Reaction-Mechanism Elucidation

The Complete Delineation of the Initiation, Propagation, and Termination Steps of the Carbomethoxy Cycle for the Carboalkoxylation of Ethene by Pd–Diphosphane Catalysts**

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Drent and Budzelaar have proposed two catalytic cycles for cationic Pd–diphosphane complex catalyzed CO–alkene coupling reactions such as CO–ethene copolymerization and methoxycarbonylation of ethene.[1] The hydride cycle is initiated by alkene insertion into a Pd–hydride bond whilst the carbomethoxy cycle is initiated by CO insertion into a Pd–methoxy bond. The two cycles may operate in parallel, for example, CO–alkene copolymerization, or one cycle may dominate, for example, the Lucite process for the methoxycarbonylation of ethene to methylpropanoate. Where the two cycles operate in tandem there exists the possibility of crossover between the cycles which has been inferred from chain end-group analysis.[1,2] Product selectivity is determined in both the initiation and termination step(s).[3–5] The chain-propagation steps, insertion of CO into a metal–alkyl bond, and insertion of alkene into a metal–acyl, bond have been extensively investigated,[6–10] whilst van Leeuwen has recently discussed termination by alcoholysis of the Pd–alkyl[11] and Pd–acyl intermediates.[4] We have recently (1) fully characterized the intermediates in and (2) delineated the initiation process of the hydride cycle.[12–14] The hydride cycle is thus well established, however, a complete cycle for the Pd–carbomethoxy mechanism has not yet been demonstrated because of the absence of suitable Pd–carbomethoxy precursors.[15–18] We report herein a simple, general procedure for the preparation of the key cationic monocarbomethoxy Pd–diphosphane compounds and present an NMR study that characterizes, for the first time, all the intermediates in the carbomethoxy cycle. We also report (1) the delineation of the propagation steps of the hydride cycle for this catalyst, and (2) for the first time, characterization of all the complexes involved in termination of the hydride cycle with concomitant crossover and initiation of the carbomethoxy cycle. It should be noted that ligands of the type used in this work give highly active catalysts in this field of chemistry.[3]

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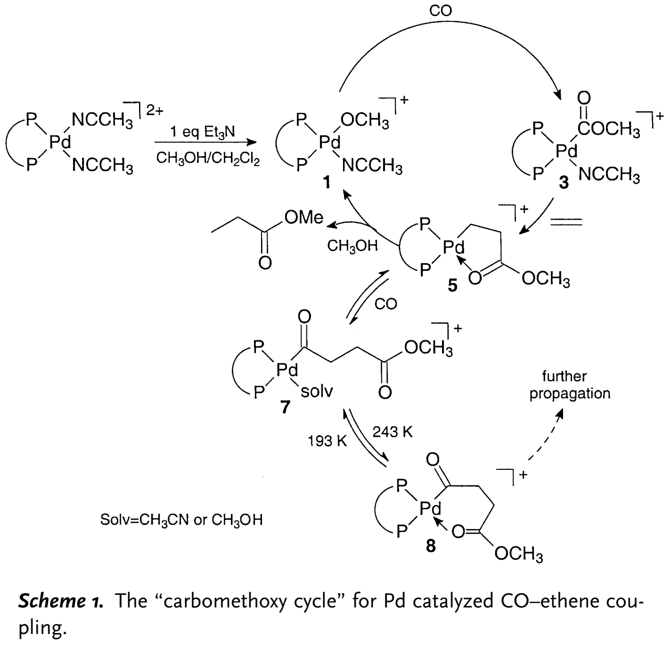
Table 1: NMR spectroscopic data for the complexes involved in Scheme 1.

Complex	δ ^{31}P [ppm]	$J(P,P)$ [Hz]	$J(P,C)$ [Hz]	δ ^{13}C [ppm][a]
1 $[Pd(dibpp)(OCH_3)(CH_3CN)][CF_3SO_3]$	3.7 dd 17.0	28 28		
3 $[Pd(dibpp)\{C(O)OCH_3\}(CH_3CN)][CF_3SO_3]$	8.3 dd −15.5 dd	47 47	9 167	191.7 dd
4 $[Pd(dibpp)\{C(O)OCH_3\}_2]$[b]	−8.2 −8.2	45 45	152 12	203.0 203.0[c]
5 $[Pd(dibpp)\{CH_2CH_2C(O)OCH_3\}][CF_3SO_3]$	13.3 d −12.0 dd	46 46	 10	193.3 d
6 $[Pd(dibpp)\{CH_2CH_2C(O)OCH_3\}(CH_3CN)][CF_3SO_3]$	12.7 dd −12.6 dd	46 46	2 4	 179.0 dd
7 $[Pd(dibpp)\{C(O)CH_2CH_2C(O)OCH_3\}(CH_3CN)][CF_3SO_3]$	4.1 dd −18.6 dd	68 68	9 116	241.5 dd 173.0 s
8 $[Pd(dibpp)\{C(O)CH_2CH_2C(O)OCH_3\}][CF_3SO_3]$	17.9 dd −14.3 dd	63 63	16 129	228.4 ddd[c] 186.0 d

[a] $^{13}C\{^1H\}$ NMR spectroscopic data and $J(PC)$ were obtained from experiments using ^{13}CO. [b] AA′XX′, the chemical shifts and coupling constants were obtained from simulation of the experimental spectrum by using gNMR 4.1. [c] $J(CC) = 6$ Hz.

The addition of one equivalent of triethylamine to a CO saturated solution of $[Pd(dibpp)(CH_3CN)_2][CF_3SO_3]_2$, (dibpp = 1,3-$(iBu_2P)_2$-$C_3H_6$) in a 9:1 mixture of dichloromethane and methanol at −78 °C, gives two new doublets at $\delta = 3.7$ and, 17.0 ppm, $^2J(P,P) = 28$ Hz in the $^{31}P\{^1H\}$ NMR spectrum (Table 1). The NMR parameters of **1** are unchanged in the presence of excess CH_3CN, which indicates that the fourth coordination site in **1** is occupied by CH_3CN rather than methanol. Complex **1** is therefore assigned as the Pd–methoxy species $[Pd(dibpp)(OCH_3)(CH_3CN)]^+$, which is too unstable to be isolated and reacts readily with ^{12}CO to give **3** (Scheme 1; the putative intermediate $[Pd(dibpp)(OCH_3)(CO)]^+$, **2**, is not observed, see also Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum of **3** shows two doublets at $\delta = 8.3$ and −15.5 ppm, $^2J(P,P) = 47$ Hz. On using ^{13}CO, these resonances are further split by ^{31}P–^{13}C coupling, Table 1, and a corresponding doublet of doublets is observed in the $^{13}C\{^1H\}$ NMR spectrum at $\delta = 191.7$ ppm, $^2J(P_{trans},C) = 167$ Hz, $^2J(P_{cis},C) = 9$ Hz, which is characteristic of the carbonyl of an ester group. Complex **3** can thus be formulated as $[Pd(dibpp)\{C(O)OCH_3\}(CH_3CN)][CF_3SO_3]$. The addition of a second equivalent of triethylamine leads to the formation of the Pd bis-carbomethoxy complex $[Pd(dibpp)\{C(O)OCH_3\}_2]$, **4**. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra of **4**, labeled with ^{13}CO, show second order AA′XX′ patterns, which have been simulated. The calculated chemical shifts and coupling constants for **4** are given in Table 1 and are similar to those found for **3**, thus substantiating the assignment of **3** and **4** as the mono and biscarbomethoxy complexes. In contrast to the ready reversibility of insertion of CO into Pd methyl bonds, **3** is stable towards decarbonylation; solutions of **3** can be taken to dryness in vacuo and extracted into dichloromethane with no change in the $^{31}P\{^1H\}$ NMR, that is, the insertion of CO into the Pd–methoxy bond is irreversible even though the fourth coordination site is occupied by CH_3CN.[19,20] The dppp (dppp = 1,3-bis(diphenylphosphinyl)propane) analogue can be prepared in a similar fashion, thus demonstrating the generality of the synthetic method (see Supporting Information).



Scheme 1. The “carbomethoxy cycle” for Pd catalyzed CO–ethene coupling.

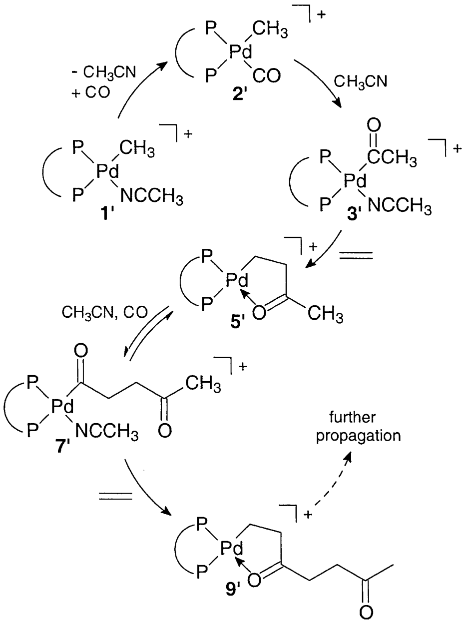
The stability of **3** makes it a promising starting point for a mechanistic NMR study of the carbomethoxy cycle (Scheme 1). On bubbling ethene through a dichloromethane solution of **3** at −78 °C, followed by warming to −30 °C for 1.5 hr, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy reveals complete conversion of **3** to a new complex **5**, $[Pd(dibpp)\{CH_2CH_2C(O)OCH_3\}]^+$ (see Table 1). The observation of a doublet for the ester carbon at $\delta = 193.3$ ppm in the $^{13}C\{^1H\}$ NMR spectrum, $J(P,C) = 10$ Hz, indicates that a five-membered chelating structure is formed in which the oxygen atom of the ester carbonyl coordinates to the metal center. This coupling is lost on addition of acetonitrile to the solution, which indicates cleavage of the chelate ring and coordination of CH_3CN to the Pd center, **6**. There are several reports of chelating structures, in which the oxygen of an acyl group coordinates to the Pd centre;[21–24] however, examples of similar chelating structures involving coordination of the oxygen atom of the ester group are rare,[11,24,25] and we believe this is the first example of such a chelating structure for a cationic diphosphane palladium system formed directly by the carbomethoxy cycle. A brief report exists of an analogous dppp compound synthesized by an alternative route.[11]

The reaction of **5** with ^{13}CO at −30 °C gives two new Pd acyl species **7** and **8** that are in equilibrium, Scheme 1. The $^{13}C\{^1H\}$ NMR spectrum of **7**, Table 1, comprises a doublet of doublets at $\delta = 241.5$ ppm, $^2J(P_{trans},C) = 116$, $^2J(P_{cis},C) = 9$ Hz, characteristic of an acyl carbonyl group coordinated to a square planar {Pd(dibpp)} fragment and a singlet at δ 173 ppm, thus indicating the carbonyl group of the ester is not coordinated to the Pd center. Complex **7** can thus be formulated as the "open" acyl complex $[Pd(dibpp)\{C(O)CH_2CH_2C(O)OCH_3\}(Solv)]^+$. Complex **8** is formulated as the "chelating" acyl $[\overline{Pd(dibpp)\{C(O)CH_2CH_2C(O}})OCH_3\}]^+$, on the basis of the downfield shift of the carbonyl of the ester group, $\delta = 186$ ppm, compare with $\delta = 173$ ppm in **7**. Addition of methanol to a dichloromethane solution of **5** at room temperature releases one equivalent of methyl propanoate as the only organic product detected by $^{13}C\{^1H\}$ NMR. In the presence of CO, **3** is regenerated smoothly in situ and can be used to initiate a new catalytic cycle, Scheme 1.

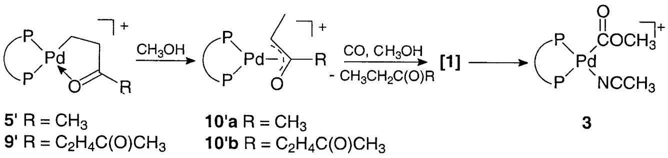
Base was required to generate the Pd-methoxy species used in the work above, however, cationic Pd–diphosphane complex catalyzed CO–alkene coupling reactions such as CO–ethene copolymerization and methoxycarbonylation of ethene are normally performed in the presence of an excess of a strong acid such as CH_3SO_3H. The same chemistry as that outlined above can be accessed in the absence of base by chain crossover from the "hydride" cycle, Scheme 2 and 3. (Primes are used throughout this work to indicate analogous intermediates in the cycles shown in Schemes 1 and 2). Although attempts to prepare the Pd(dibpp)–hydride cation were unsuccessful, the methyl complex $[Pd(dibpp)(CH_3)(CH_3CN)][CF_3SO_3]$ **1′**, provides a clean entry point into the chemistry of the hydride cycle[4–7,11] (with the exception of the initial insertion of C_2H_4 into the Pd−H bond). **1′** was prepared in a manner similar to that described by Brookhart and co-workers.[26] Sequential insertions of CO and ethene were then monitored at low temperature (−78 °C to −30 °C) by $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopy, and gave the reaction sequence **1′**→**2′**→**3′**→**5′**→**7′**→**9′** (Scheme 2, Table 2) in agreement with reports on other diphosphane ligands.[6,7,12,14,15,26–31]

Importantly however, we have been able to characterize, for the first time, all the organometallic species involved in the methanolysis of the chelate complexes **5′** and **9′**, that is, **5′**→**10a′**→**[1]**→**3**, and **9′**→**10b′**→**[1]**→**3** with the exception of **1** (the involvement of which can be inferred from the work above; see Scheme 3). Van Leeuwen and co-workers have previously shown that methanolysis of the Pd-chelated alkyl species proceeds via an enolate intermediate but were unable to characterize the organometallic products of solvolysis of the enolate.[11] Isomerization of the β-chelate complexes **5′** and **9′** to the enolates **10′a** and **10′b**, respectively, occurs in the presence of excess methanol (Scheme 3); in the absence of methanol decomposition of the β-chelate was observed. The methoxy species **1** was not observed presumably because of its instability and readiness to react with CO (see above)[32] to give **3**, from which we have been able to restart the carbomethoxy cycle described above.

All of the steps in both the hydride and carbomethoxy catalytic cycles for Pd-catalyzed CO–ethene coupling for a single, highly active catalyst have thus been fully characterized by NMR for the first time. The characterization of the active catalytic species resulting from chain termination through protonolysis of the Pd–alkyl intermediate in the hydride cycle has allowed the pathway from the hydride to the carbomethoxy cycle through a methanolysis chain-transfer step to be demonstrated for the first time. Termination of the carbomethoxy cycle by methanolysis of the alkyl intermediate also gives **3**. It has previously been noted that alcoholysis of the acyl intermediate gives ester product and a Pd–hydride



Scheme 2. The "hydride" cycle (initiated from $[Pd(dibpp)(CH_3)(CH_3CN)][CF_3SO_3]$ **1′**) for Pd-catalyzed CO–ethene coupling. (Primes indicate analogous complexes to those in Scheme 1.)



Scheme 3. Termination of the hydride cycle and crossover to the carbomethoxy cycle.

Table 2: NMR spectroscopic data for the complexes involved in Scheme 2 and 3.

Complex	δ ^{31}P [ppm]	J(P,P) [Hz]	J(P,C) [Hz]	δ ^{13}C [ppm][a]
1′ $[Pd(dibpp)(CH_3)(CH_3CN)][CF_3SO_3]$	11.1 d −15.6 d	42 42		
2′ $[Pd(dibpp)(CO)(CH_3)][CF_3SO_3]$	−0.5 dd −12.3 dd	47 47	114 16	181.6 dd
3′ $[Pd(dippp)\{C(O)CH_3\}(CH_3CN)][CF_3SO_3]$	5.4 dd −19.6 dd	70 70	10 112	242.6 dd
5′ $[\overline{Pd(dibpp)\{CH_2CH_2C(O}})CH_3\}][CF_3SO_3]$	12.7 d −13.5 dd	46 46	 10	236.0 d
7′ $[Pd(dippp)\{(C(O)CH_2CH_2C(O)CH_3)\}(CH_3CN)][CF_3SO_3]$	3.9 dd −19.1 dd	69 69	10 114	240.3 dd
9′ $[\overline{Pd(dibpp)\{CH_2CH_2C(O}})CH_2CH_2C(O)CH_3\}(CH_3CN)][CF_3SO_3]$	14.7 d −13.6 dd	47 47	 10	237.4 dd
10a′ $[Pd(dibpp)\{CH_2CH_2C(O)\ CH_3\}][CF_3SO_3]$	12.8 d −15.2 d	44 44		208.4 s
10b′ $[Pd(dibpp)\{CH_2CH_2C(O)CH_2CH_2C(O)CH_3\}][CF_3SO_3]$	12.5 d −16.5 d	52 52		206.3 s
3 $[Pd(dibpp)\{C(O)OCH_3\}(CH_3CN)][CF_3SO_3]$	7.8 dd −15.7 dd	48 48	9 167	190.8 dd

[a] $^{13}C\{^1H\}$ NMR spectroscopic data and J(PC) were obtained from experiments by using ^{13}CO.

species "locking" the catalysis into the hydride cycle,[4,33] this work shows that methanolysis of the alkyl intermediate in both cycles gives a Pd–methoxy species, thus locking the catalysis into the carbomethoxy cycle.

Qualitatively, the rate of ethene insertion into the Pd–carbomethoxy bond in **3** is found to be similar to that of insertion into the Pd–acyl bond in **3′**, that is, insertion occurs at low temperature on the timescale of tens of minutes. This contrasts with literature precedent, in which insertion of alkene into the Pd–carbomethoxy bond is reported not to occur at room temperature on a timescale of days, if at all.[15,18] Although we cannot rule out that the high reactivity we observe is due to the different ligand used—dialkyl versus diaryl diphosphane—it seems likely that the low reactivity toward alkene insertion of Pd carbomethoxy complexes reported in previous work may reflect the presence of a strongly coordinating anion or ligand in the fourth coordination site rather than the intrinsic reactivity of the Pd–carbomethoxy bond.

The β-chelate has been proposed to be a resting state in catalytic cycle,[21] it is therefore interesting to compare the reactivity of $[\overline{Pd(dibpp)\{CH_2CH_2C(O}})OCH_3\}]^+$ **5** with that of the analogous β-chelate in the hydride cycle $[\overline{Pd(dibpp)\{CH_2CH_2C(O}})CH_3\}]^+$ **5′**. The chelate ring in **5** can be easily opened by the addition of acetonitrile to a dichloromethane solution of **5** to give **6** quantitatively. Complex **6** is formulated as the ring opened cation $[Pd(dibpp)\{CH_2CH_2C(O)OCH_3\}(CH_3CN)]^+$ based on the upfield shift of the carbonyl carbon ($\delta = 179$ ppm) in **6** relative to that in **5**, and loss of the 10 Hz P,C coupling characteristic of a dative bond from the oxygen of the ester group to the Pd centre. This contrasts with the stability of **5′**, in which the chelating structure is preserved in the presence of strongly coordinating solvents (e.g. acetonitrile) or anions (e.g. trifluoroacetate). These results indicate that the ketonic group is a stronger Lewis base toward the metal centre than the ester carbonyl group in this system, compare Scheme 1 and 2.

Several six-membered chelates formed by coordination of the oxygen atom of a ketone to the metal centre have been reported during the stepwise insertion of alkenes and CO into metal–acyl compounds[34,35] and we report herein an analogous structure **8** involving coordination of an ester carbonyl group formed directly from successive insertions of ethene and CO into a Pd carbomethoxy species. The six-membered Pd–acyl chelates derived from the hydride cycle are reported to promote methanolysis relative to further ethene insertion,[3] however, our preliminary results show that further ethene insertion into **7** is preferred over methanolysis. These findings indicate that the oxochelates (**5** and **8**) formed in the carbomethoxy cycle are more susceptible to nucleophilic attack by substrates such as ethene, strong coordinating solvents, and anions, than their counterparts in the hydride cycle.

A Pd–carbomethoxy compound **3** has been synthesized by a simple methodology; this has allowed the Pd carbomethoxy cycle in CO–ethene coupling to be demonstrated for the first time and all important intermediates in both the carbomethoxy and hydride cycles to be characterized by ^{31}P and ^{13}C NMR spectroscopy. In contrast to previous reports, comparable reactivity towards ethene insertion was observed for the Pd carbomethoxy complex **3** and the Pd acetyl complex **3′** and is attributed to the absence of a strongly coordinating ligand in the fourth coordination site of **3**. In copolymerization and methoxycarbonylation reactions, the chain termination steps are as important as initiation and propagation since they can govern the product selectivity and regeneration of the catalytically active species. Methanolysis of the Pd β-chelate complexes occurs in both cycles regenerating the Pd−OCH$_3$ species **1** which, in the presence of CO, forms the Pd−C(O)OCH$_3$ species initiating a new catalytic cycle.

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