrylate during 5 days." and Cavinato and Toniolo report that "When [*trans*-$[PdCl\{C(O)OCH_3\}(PPh_3)_2]$] is treated at 95 °C with 1-hexene…the starting complex is recovered almost quantitatively (92 %)."[13] This lack of reactivity has been cited as evidence for hydroalkoxycarbonylation of alkenes not proceeding by a carboalkoxy cycle.[7,12–14] In contrast, we find ready insertion of ethene into the Pd–carbomethoxy compounds **8-CH_3CN** and **8-CO**, at 243 K, to give $[Pd(dibpp)(CH_2CH_2C(O)OCH_3)]^+$ (**11**) quantitatively after 30 min. Complex **11** has been characterized by using $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy (Table 4). Similarly, $[Pd(dppp)(CH_2CH_2C(O)OCH_3)]^+$ (**12**) can be obtained from **9** under identical conditions (Table 4). The organic ligand chelates Pd through coordination of the oxygen atom of the carbonyl group as evidenced by the presence of coupling between the carbonyl carbon and the phosphine ligand at $\delta_P = -12.0$ ppm (J(P,C) = 10 Hz) and by the downfield shift of the carbonyl carbon, $\delta_C = 193.3$ ppm, in **11**

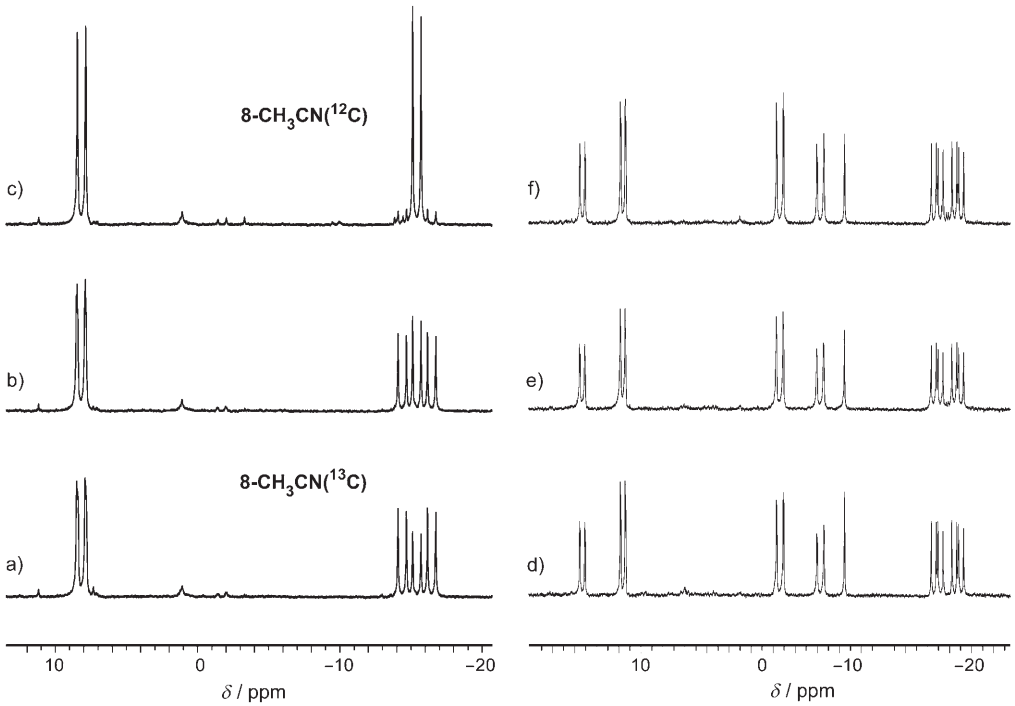


Figure 3. Scrambling of ^{12}CO with **8-CH_3CN** and **8-PPh_3** labeled with ^{13}C at the carbonyl group of the carbomethoxy ligand. a)–c) **8-CH_3CN** after 1, 2.5, and 60 h, respectively; d)–f) **8-PPh_3** after 1, 2.5, and 60 h, respectively.

(Table 4). Inspection of the values in Table 1 suggests that the phosphine oriented *trans* to the alkyl carbon is expected to show a δ_P signal in the region −11 to −16 ppm. We therefore assign the P,C coupling to the phosphorus ligand oriented *cis* to the carbonyl group in accord with earlier work.[42] Although chelation is well known in β-ketone complexes, there have been few reports of such chelation in β-ester compounds.[59] The chelating structure in **11** is readily disrupted. Thus, addition of 0.05 mL CH_3CN (30 equiv with respect to palladium) to a solution of **11** in dichloromethane results in immediate replacement of the NMR spectroscopic resonances of **11** by those of $[Pd(dibpp)\{CH_2CH_2C(O)OCH_3\}(CH_3CN)]^+$ (**13**) (Table 4) as a result of displacement of the chelating carbonyl of the ester ligand from Pd by CH_3CN. Thus, the doublet at $\delta_C = 193.3$ ppm in the $^{13}C\{^1H\}$ NMR spectrum due to the chelating carbonyl of ester **11** is replaced by a doublet of doublets $\delta_C = 179.0$ ppm, a shift characteristic of the carbonyl group of a free ester. Interestingly, long-range coupling to both phosphorus atoms is well resolved in **13**, $^4J(P,C) = 2$ and 4 Hz, and is assigned to coupling to the phosphorus donor oriented *cis* and *trans* to the ester ligand, respectively. The absence of observable coupling to the *trans* P in **11** may reflect cancellation of the coupling through the organic backbone of the chelate by coupling through Pd, a coupling pathway not present in **13**.

The five-membered ring structure can be regenerated by evaporation of the solvents and redissolution of the solid residue in dichloromethane, thus supporting our assignments of **11** and **13** as the chelate and open structures, respectively. The stability of the chelating structure in the β-ester complex is, however, quite weak compared with that of the β-ketone compounds **3**, which can be dissolved in CH_3CN/CH_2Cl_2 (10% v/v) without change.

Although palladium complexes analogous to **11** have been prepared by insertion of methyl acrylate into a Pd–methyl bond,[60] and insertion of norbornadiene into a Pd–carboalkoxy bond has been reported,[22] we believe **11** is the first example of such a complex being formed from insertion of ethene into a Pd–$C(O)OCH_3$ bond at ambient pressure. The formation of **11** from **8-CH_3CN** is in stark contrast to the reports of Cavinato and Toniolo and Elsevier et al. We were therefore interested to investigate the origins of this difference in reactivity.[13,22]

Mechanism of insertion of C_2H_4 into the Pd–C(O)OR bond: Theoretical studies indicate that insertion at square planar d^8 metal centers has a lower energy barrier than insertion in the analogous five-coordinate complex,[58] that is, in the lowest-energy pathway the incoming alkene must first displace the ligand occupying the fourth site in the square plane around the Pd center. The relative affinity for the fourth coordination site at Pd of this "spectator" ligand can, therefore, have a pronounced influence on the chemistry.

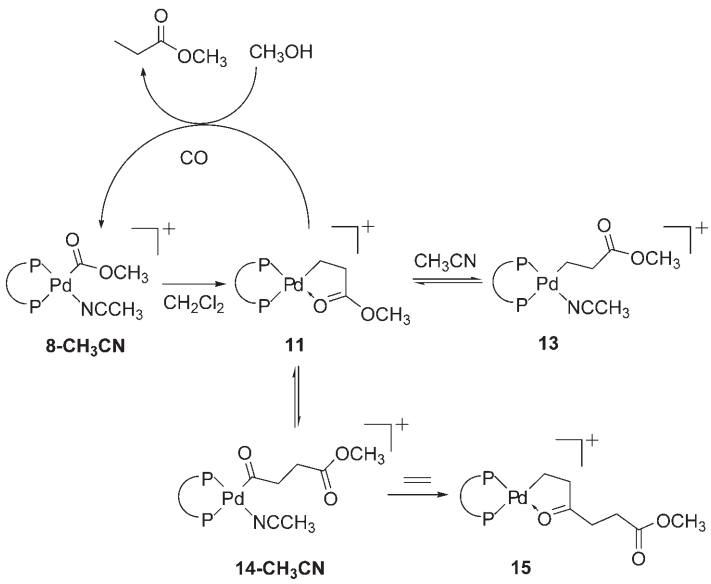
We have previously shown by means of competition studies that the relative affinities for the Pd(dibpp) center of the various coordinating groups used in this study is $TFA^- > CH_3CN > CO > OTs^- > CH_3OH > OTf^-$.[24] We have now extended these studies and find, as expected, that, in the solvent systems used, the affinities for Pd^{II} of Cl^- and PPh_3 are comparable, and much greater than all other monodentate ligands used in this work. The ordering of ligands is determined by both enthalpic and entropic factors. For example, the equilibrium constant for Equation (1) was measured over the temperature range 193–233 K, allowing ΔG (at 193 K), ΔH, and ΔS to be determined as $-5.1\ kJ\,mol^{-1}$, $15.8\ kJ\,mol^{-1}$, and $108.2\ KJ\,mol^{-1}$ respectively. The large, positive entropy change presumably reflects changes in solvation on coordination of the TFA^- anion to the Pd center. The position of the anions with respect to the neutral ligands in the series above will therefore be solvent dependent.

$$\textbf{1-CH}_3\textbf{CN} + TFA \rightleftharpoons \textbf{1-TFA} + CH_3CN \quad (1)$$

This ordering of ligand affinities allows us to account for the difference between the results of van Leeuwen et al. and Toniolo et al., and ours. In the former, a tightly bound ligand, that is, chloride or phosphine, imposes a high energy barrier on the reaction. Whereas, in **8-CH_3CN**, the absence of a strongly bound ligand in the fourth coordination site on Pd allows the intrinsic activity toward migratory insertion of ethene into the Pd–$C(O)OCH_3$ bond to be observed for the first time. In accord with this explanation, we find **8-PPh_3** does not react with ethene.

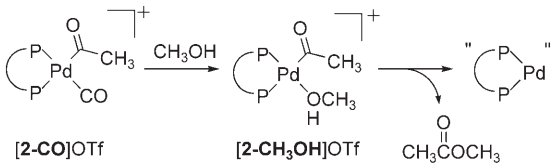
Our result is clearly incompatible with the existing consensus that slow, or nonexistent, alkene insertion into the Pd–C(O)OR bond is responsible for the dominance of the hydride pathway in hydroesterification. Clearly, the reason for this dominance must lie elsewhere in the reaction pathway. We therefore next investigated insertion of CO into the Pd–carbon bond of **11** and **13**.

Insertion of CO into palladium β-ester complexes: On exposure of a mixture of **11** and **13** in CH_3CN/CH_2Cl_2 (10% v/v) to CO at 243 K, insertion of CO into the chelate complex **11** occurs immediately (Scheme 5). This is evidenced by the disappearance of the resonances of the chelate from the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra and their replacement by the resonances of a new complex that can be assigned to the Pd–acyl cation $[Pd(dibpp)\{C(O)CH_2CH_2C(O)OCH_3\}(CH_3CN)]^+$ (**14-CH_3CN**) on the basis of resonances at $\delta_C = 173.0$ (singlet, ester carbonyl) and 241.5 ppm (doublet of doublets, $^2J(P,C) = 116$, 9 Hz, acyl carbon; Table 4). However, the resonances of **13**, the open ester, remain unchanged over the same period of reaction indicating that, under these conditions, CO is unable to displace the coordinated CH_3CN; this is in agreement with the relative ordering of affinities of the ligands for palladium discussed above and the relatively weak chelating ability of the ester carbonyl, and with our mechanistic proposal above, that is, that ethene cannot access a site in the square plane of Pd in **13** prior to insertion due to the presence of the "hard to displace" acetonitrile ligand. In a CH_2Cl_2/CH_3OH (1:1) mixture



Scheme 5. Reactions and intermediates involved in the carboalkoxy pathway.

Methanolysis of Pd–acyl complexes: Alcoholysis of the acyl intermediate has been studied by both van Leeuwen et al. and Bianchini et al. Van Leeuwen et al. concluded that methanolysis of the acyl group must occur by intramolecular attack of *cis*-coordinated CH_3OH on the acyl carbon atom (Scheme 6).[14,44] However, in a later paper, Bianchini et al. showed that direct intermolecular attack of CH_3OH at the acyl carbon atom probably occurs in [Pd(dppomf)-{C(O)CH_3}]OTs (dppomf = 1,1′-bis(diphenylphosphino)octamethylferrocene) because methanolysis is fast whereas the cation is unreactive toward ethene.[62,63]



Scheme 6. Methanolysis of the palladium–acyl intermediate.

or pure CH_3OH, CO insertion into **11** occurs smoothly to give a new acyl complex that can be assigned as [Pd(dibpp){C(O)CH_2CH_2C(O)OCH_3}(CO)]$^+$ (**14-CO**) on the basis of its $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra (Table 4). Bubbling ethene through a solution of **14** gives the second-generation palladium β-chelate **15**, with a pendent ester group (Scheme 5); further chain propagation is essentially identical to that of the Pd–hydride cycle, thus alkene/CO copolymerization through the carboalkoxy cycle is demonstrated.

On the whole, our results indicate that there is no intrinsic barrier to reaction in the propagation steps of the carboalkoxy pathways for hydroesterification and copolymerization. Indeed the propagation steps in both cycles, namely, CO insertion into a Pd−OMe or Pd−alkyl bond, and ethene insertion into a Pd−H or Pd−COOR bond all occur readily at or below 243 K. We therefore next investigated the termination steps in both pathways.

Termination: The termination steps of the reaction have been little studied in comparison with the propagation steps, with most information being derived from an analysis of the end groups of the polymer chain.[5] Notable exceptions to this are the recent studies by the groups of van Leeuwen and Zuideveld[14,61] and Bianchini,[62] and ourselves[23,24] that have succeeded in identifying some or all of the intermediates involved in alcoholysis of the acyl and alkyl intermediates.

We were particularly interested in whether or not there were any significant, qualitative differences in the rates of termination leading to an ester product in the two pathways; termination leading to an ester product in the hydride cycle requires methanolysis of the Pd–acyl intermediate, and regenerates a Pd−H initiator, whereas methanolysis of the Pd–β-chelate intermediate, regenerating a Pd−OMe initiator, is required in the carbomethoxy cycle.

The preparation of the series of acyl complexes **2** (Table 2), and the ordering of the relative affinities of the various potential ligands for the Pd^{II} center, described above, allows us to probe directly, for a highly active catalytic system, whether or not coordination of methanol to palladium is a prerequisite for methanolysis of the acyl ligand or whether direct attack by methanol from the solvent on the acyl group is responsible for the methanolysis. Effects due to variation of, for example, the diphosphine ligand are excluded, that is, the system has a "free choice" between inter- and intramolecular pathways.

In a typical reaction, methanol (10% v/v) was added at low temperature to a solution of the Pd–acyl complex **2** in CH_2Cl_2 and the progress of the reaction was monitored by using $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy. We found that if the ligand in the fourth site is weakly coordinating, methanolysis occurs on the timescale of tens of minutes at 243 K; methyl acetate was detected by means of $^{13}C\{^1H\}$ NMR spectroscopy as the only organic product of the reaction. The methanol complex [**2-CH_3OH**]OTf is observed as an intermediate in the reaction (Scheme 6).[64] However, in the presence of a moderately coordinating ligand such as TFA^- or CH_3CN, the fourth coordination site, in CH_2Cl_2, is blocked to the methanolysis reaction; **2-MeOH** is not observed. On warming these solutions to 293 K, decarbonylation reactions dominate, in line with the ready reversibility of migratory insertion in these systems in the absence of CO.[14]

Thus, in the Pd–dibpp hydride pathway, methanolysis proceeds at 243 K by coordination of CH_3OH to Pd, followed by intramolecular nucleophilic attack on the acyl carbon atom and the pathway is not affected by the acid (HOTs, HOTf) used, that is, as proposed by van Leeuwen et al. (Scheme 6).[14,65]

The reactivity of the trifluoroacetate complex **2-TFA** with CH_3OH in both CH_2Cl_2 and CH_2Cl_2/CH_3CN requires further comment. No reaction was observed at 243 K on addition of 1–10 equivalents of CH_3OH to a solution of **2-TFA** in CH_2Cl_2. However, addition of CH_3OH (10% v/v) to a solution of **2-TFA** in CH_2Cl_2 in the presence of ^{13}CO[66] resulted in immediate formation of [**2-CO**]TFA, detected in situ by using $^{31}P\{^1H\}$ NMR spectroscopy, followed by methanolysis to give methyl acetate. Thus, in the presence of near stoichiometric amounts of CH_3OH, TFA^- cannot be displaced because there is insufficient CH_3OH present to solvate the anion; the fourth coordination site on Pd is effectively blocked to incoming CH_3OH. However, in the presence of a large excess of CH_3OH, solvation by methanol (see above) aids displacement of the anion to give, in the presence of excess CO, [**2-CO**]TFA. Methanolysis of [**2-CO**]TFA then occurs by the mechanism shown in Scheme 6. This interpretation is supported by the observation that addition of CH_3OH (10% v/v) to a mixture of [**2-CH_3CN**]TFA and **2-TFA** in CH_2Cl_2/CH_3CN (9:1) results in complete conversion of **2-TFA** to [**2-CH_3CN**]TFA, which is resistant to methanolysis. These observations also provide an explanation for the previous reports of van Leeuwen et al.[14] and Clegg et al.[67] who found "surprisingly" that fast alcoholysis of Pd–acyl complexes was not retarded by TFA^-. It is now evident that the coordination strength of the TFA^- was lessened as a result of solvation by the alcoholic solvent used in those reports.

The organometallic product of the methanolysis is presumably the Pd–hydride $[Pd_2(\mu\text{-}H)(\mu\text{-}CO)(dibpp)_2]^{2+}$ by analogy with the report by Bianchini et al.[62] However, the major organometallic species isolated after the methanolysis reaction shows a singlet at $\delta = 21.1$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. An X-ray crystal-structure determination showed that the crystals contain the dicationic complex $[\{Pd(dibpp)(\mu\text{-}OH)\}_2]^{2+}$ in which the two Pd^{II} centers are bridged by two hydroxide ions. Coordination to the bidentate diphosphine ligands completes the square-planar environment of the Pd centers. The Pd–O distances within the planar four-membered Pd_2O_2 ring are on average 2.10 Å and thus similar to those of related complexes $[\{Pd(\widehat{LL})(\mu\text{-}OH)\}_2]^{2+}$ containing diphosphine ligands.[67–69] There are two triflate ions for every dicationic complex in the crystal structure. Both interact through hydrogen bonds with the hydroxide ions of the Pd complex (see the Supporting Information, Figure S15). $[\{Pd(dibpp)(\mu\text{-}OH)\}_2](OTf)_2$ is presumably formed by a decomposition pathway involving adventitious water. Other bond lengths and interbond angles mirror those reported by Bianchini et al. for similar μ-OH species and are given in the Supporting Information. Bianchini et al. have shown, in an in situ NMR spectroscopic study of ethene–CO copolymerization, that such species can act as catalyst precursors.[44]

Methanolysis of the Pd–β-chelate complexes: The methanolysis of Pd–alkyl complexes in the hydride pathway has been studied for diaryl phosphine ligands such as dppp and dppf (dppf = 1,1′-bis(diphenylphosphino)ferrocene),[62,63] and the intermediacy of a palladium enolate complex has been established by using deuterium labeling. Little work has been done, however, with complexes containing dialkyl diphosphines and the reaction in the carbomethoxy pathway has not previously been studied. Methanolysis of a mixture of the second- and third-generation Pd–alkyl complexes **3** and **5** was monitored periodically by using $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy as the temperature was raised from 193 to 292 K. The resonances of **3** disappear first to be replaced by two new doublets at $\delta = 12.8$ and -15.2 ppm ($^2J(P,P) = 52$ Hz), which can be attributed to a palladium–enolate intermediate by analogy with the work of van Leeuwen et al.[61] Concomitant with the disappearance of the resonances of **3**, a resonance at $\delta = 211.8$ ppm attributed to methyl ethyl ketone[71] appears in the $^{13}C\{^1H\}$ NMR spectrum. Almost complete methanolysis of **3** occurs at 292 K on the timescale of tens of minutes before significant methanolysis of **5** occurs. The large difference in methanolysis rates of the second- and third-generation β chelates, may indicate a trend which, if continued, would imply this termination pathway becomes less efficient as chain length increases, thus favoring copolymerization reactions.

When the methanolysis is performed under a CO atmosphere, the characteristic resonances of the Pd–carboalkoxy cation **8** are seen in both the $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra (Supporting Information, Figure S10). On bubbling ethene through the solution, insertion to give the β-chelate **11** is observed. Thus, crossover from the hydride to the carbomethoxy cycle is demonstrated, we believe, for the first time.

Methanolysis of palladium β-ester chelate: In contrast to methanolysis of the β-chelate complex **3** in the hydride cycle, methanolysis of **11** is found to be extremely slow, requiring several days at room temperature to reach completion, during which time methyl propanoate is the only identified organic product detected by $^{13}C\{^1H\}$ NMR spectroscopy. This difference in rate is in accord with the expected reactivities of α–β-unsaturated ketones and esters in the β-elimination/hydride conjugate addition mechanism for enolate formation as proposed by van Leeuwen et al. However, given the slowness of the reaction, which takes several days at 293 K, we have been unable to demonstrate conclusively, by using deuterium labeling, that the enolate pathway is followed exclusively, due to extensive decomposition/side reactions occurring. These have also prevented characterization of the organometallic products of the methanolysis reaction.

Thus, methanolysis of the β chelate, which is required in the carbomethoxy cycle to give an ester, is extremely slow relative to the insertion of CO into the Pd–alkyl bond, a situation that favors propagation and leads ultimately to the copolymer product. Whereas the required methanolysis of the Pd–acyl in the hydride cycle is competitive with further propagation. Bianchini and van Leeuwen et al. have previously noted the difference in rates of reaction of the acyl and alkyl intermediates with methanol.[44] We believe this

difference, which is even greater between the acyl in the hydride cycle and alkyl in the carbomethoxy cycle, is the explanation for the importance of the carboalkoxy cycle in copolymerization, in which propagation dominates, and the consensus that alkoxycarbonylation occurs almost exclusively by the hydride pathway, because termination by methanolysis of a Pd–acyl complex locks the catalysis into the hydride cycle. It is noteworthy that Cavinato et al. have recently shown that, although a Pd–carbomethoxy species [Pd(PPh$_3$)$_2${C(O)OCH$_3$}(OTs)] can be isolated from hydromethoxycarbonylation reactions starting from any of [Pd(PPh$_3$)$_2$(OTs)$_2$], [Pd(PPh$_3$)$_2${C(O)CH$_3$}(OTs)], or [Pd(PPh$_3$)$_2${C(O)OCH$_3$}(OTs)], this complex is converted into a Pd–hydride initiator through a water–gas shift mechanism.[45]

Conclusions

The intermediates involved in all the essential steps in the hydride cycles for ethene hydromethoxycarbonylation and CO–ethene copolymerization, namely, alternating insertions of CO and ethene to give first-, second-, and third-generation acyl and alkyl complexes; chain termination by methanolysis of the acyl intermediate via a Pd–acyl-methanol intermediate giving a Pd–hydride complex; and methanolysis of the alkyl intermediate via an enolate complex to give a presumed Pd–methoxy complex, which is transformed into a Pd–carbomethoxy complex **8** in the presence of CO, have been characterized by using ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR spectroscopy. The carbomethoxy complex can be used to initiate, and study, the carboalkoxy catalytic cycle, thus **8** reacts with ethene, giving **11**. Therefore, the palladium complexes involved in chain crossover from the hydride to the carboalkoxy cycles have been characterized for the first time.

Compound **8** has also been prepared by insertion of CO into the Pd−OMe bond of [Pd(dibpp)(OCH$_3$)(CH$_3$CN)]$^+$ **6**, which has allowed the Pd complexes involved in the carboalkoxy cycle for the hydrocarboxylation of alkenes/alkene–CO copolymerization and the interconversions between them to be established for the first time by using NMR spectroscopy. This has allowed the analogous reactions in the two pathways to be directly compared, for the same catalyst system, for the first time. This has revealed that alkene insertion into the Pd–carboalkoxy bond occurs readily, under similar conditions as, and on a similar timescale to, insertion of an alkene into the Pd−H bond. This is entirely consistent with the reported product distribution of the copolymerization reaction under actual catalytic conditions and contrasts with previous reports that insertion of simple alkenes into the Pd−C(O)OCH$_3$ bond was slow or did not occur. This latter observation has been shown to correlate with the presence of a strongly bound ligand in the fourth coordination site of the square-planar Pd center rather than an intrinsic barrier to insertion. Indeed, an intrinsic barrier to alkene insertion into the Pd−C(O)OCH$_3$ bond in the hydromethoxycarbonylation reaction would be remarkable given the necessity for such insertion to occur in the copolymerization reaction in order to explain the occurrence of diester- and diketone-terminated copolymer.

The observation that methanolysis of the β chelate in the carboalkoxy cycle is extremely slow relative to methanolysis of the Pd–acyl in the hydride cycle provides an alternative explanation for the importance of the carboalkoxy cycle in copolymerization, in which propagation dominates, and the consensus that alkoxycarbonylation occurs almost exclusively by the hydride pathway, because termination by methanolysis of a Pd–acyl complex locks the catalysis into a hydride pathway. The previously held explanation, that slow olefin insertion into the Pd–carboalkoxy bond was responsible for the dominance of the hydride pathway in hydrocarboxylation is clearly inconsistent with our results.

If this proves to be a general result, then it follows that any catalyst system that favors the carbomethoxy cycle must give copolymer, conversely, only catalyst systems that favor the hydride cycle are potential candidates for hydroesterification/hydroalkoxycarbonylation. This is an important result that has not previously been recognized, that overturns a previously widely held opinion, and has implications for the design of catalysts for these systems.

Experimental Section

General procedures: All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere by using Schlenk techniques. All solvents were carefully purified by means of appropriate procedures. CD_2Cl_2 was subjected to three freeze–pump–thaw cycles and stored over 4 Å molecular sieves. Air-sensitive compounds were stored under nitrogen at 243 K. NMR spectra were recorded on a Bruker AMX2-200 WB spectrometer. ^{13}CO (99 %) was used in experiments in which ^{13}C NMR data was recorded; for simplicity, CO is used to designate both natural abundance and enriched carbon monoxide. ^{13}CO was purchased from ISOTEK, ethene from BOC. 1,3-Bis(diisobutylphosphino)propane (dibpp) was prepared by reaction of diisobutylphosphine with 1,3-dibromopropane to give the double HBr salt, which was subsequently neutralized with sodium hydroxide and distilled to give the diphosphine product.[4] The Pd–dimethyl complexes [Pd(dibpp)(CH$_3$)$_2$] and [Pd(dibpp)(CH$_3$CN)$_2$](OTf)$_2$ were synthesized as described in the literature.[4] All other chemicals were purchased from Aldrich.

Preparation of [Pd(dibpp)(CH$_3$)(CF$_3$SO$_3$)] (1-OTf): [Pd(dibpp)(CH$_3$)$_2$] (64 mg, 0.14 mmol) was dissolved in CH_2Cl_2 (2 mL) in a 10 mm NMR tube and then cooled to 195 K. CF_3SO_3H (1 equiv, 7 μL) was then added and the solution was warmed to RT briefly until the ^{31}P{^{1}H} NMR spectrum indicated that the reaction had gone to completion. ^{31}P{^{1}H} NMR: δ_P = 18.8 (d, ^2J(P,P) = 41 Hz), −16.6 ppm (d, ^2J(P,P) = 41 Hz); ^{1}H NMR (CD_2Cl_2): δ_H = 0.36 ppm (d, ^3J(H,P) = 7 Hz; Pd−CH$_3$). The series of monomethyl complexes **1-X** and [**1-L**]**X** were prepared in a similar manner; specific details are given in the Supporting Information.

Preparation of [Pd(dibpp){C(O)CH$_3$}(CH$_3$CN)]$^+$[CF$_3$SO$_3$]$^-$ ([2-CH$_3$CN]OTf): Carbon monoxide was bubbled thoroughly (for a few minutes) through a solution of **1-CH$_3$CN** in a mixture of dichloromethane and acetonitrile (9:1) at 195 K, the solution was warmed to 243 K for 1 h when the ^{31}P{^{1}H} NMR revealed the quantitative formation of **2-CH$_3$CN**. ^{31}P{^{1}H} NMR: δ_P = 5.4 (d, ^2J(P,P) = 70 Hz), −19.6 ppm (d, ^2J(P,P) = 70 Hz); ^{13}C{^{1}H} NMR: δ_C = 242.6 ppm (dd, $^2J(P_{trans},C(O)CH_3)$ = 112 Hz, $^2J(P_{cis},C(O)CH_3)$ = 10 Hz). The series of acyl complexes **2-X** and [**2-L**]**X** were prepared in a similar manner; specific details are given in the Supporting Information.

Preparation of [Pd(dibpp)($CH_2CH_2C(O)CH_3$)]OTf (3): Ethene was bubbled through the solution of **[2-CH_3CN]**OTf at 195 K, and the progress of the reaction was monitored by using $^{31}P\{^1H\}$ NMR spectroscopy. **3** started to form after 15 min at 195 K; the reaction went to completion after 10 h at 243 K. $^{31}P\{^1H\}$ NMR: δ_P = 12.7 (d, ^2J(P,P) = 46 Hz), −13.5 ppm (d, ^2J(P,P) = 46 Hz); $^{13}C\{^1H\}$ NMR: δ_C = 236.0 ppm (d, $^2J(P,CH_2CH_2C(O)CH_3)$ = 10 Hz). Further CO and ethene insertions, performed in a similar manner to that described above, result in the formation of **4** and **5**. Experimental details and full multinuclear NMR spectroscopic characterization of all intermediates are given in the Supporting Information.

[Pd(dibpp){C(O)OCH_3}(CH_3CN)]OTf (8-CH_3CN): [Pd(dibpp)-($CH_3CN)_2$]($OTf)_2$ (42 mg, 0.05 mmol) was dissolved in a $CH_2Cl_2/CH_3OH/CH_3CN$ (9:1:trace) mixture saturated with CO at 193 K. Et_3N (1 equiv, 6.5 μL) was then added to give a clear yellow solution. Additional CO was bubbled through the solution to drive the reaction to completion. The solvents were evaporated quickly and the red oily residue extracted into CH_2Cl_2 (2 mL) as a yellow solution. $^{31}P\{^1H\}$ NMR: δ_P = 8.3 (d, ^2J(P,P) = 47 Hz), −15.5 ppm (d, ^2J(P,P) = 47 Hz); $^{13}C\{^1H\}$ NMR: δ_C = 191.7 ppm (dd, $^2J(P_{trans},C(O)OCH_3)$ = 167 Hz, $^2J(P_{cis},C(O)OCH_3)$ = 9 Hz). Analogous compounds **8-CO, 8-PPh_3**, and **9** were synthesized similarly. See the Supporting Information for specific details of their characterization and reactions. Subsequent ethene/CO insertions were performed in an analogous manner to **3** as described above. Full experimental details and characterization data are given in the Supporting Information.

CCDC-293551 contains the supplementary crystallographic data for [{Pd-(dibpp)(μ-OH)}$_2$]($OTf)_2$. These data may be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

The financial support of EPSRC, grant RG/R37685, is gratefully acknowledged.

[1] E. Drent, P. H. M. Budzelaar, *Chem. Rev.* **1996**, *96*, 663–681.
[2] A. Sen in *Catalytic Synthesis of Alkene–Carbon Monoxide Copolymers and Cooligomers, Vol. 27* (Ed.: A. Sen), Kluwer, Dordrecht, **2003**.
[3] a) "Special Report on the Industry's campaign for a better image": B. Wassener, *FT Chemicals*, Wed., September 8, **2004**, p. 3; b) *Hydrocarbon Process.* **2003**, *82*, 25; c) *Plast. Rubber Wkly.*, 1 July, **2005**.
[4] E. Drent, J. A. M. Vanbroekhoven, M. J. Doyle, *J. Organomet. Chem.* **1991**, *417*, 235–251.
[5] W. P. Mul, E. Drent, P. J. Jansens, A. H. Kramer, M. H. W. Sonnemans, *J. Am. Chem. Soc.* **2001**, *123*, 5350–5351.
[6] Z. Freixa, P. van Leeuwen, *Dalton Trans.* **2003**, 1890–1901.
[7] I. del Rio, C. Claver, P. van Leeuwen, *Eur. J. Inorg. Chem.* **2001**, 2719–2738.
[8] A. Seayad, A. A. Kelkar, L. Toniolo, R. V. Chaudhari, *J. Mol. Catal. A* **2000**, *151*, 47–59.
[9] A. Vavasori, L. Toniolo, G. Cavinato, F. Vistentin, *J. Mol. Catal. A* **2003**, *204*, 295–303.
[10] G. Cavinato, A. Vavasori, L. Toniolo, F. Benetollo, *Inorg. Chim. Acta* **2003**, *343*, 183–188.
[11] A. Seayad, S. Jayasree, K. Damodaran, L. Toniolo, R. V. Chaudhari, *J. Organomet. Chem.* **2000**, *601*, 100–107.
[12] G. Kiss, *Chem. Rev.* **2001**, *101*, 3435–3456.
[13] G. Cavinato, L. Toniolo, *J. Organomet. Chem.* **1990**, *398*, 187–195.
[14] P. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, A. L. Spek, *J. Am. Chem. Soc.* **2003**, *125*, 5523–5539.
[15] C. Bianchini, A. Meli, *Coord. Chem. Rev.* **2002**, *225*, 35–66.
[16] C. Bianchini, A. Meli, W. Oberhauser, *Dalton Trans.* **2003**, 2627–2635.
[17] R. A. M. Robertson, D. J. Cole-Hamilton, *Coord. Chem. Rev.* **2002**, *225*, 67–90.
[18] I. del Rio, C. Claver, P. W. M. N. van Leeuwen, *Eur. J. Inorg. Chem.* **2001**, 2719–2738.
[19] G. Consiglio, *Chimia* **2001**, *55*, 809–813.
[20] D. Milstein, *Acc. Chem. Res.* **1988**, *21*, 428–434.
[21] S. Otsuka, A. Nakamura, T. Yoshida, M. Naruto, K. Ataka, *J. Am. Chem. Soc.* **1973**, *95*, 3180–3188.
[22] G. Dekker, C. J. Elsevier, K. Vrieze, P. Vanleeuwen, C. F. Roobeek, *J. Organomet. Chem.* **1992**, *430*, 357–372.
[23] J. K. Liu, B. T. Heaton, J. A. Iggo, R. Whyman, *Angew. Chem.* **2004**, *116*, 92–96; *Angew. Chem. Int. Ed.* **2004**, *43*, 90–94.
[24] J. K. Liu, B. T. Heaton, J. A. Iggo, R. Whyman, *Chem. Commun.* **2004**, 1326–1327.
[25] W. Clegg, G. R. Eastham, M. R. J. Elsegood, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman, S. Zacchini, *J. Chem. Soc. Dalton Trans.* **2002**, 3300–3308.
[26] G. R. Eastham, B. T. Heaton, J. A. Iggo, R. P. Tooze, R. Whyman, S. Zacchini, *Chem. Commun.* **2000**, 609–610.
[27] J. A. Iggo, Y. Kawashima, J. Liu, T. Hiyama, K. Nozaki, *Organometallics* **2003**, *22*, 5418–5422.
[28] C. S. Shultz, J. Ledford, J. M. DeSimone, M. Brookhart, *J. Am. Chem. Soc.* **2000**, *122*, 6351–6356.
[29] J. Ledford, C. S. Shultz, D. P. Gates, P. S. White, J. M. DeSimone, M. Brookhart, *Organometallics* **2001**, *20*, 5266–5276.
[30] K. Nozaki, Y. Kawashima, K. Nakamoto, T. Hiyama, *Polym. J.* **1999**, *31*, 1057–1060.
[31] The ligand L occupying the fourth coordination site in the methyl **1**, acyl **2**, and so forth, compounds is given as part of the compound number. Thus, [Pd(dibpp)CH_3(CH_3CN)]OTf is designated as **1-CH_3CN** or **[1-CH_3CN]**OTf, and [Pd(dibpp)CH_3(TFA)] as **1-TFA**.
[32] Traces of water in the triflic acid seem to be unavoidable. [Pd-(dibpp)Me(H_2O)]OTf is always present as a minor species when dichloromethane is used as the solvent. The intensities of the resonances of this complex correlate with the amount of water present in the system; see the Supporting Information p. S38, S39. The AB pattern observed, and the close similarity of δ_P and ^2J(P,P) with those of other complexes **1-L**, strongly suggest a monomeric, rather than a bridged structure.
[33] W. P. Mul, H. Oosterbeek, G. A. Beitel, G. J. Kramer, E. Drent, *Angew. Chem.* **2000**, *112*, 1919–1922; *Angew. Chem. Int. Ed.* **2000**, *39*, 1848–1851.
[34] C. Bianchini, H. M. Lee, A. Meli, W. Oberhauser, M. Peruzzini, F. Vizza, *Organometallics* **2002**, *21*, 16–33.
[35] a) I. Toth, C. J. Elsevier, *J. Am. Chem. Soc.* **1993**, *115*, 10388–10389; b) I. Toth, C. J. Elsevier, *J. Chem. Soc. Chem. Commun.* **1993**, 529–531.
[36] R. I. Pugh, E. Drent, *Adv. Synth. Catal.* **2002**, *344*, 837–840.
[37] Henceforth ^{12}CO and ^{13}CO are not differentiated, all $^{13}C\{^1H\}$ NMR spectra and the $^2J_{P,C}$ in the $^{31}P\{^1H\}$ NMR spectra are obtained by using isotopically enriched ^{13}CO.
[38] K. Nozaki, H. Komaki, Y. Kawashima, T. Hiyama, T. Matsubara, *J. Am. Chem. Soc.* **2001**, *123*, 534–544.
[39] M. J. Green, G. J. P. Britovsek, K. J. Cavell, F. Gerhards, B. F. Yates, K. Frankcombe, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1998**, 1137–1144.
[40] F. C. Rix, M. Brookhart, P. S. White, *J. Am. Chem. Soc.* **1996**, *118*, 4746–4764.
[41] P. Braunstein, C. Frison, X. Morise, *Angew. Chem.* **2000**, *112*, 2989–2992; *Angew. Chem. Int. Ed.* **2000**, *39*, 2867–2870.
[42] K. Nozaki, N. Sato, Y. Tonomura, M. Yasutomi, H. Takaya, T. Hiyama, T. Matsubara, N. Koga, *J. Am. Chem. Soc.* **1997**, *119*, 12779–12795.
[43] R. I. Pugh, E. Drent in *Catalytic Synthesis of Alkene–Carbon Monoxide Copolymers and Cooligomers, Vol. 27* (Ed.: A. Sen), Kluwer, Dordrecht, **2003**, Chapter 2.
[44] C. Bianchini, A. Meli, W. Oberhauser, P. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev, A. M. Kal'sin, *Organometallics* **2003**, *22*, 2409–2421.

[45] G. Cavinato, L. Toniolo, A. Vavasori, *J. Mol. Catal. A* **2004**, *219*, 233–240.
[46] R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, *J. Mol. Catal.* **1993**, *84*, 165–176.
[47] A. Seayad, S. Jayasree, K. Damodaran, L. Toniolo, R. V. Chaudhari, *J. Organomet. Chem.* **2000**, *601*, 100–107.
[48] W. R. Moser, A. W. Wang, N. K. Kildahl, *J. Am. Chem. Soc.* **1988**, *110*, 2816–2820.
[49] W. Keim, J. Becker, A. M. Trzeciak, *J. Organomet. Chem.* **1989**, *372*, 447–451.
[50] G. D. Smith, B. E. Hanson, J. S. Merola, F. J. Waller, *Organometallics* **1993**, *12*, 568–570.
[51] A. Dervisi, P. G. Edwards, P. D. Newman, R. P. Tooze, S. J. Coles, M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.* **1999**, 1113–1120.
[52] A. Sacco, G. Vasapollo, C. F. Nobile, A. Piergiovanni, M. A. Pellinghelli, M. Lanfranchi, *J. Organomet. Chem.* **1988**, *356*, 397–409.
[53] J. E. Byrd, J. Halpern, *J. Am. Chem. Soc.* **1971**, *93*, 1634–1636.
[54] H. E. Bryndza, *Organometallics* **1985**, *4*, 1686–1687.
[55] H. C. Clark, R. J. Puddephatt, *Inorg. Chem.* **1970**, *9*, 2670–2675.
[56] Bianchini has reported that the reaction of $[Pd(H_2O)_2(dppomf)](OTs)_2$ with CO/C_2H_4 (40 atm) in MeOH gives a carbomethoxy complex, as observed from high-pressure ^1H and ^{31}P NMR spectroscopic data, presumed to be formed by an insertion pathway. No evidence for any of the proposed intermediates was reported.
[57] S. A. Macgregor, G. W. Neave, *Organometallics* **2003**, *22*, 4547–4556.
[58] D. L. Thorn, R. Hoffmann, *J. Am. Chem. Soc.* **1978**, *100*, 2079–2090.
[59] E. G. Lundquist, K. Folting, W. E. Streib, J. C. Huffman, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1990**, *112*, 855–863.
[60] S. Mecking, L. K. Johnson, L. Wang, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 888–899.
[61] M. A. Zuideveld, P. C. J. Kamer, P. W. M. N. van Leeuwen, P. A. A. Klusener, H. A. Stil, C. F. Roobeek, *J. Am. Chem. Soc.* **1998**, *120*, 7977–7978.
[62] C. Bianchini, A. Meli, W. Oberhauser, *Dalton Trans.* **2003**, 2627–2635.
[63] C. Bianchini, A. Meli, W. Oberhauser, P. van Leeuwen, M. A. Zuideveld, Z. Freixa, P. C. J. Kamer, A. L. Spek, O. V. Gusev, A. M. Kal'sin, *Organometallics* **2003**, *22*, 2409–2421.
[64] A small amount of **2-H_2O** was also observed, presumably as a result of traces of water in the triflic acid and/or methanol used, see ref. [32] above. A simple AB NMR spectrum is observed for this complex. A symmetrical bridging complex would give either an AA′BB′ or A_4 spectrum depending on the existence or not of coupling between the phosphorus nuclei, whereas an unsymmetrically bridged complex would give an AA′XX′ spectrum. We prefer unbridged structures because 1) Bianchini et al. report A_4 spectra in related studies in which hydroxy-bridged complexes are observed; 2) we report here the crystal structure of $[\{Pd(dibpp)(\mu\text{-}OH)\}_2](OTf)_2$, the ^{31}P NMR spectrum of which shows a singlet at δ = 21.1 ppm; and 3) bridged complexes seem to be the exception rather than the rule in this chemistry.
[65] The situation with regard to $[Pd(dppomf)\{C(O)CH_3\}]OTs$ is complicated by the presence of an intramolecular Fe–Pd bond, which reasonably accounts for the observed reactivity of that system.
[66] Carbon monoxide was added to suppress the migratory deinsertion back reaction.
[67] J. G. Knight, S. Doherty, A. Harriman, E. G. Robins, M. Betham, G. R. Eastham, R. P. Tooze, M. R. J. Elsegood, P. Champkin, W. Clegg, *Organometallics* **2000**, *19*, 4957–4967.
[68] C. Pisano, G. Consiglio, A. Sironi, M. Moret, *J. Chem. Soc. Chem. Commun.* **1991**, 421–423.
[69] A. Fujii, E. Hagiwara, M. Sodeoka, *J. Am. Chem. Soc.* **1999**, *121*, 5450–5458.
[70] G. Pieri, M. Pasquali, P. Leoni, U. Englert, *J. Organomet. Chem.* **1995**, *491*, 27–30.
[71] Solutions resulting from methanolysis of **3** may be stored at low temperature for three weeks with no visible formation of palladium black. The NMR spectra indicate the presence of many complexes. On exposure to ^{13}CO, some **8** is formed. However, the quality of the NMR spectra after such a long sequence of reactions is poor.
[72] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512–7515.

Received: November 9, 2005
Published online: March 24, 2006

