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Palladium Catalyzed Oxidative Carbonylation of Alcohols: Effects of the Diphosphine Ligands

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The catalytic activity of a series of palladium diphosphine complexes of the type [PdX_2(P∩P)] has been studied in the oxidative carbonylation of *i*–PrOH with *p*–benzoquinone as oxidant. Diphosphine ligands have been chosen in order to cover a wide range of bite angles, electronic and steric parameters. Their properties have been correlated to the catalytic activity and selectivity of the reaction. The best catalytic performance has been achieved with weakly coordinating anions, non bulky and electron donating P∩P ligands with a relatively wide bite angle yet capable of maintaining *cis*–coordination, such as *cis*–[$Pd(OTs)_2$(*p*MeO–dppf)]. These results and those on the reactivity of the dicarboalkoxy species of the type *cis*–[$Pd(COOMe)_2$(P∩P)] toward the reductive elimination, a crucial step in the oxalate formation, suggest that the slow step of the catalysis depends on the nature of the P∩P ligand.

1. Introduction

As far as catalysis is concerned, palladium is one of the most versatile elements of the transition metal series. In particular, it catalyses a wide spectrum of carbonylation reactions, such as the Reppe reaction with alkenes, alkynes, conjugated dienes, and aryl–substitutes alkenes,[1] the copolymerization of CO and alkenes to alternating and nonalternating polyketones (PKs),[2] the oxidative carbonylation of alkenes, alkanols and alkynes,[3] and the carbonylative cross–coupling,[4] just to mention some representative examples.

The nature of the ligand plays a role of paramount importance in governing the catalyst activity and selectivity,[5] as exemplified by the carbonylation of ethene. In fact, by carefully increasing the steric hindrance around the metal center of catalysts suitable for the synthesis of PKs, it has been possible to reduce the propagation chain rate to the extreme point that methyl propanoate is formed.[6]

Whereas the carbonylation of alkenes has been thoroughly investigated both in industry and academia, particularly for the synthesis of PKs and of methyl propanoate,[6,7] an intermediate to methyl methacrylate (Lucite process), the oxidative carbonylation of alkanols received less attention, in spite of the interest in synthesising organic carbonates *via* a one step environmentally friendly phosgene–free technology.[8] Another product of the oxidative carbonylation of an alkanol is the corresponding oxalate, which is prepared in industry using a Pd/C catalyst.[9]

Even though the use of palladium catalysts for the synthesis of organic oxalates is known since the seventies,[10] only a few examples have been reported later.[11] More recently, the interest for this chemistry has received further impulse using well defined Pd(II)–PPh_3 systems in combination with a base, NEt_3, and 1,4–benzoquinone (BQ) as a stoichiometric oxidant. The main product, oxalate, is formed together with carbonate, through the intermediacy of mono– and di–carboalkoxy palladium(II) species (Scheme 1).[11g,12]

Insert Scheme 1

Scheme 1. Carboalkoxy palladium(II) intermediates involved in the products forming steps.

It was established that both BQ and the base play a role of paramount importance in controlling the product distribution. Both favor the formation of a $Pd(COOR)_2$ species and BQ, in addition to being the oxidant, promotes the reductive elimination step of a dicarboalkoxy–Pd(II) species to oxalate.[12h]

While the oxidative carbonylation of alcohols has been explored using Pd(II)–monophosphine complexes, only little attention has been given to the use of diphosphine ligands,[12g] though their potentiality in governing the catalyst performance is well recognized.[5,13] This lack of knowledge prompted us to study, for the first time in an exhaustive manner, the performance of Pd(II)–diphosphine catalysts with the aim to correlate their properties with the activity and selectivity of the reaction. A large

variety of diphosphine ligands, chosen to cover a wide range of bite angles, electronic and steric properties, have been used in order to establish a correlation between these properties and the catalysts activity and selectivity. The effect of the nature of the counter anion and CO pressure on the catalytic outcome have also been studied. Most of the catalytic experiments have been carried out in isopropanol (*i*PrOH). Diisopropyl oxalate (**O**) is formed as the major product, together with diisopropyl carbonate (**C**). Also formation of acetone (**A**) from *i*PrOH occurs as a side reaction (Scheme 2).

Insert Scheme 2

Scheme 2. Products formed in the palladium–catalyzed oxidative carbonylation of *i*PrOH .

The synthesis and reactivity of Pd(II)–dicarboalkoxy complexes have been also investigated in order to determine the relationship between the bite angle of the ligand and the reactivity toward reductive elimination to oxalate and "Pd(0)(P∩P)", a crucial step in the "oxalate catalytic cycle".

2. Results and Discussion

2.1. Influence of the anion of the catalyst precursor [PdX_2(dppf)] (dppf = 1,1'–bis(diphenylphosphino)ferrocene)

Graph 1 shows the results using the precursors [PdX_2(dppf)] (X or X_2 = TsO,[‡] SO_4, AcO, C_2O_4, Cl). The highest TOF to **O** was achieved with the most weakly coordinating TsO anion. This result is not surprising since strongly coordinating anions compete with CO and the alcohol for coordination, a prerequisite for the formation of the products. This behavior is opposite to that observed with monophosphine–based precursors [$PdX_2(PPh_3)_2$], in which the highest catalytic activity was achieved with X = Br and the lowest with TsO.[12i]

Insert Graph 1

Graph 1. Effect of the anion on the catalytic activity using *cis*–[PdX_2(dppf)]. Conditions: [Pd] = $2\cdot10^{-4}$ mol/L, Pd/BQ/NEt_3 = 1/700/2, P_{CO} = 80 atm, T = 80 °C, 1 h, 5 mL anhydrous *i*PrOH.

With a strongly coordinating anion such as Cl^- both the activity and the selectivity toward the formation of **O** were significantly suppressed, whereas the TOFs for the formation of **C** and **A** were less influenced. A reasonable explanation is the following. The formation of the products occurs through a common Pd–OR intermediate **a** (Scheme 3). β–hydride elimination from Pd–OR gives the side product **A** and a Pd–H species,[14] which is oxidized by BQ restoring the catalyst or deprotonated to Pd(0). If a migratory insertion of coordinated CO into the Pd–OR bond takes place before β–hydride elimination, a monocarboalkoxy intermediate Pd–COOR **b** is formed. Addition of the OR nucleophile to palladium followed by reductive elimination rather than a direct nucleophilic abstraction process[15] gives **C** and Pd(0), which is oxidized by BQ to the initial Pd(II). For the formation of **O** it is necessary that a dicarboalkoxy species **d** is formed before the formation of **C** occurs. Moving from TsO^- to Cl^- the activity toward **C** and **A** was little influenced, while a dramatic lowering of the TOF toward **O** was detected. This fact suggests that once a Pd–COOR intermediate is formed, Cl^- competes more strongly than TsO^- for the coordination of another molecule of ROH or CO necessary to give the $Pd(COOR)_2$ species leading to **O**. This might be due to the electron withdrawing properties of COOR ligand, which makes the displacement of Cl^- more difficult. In Scheme 3, Pd(0) may be coordinated by the diphosphine and BQ, similar to what was found using Pd(II)–monophosphine catalysts, for which a mechanism for the reoxidation of Pd(0) was proposed.[12h,i]

2.2. Effect of the pressure of carbon monoxide

Graph 2 shows that upon increasing the pressure of CO the activity and the selectivity toward **O** increases (TOF = 245 h^{-1} and 93 % selectivity), with concomitant decrease of the formation of **A**. Instead, the formation of carbonate is little influenced and remains low (maximum selectivity 3%).

Insert Graph 2

Graph 2. Effect of P_{CO} on the activity of the oxidative carbonylation reaction using *cis*–[$Pd(OH_2)$(OTs)(dppf)](TsO). Conditions: [Pd] = $2\cdot10^{-4}$ mol/L, Pd/BQ/NEt_3 = 1/700/2, 80 °C, 1 h, 5 mL anhydrous *i*PrOH.

These trends suggest that the formation of **O** is connected to that of **A** and that they hardly interfere with the formation of **C**. As already mentioned, acetone is formed through β–hydride elimination from the Pd–OR species **a** (Scheme 3). Alternatively, this species undergoes CO insertion giving monocarboalkoxy intermediates (Pd–COOR) **b** and **b′**. Since species **b** is the most abundant, its concentration is not much affected by CO pressure. **b** interacts with ROH giving the intermediate Pd(COOR)(OR) (**c**), which forms C and Pd(0) in a relatively slow step. Species **b′**, in which CO is already coordinated, interacts with ROH giving intermediate $Pd(COOR)_2$ (**d**) which yields **O** and Pd(0). The CO pressure influences significantly the equilibrium between **a** and **b′**, so that, upon increasing CO pressure, the selectivity toward **O** increases at the expenses of **A**.

Insert Scheme 3

Scheme 3. Proposed catalytic cycles for the formation of **O**, **C** and **A** (R = *i*Pr).

2.3. Influence of the diphosphine ligand

As already mentioned, the main goal of this investigation was to correlate the catalyst performance to ligand features. To this end, several diphosphine ligands P∩P were selected covering a wide range of bite angles, electronic and steric properties. The selected P∩P ligands span from the typically *cis*–chelating dppe to the *trans*–chelating SPANPhos (Figure 1).

Insert Figure 1

Figure 1. Diphosphine ligands used in this study.
[a] The natural bite angle (β_n) is taken from ref.16. [b] Extracted from the X–ray structure of *trans*–[$PdCl_2$(SPANphos)].[17]

When chelating diphosphine–based catalysts are used, the bite angle is a key parameter since it may influence significantly the electronic and steric properties and therefore the reactivity of the metal center.[5,13] In more detail, an increment of the bite angle can exert two distinct effects: *i)* it increases the effective steric bulk and *ii)* it electronically favours or disfavours certain geometries especially the ones involved in reductive elimination.[18] For instance, in the case of palladium complexes, using ligands with small bite angle (dppe, dppp and dppb), the complexes typically show a stable *cis* coordination to Pd(II), while wider bite angles lead to rapid reductive elimination.[19] Also, for larger bite angle diphosphines, such as DPEphos or Xantphos, the *cis* species might eventually get involved in a *cis*–*trans* isomerisation equilibrium promoted by the formation of a palladium–oxygen bond.[15,20]

By contrast, an extreme case is observed with SPANphos, typically considered a *trans* diphosphine, which forms *cis*–complexes only when *cis*–enforcing conditions are used.[21] These different ligand coordination features should therefore influence the reactivity of the resulting palladium complexes. In Graph 3 (Table 1S Supporting Information), the dependence of the catalyst performance from the ligand bite angle is presented.

Insert Graph 3

Graph 3. Bite angle effect on the catalytic activity. Conditions: [Pd] = 2.10^{-4} mol/L, Pd/BQ/NEt_3 = 1/700/2, PCO = 80 atm, T = 80 °C, 1 h, 5 mL anhydrous *i*PrOH.

Both the activity and the selectivity toward oxalate are strongly dependent on the bite angle. Dppf presents the optimal value, whereas narrower or wider bite angles dramatically decrease the catalysts performance. The trend observed is consistent with the hypothesis that oxalate formation is favoured by wide bite ligands, but it requires stable *cis*–geometry of the intermediates involved in the reaction. Bite angles of around 100° appear to be the best compromise. Similar bite angle effects, though only partially explored, were reported in literature when studying the oxidative carbonylation of MeOH to dimethyl carbonate/oxalate with nitrobenzene as oxidant[12g] and the cross–coupling and C–C reductive elimination reactions using palladium complexes,[13, 16b,19] although for these reactions slightly wider bite angles were optimal, *e.g.* DPEphos or Xantphos.

2.4. Electronic and steric effects of the diphosphine ligand

As already mentioned, in order to evaluate the role of the catalyst´s properties in controlling the catalytic activity and selectivity, also the electronic and steric properties should be taken into account. Insight into these effects has been obtained from catalytic experiments employing a variety of palladium complexes with ferrocenyl ligands bearing different alkyl or aryl substituents, as shown in Figure 2.

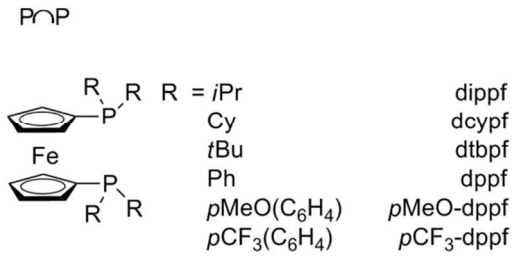


Figure 2. Ferrocenyl–diphosphine ligands.

The results are reported in Table 1, together with those relevant to the dppf–based catalyst for comparative purposes. The notable differences observed in activity and selectivity when aryl–substituted ferrocenyl phosphines were employed (all with identical steric properties) suggest that electronic rather than steric effects play a dominant role in controlling the oxalate formation.

Table 1. Electronic and the steric effects on the oxidative carbonylation reaction

En.	P∩P	θ [a]	χ [a]	TOF [mol/(mol·h)]			Selectivity [%]		
				O	**C**	**A**	**O**	**C**	**A**
1	*p*CF_3–dppf	145	20.5	4	8	10	18	36	45
2	dppf	145	13.2	245	6	15	92	2	6
3	*p*MeO–dppf	145	10.5	291	7	5	96	2	6
4	dippf	160	3.4	3.5	1.0	1.1	62	18	20
5	dcypf	170	1.4	1.7	2.2	4.3	21	27	52
6	dtbpf	182	0.0	0.9	1.3	3.7	16	21	62

Conditions: $[Pd(OH_2)_n(OTs)_{2-n}(P\cap P)](TsO)_n$ (n = 0, 1)] = $2*10^{-4}$ mol/L, Pd/BQ/NEt_3 = 1/700/2, P_{CO} = 80 atm, T = 80 °C, t = 1h, 5 mL anhydrous *i*PrOH. [a] Tolman's cone angle θ (steric parameter) and the χ values (electronic parameter) are taken from reference 22 and 23 respectively, considering the corresponding PAr_3.

The aryl ferrocenyl ligand with electron–withdrawing substituents (*p*CF_3) strongly inhibits the catalysis, whereas the ligand with electron–releasing groups (*p*MeO) presents a slightly accelerating effect (Entries 1–3, Table 1).

In order to rationalize the data from a mechanistic point of view, it should be noted that electron acceptor groups accelerate the reductive elimination,[24] while electron donors favour the reoxidation. Thus, for the aryl ferrocenyl ligands the reductive elimination to oxalate might not be the rate determining step because a higher activity would be expected when using *p*CF_3–dppf, which is not the case. On the contrary, the rate limiting step might be the reoxidation of Pd(0) that is formed in the product forming step.

All the explanations given above seem in contrast with the results obtained using the more basic alkyl ferrocenyl ligands (dippf, dcypf, dtbpf; entries 4–6 in Table 1). However, it has been

already proved that these strong Lewis Base ferrocenyl ligands may coordinate palladium centre through both *cis* k^2–P,P and *trans* k^3–P,P,Fe bonding modes and that this equilibrium is favoured when electron–withdrawing COOMe moiety is present in the complex as shown in Scheme 4. [25]

Since Pd–COOR type intermediates are involved in the reaction mechanism, it is reasonable to presume that the observed modest catalytic performances are mainly due to the *in situ* formation of these more stable but less active *trans* isomers.

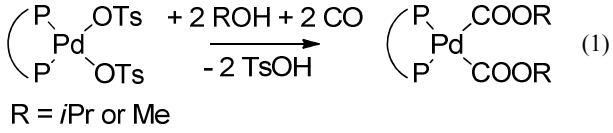
Insert Scheme 4

Scheme 4. Equilibrium between *cis* k2–P,P and *trans* k3–P,P,Fe bonding modes (R = *t*Bu, *i*Pr, Cy; R' = Alcohol residue).

Despite the low activity, it is interesting to observe that, within the dippf, dcypf, dtbpf series (entries 4–6 in Table 1), the increase in the steric hindrance favours the formation of acetone, *via* β–hydride elimination of a Pd–O*i*Pr moiety and therefore disfavouring the formation of carbonate and oxalate which required the formation of bulkier Pd–COO*i*Pr moieties as intermediates. It can be suggested that in this case β–hydride elimination diminishes steric strain in the complex.

2.5. Mechanistic investigation of the oxalate forming step

With the aim to rationalize the large bite angle effect and to gain more insight into the role of the dicarboalkoxy species in oxalate formation, we attempted their synthesis under conditions close to those used in catalysis, *i.e.* from $[Pd(OTs)_2(P\cap P)]$ dissolved in *i*PrOH, under carbon monoxide, either in the presence or absence of NEt_3, but always in the absence of BQ (reaction 1).



(1)

In spite of the wide spectrum of conditions explored, when using *i*PrOH as solvent all synthesis attempts gave unsatisfactory results. In contrast, with MeOH it was possible to isolate two complexes, *cis*–$[Pd(COOMe)_2(P\cap P)]$ (P∩P = dppe, and dppp) (Supporting Information). Therefore, it was decided to use the "carbomethoxy species" as models for mechanistic investigations.

The reactivity of preformed *cis*–$[Pd(COOMe)_2(P\cap P)]$ (P∩P = dppe, dppp) was studied by NMR spectroscopy. The dppe based complex in CD_2Cl_2 at 25 °C is stable for days, whereas the dppp one gave 80% of **DMO** (dimethyl oxalate) and unidentified Pd complexes after 24 hours. The *cis*–$[Pd(COOMe)_2(dppp)]$ complex was dissolved in CD_2Cl_2 (0.01 mmol in 1 mL) at –78 °C and the decomposition was followed in time upon increasing the temperature. The ^1H (Figure 3) and the $^{31}P\{^1H\}$ (Figure 1S, Supporting Information) spectra showed a slight shift of both $^{31}P\{^1H\}$ and methoxy "Pd-COOMe" signals with increasing temperature but no decomposition products were observed below 25 °C. However, after 24 h the intensity of the "Pd-carbomethoxy" signal decreased with concomitant appearance of a new singlet at 3.92 ppm assigned to **DMO**. The $^{31}P\{^1H\}$ spectra revealed the formation of ill defined compounds.

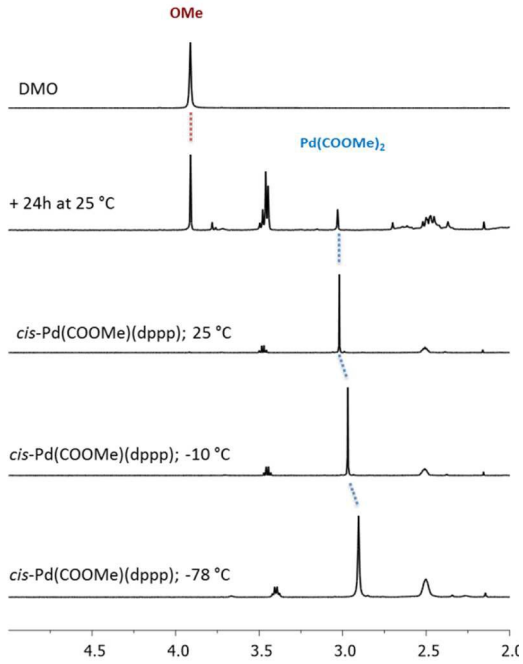


Figure 3. ^1H NMR spectra relevant to the stability of *cis*–$[Pd(COOMe)_2(dppp)]$ in $CDCl_2$.

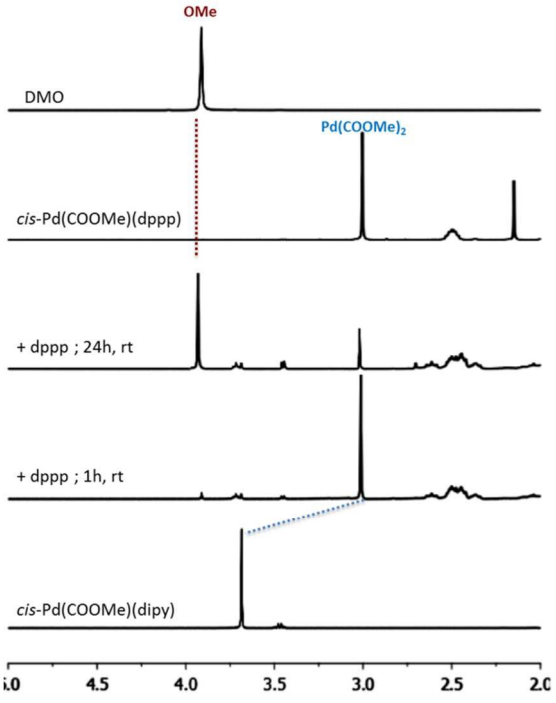


Figure 4. ^1H NMR spectra relevant to the reaction between the *cis*–$[Pd(COOMe)_2(dipy)]$ and dppp in $CDCl_2$.

The same results were observed when a 2,2'–dipyridyl dicarbomethoxy complex (0.01 mmol), prepared separately,[26] was reacted with one equivalent of either dppe or dppp (Scheme 5) in CD_2Cl_2. In both cases, the formation of the corresponding *cis*–[Pd(COOMe)$_2$(P∩P)] was immediate and complete. In more detail, upon the addition of dppe or dppp an upper shift of the methoxy signals occurred due to the formation of cis–[Pd(COOMe)$_2$(P∩P)]. The ^{31}P-NMR analysis definitely confirmed their formation. (See Figure 4 and Figure 2S, 3S, Supporting information). As was already observed when starting from preformed *cis*–[Pd(COOMe)$_2$(dppp)], after 24 hours at room temperature also the *in situ* formed complex decomposed giving *ca.* 80 % of **DMO.**

Insert Scheme 5

Scheme 5. Synthesis of [Pd(COOMe)$_2$(P∩P)] complexes and their reactivity toward the reduction elimination step.

In view of the same reactivity observed for both pre– or *in situ*–formed dppe and dppp complexes it was decided to extend this simple synthetic approach to the other P∩P ligands (The procedure used is described in Supporting Information). The results are reported in Table 2.

Table 2. Reactivity of *in situ* formed [Pd(COOMe)$_2$(P∩P)]

Entry	P∩P	β_n [a] [°]	Stability	time	Yield **DMO** [%]
1	dppe	78. 1	stable	24 h	0
2	dppp	86.2	moderately stable	24h	80
3	dppb	98.7	unstable	immediately	100
4	dppf	99.1	unstable[b]	immediately[b]	100[b]
5	DPEphos	102.9	unstable	immediately	100
6	Xantphos	110.0	unstable	immediately	100
7	SPANphos	171.9[c]	stable	24 h	0

Conditions: [Pd] = $1{\cdot}10^{-2}$ molL^{-1}, T = 25 °C, 1 mL anhydrous CD_2Cl_2. [a] The natural bite angle (β_n) are taken from ref 16. [b] Even at –78 °C and at 50 atm of CO. [c] Extracted from the X–ray structure of *trans*–[PdCl$_2$(SPANphos)].[17]

The reactivity of these complexes provides valuable information. Compared to the others, the dppe– and dppp–dicarbomethoxy complexes are relatively stable. These results and the poor performance of the dppe–and dppp–based catalysts (Table 1) indicate that when using these diphosphines the reductive elimination of oxalate might be the slow step of the catalysis.

When using wider bite angle diphosphines, the dicarboalkoxy complexes are unstable and they decompose immediately, with dppf even at -78 °C and in presence of 50 atm of CO, giving oxalate product (except with SPANphos in which the disappearance of Pd-COMe signals occurs without formation of defined products). All attempts to define the nature of the in situ formed Pd(0) through ESI and MALDI analysis gave unsatisfactory results. In Figure 5 the ^{1}H-NMR spectra registered after the addition of P∩P to the 2,2'–dipyridyl dicarbomethoxy palladium complex precursor are shown.

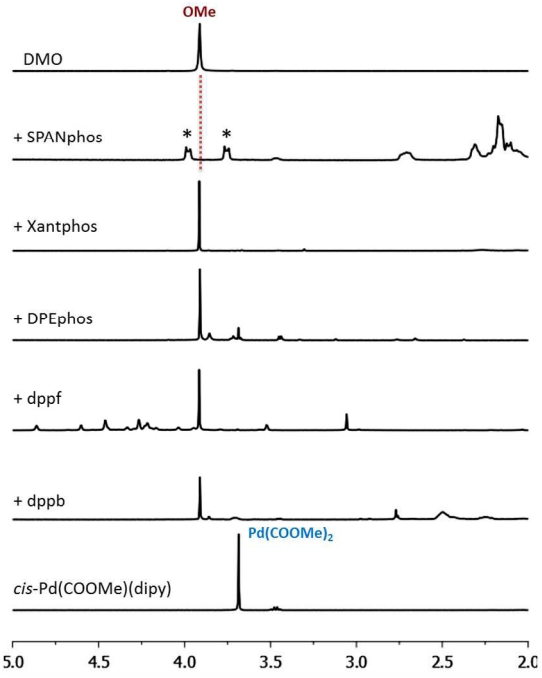


Figure 5. ^{1}H NMR spectra relevant to the *in situ* formation and stability of [Pd(COOMe)$_2$(P∩P)] complexes in $CDCl_2$. * = Ligand signals.

This is in line with the above reported hypothesis that, at least for the ferrocenyl ligands, the slow step in catalysis is not the reductive elimination but might be the reoxidation step.

In order to gain some insight in the reoxidation step, the productivity of the dppf–based catalyst was studied using different BQ/Pd ratios and different reaction times (Table 3).

Table 3. Influence of BQ/Pd ratio and reaction times on the oxidative carbonylation reaction

Entry	BQ/Pd [mol/mol]	time [h]	TON [mol/mol]			Selectivity [%]		
			O	**C**	**A**	**O**	**C**	**A**
1	1400	1	253	6	13	93	2	5
2	1000	1	253	6	12	93	2	4
3	900	1	248	5	10	94	2	4
4	700	1	245	6	15	92	2	6
5	600	1	250	5	16	92	2	6
6	500	1	247	4	15	93	2	6

7	1400	2	537	11	25	94	2	4
8	700	2	543	9	31	93	2	5
9	1400	3	846	16	49	93	2	5

Conditions: [*cis*–[Pd(OH$_2$)(OTs)(dppf)](TsO)] = 2*10^{-4} mol/L, Pd/NEt$_3$ = 1/2, P_{CO} = 80 atm, T = 80 °C, t = 1h, 5 mL anhydrous *i*PrOH.

The results show that the productivity toward **O** does not depend on the BQ/Pd initial ratio (entries 1–6) and exhibits a linear trend with time (entries 4, 7 and 1, 8, 9). Even though these data do not suggest that the reoxidation step is the slow one, this cannot be excluded because it might be that either *i)* uncoordinated BQ is not involved or more likely *ii)* palladium is present as a species in which Pd(0) is coordinated to BQ, for instance [Pd(BQ)(P∩P)]. Indeed, the Pd(0)-BQ complexes with mono- or bidentate ligands are well known[27] and recently it has been demonstrated that they able to promote oxidative carbonylation reactions.[12f, 28] Other hypotheses can be imagined, but in the absence of more significant data, this discussion would be speculative.

Going back to the reactivity of the *in situ* formed Pd-carbomethoxy species, only with SPANphos the formation of oxalate was not observed, not even after 24 hours. This fact was at first attributed to the formation of a *trans*–palladium compound such as *trans*–[Pd(COOMe)$_2$(SPANphos)] unable to undergo elimination of oxalate. However, the nature of the complexes formed *in situ* has not been determined. In order to gain more insight, the reactivity of *trans*–[Pd(OTs)$_2$(SPANphos)] was studied by VT $^{31}P\{^1H\}$ and ^1H NMR spectroscopy under conditions closer to those of catalysis (MeOH/CD_2Cl_2 = 1/10, v/v, P_{CO} = 5 atm). At –78 °C the monocarbomethoxy complex *trans*–[Pd(COOMe)(OTs)(SPANphos)] is formed (Supporting Information), which is stable even in presence of NEt$_3$ up to 60 °C. Above this temperature decomposition takes place, without formation of **DMO**, dimethyl carbonate, or formaldehyde. No dicarboalkoxy Pd–complexes were observed either. It is supposed that the formation of *trans*–monocarboalkoxy species occurs through a five–coordinated intermediate in which CO and MeO are in *cis* position so they can react to give a Pd–COOMe moiety (Scheme 6).[29] Probably, the square–planar *trans*–[Pd(COOMe)(OTs)(SPANphos)] complex is a stable complex, thus preventing further transformation (*i.e.* its conversion to dicarboalkoxy species and oxalate or formation of carbonate by alcoholysis).

Insert Scheme 6

Scheme 6. Putative mechanism of the formation of *trans*–[Pd(COOR)(OTs)(SPANphos)] R = Me.

The fact that reductive elimination takes place immediately with Xantphos or DPEphos seems in contrast with the poor catalytic performance obtained with these wide bite angle bidentates.[19] This observation suggests that in these cases the slow step in catalysis might be the formation of a dicarboalkoxy species or any species that leads to its formation, and as expected from previous work, reductive elimination is fast for Xantphos and DPEphos complexes.

Conclusions

The oxidative carbonylation of *i*PrOH catalysed by [PdX$_2$(P∩P)] gives the corresponding oxalate as the major product and carbonate. Acetone is also formed as a minor by–product. The catalytic performance is strongly influenced by the properties of the diphosphine ligand (bite angle, electronic and steric parameters), the nature of the counter anion and the pressure of carbon monoxide. Specifically, high activity and selectivity toward oxalate are achieved *i)* with weakly coordinating anions, *ii)* electron–donating and non bulky P∩P ligands with a relatively wide bite angle capable of maintaining *cis*– geometry, and *iii)* under relatively high CO pressure. The best results were obtained with *cis*–[Pd(OTs)$_2$(pMeO–dppf)]. These results and those on the reactivity of the dicarboalkoxy species of the type *cis*–[Pd(COOMe)$_2$(P∩P)] suggest that the slow step of the catalysis is related to the nature of P∩P. For dppe and dppp the reductive elimination to oxalate in the product forming step may be rate limiting, while for dppb, dppf and substituted dppf the limiting step might be the reoxidation. For wider bite angles ligands such as DPEphos, Xantphos and SPANphos the difficult step may be the formation of a dicarboalkoxy species or any species leading to its formation.

The importance of the *cis*– chelation has been shown studying the reactivity of the SPANphos–based catalyst. Although in this case the monocarbomethoxy complex *trans*–[Pd(COOMe)(OTs)(SPANphos)] can be isolated, catalysis does not occur to a significant extent, probably because the *trans* geometry does not favour the steps required for the advancement of the catalysis.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [Bite angle effect on the activity or selectivity, experimental details and spectroscopic characterization for P∩P, [PdX$_2$(P∩P)] and [Pd(COOMe)$_2$(P∩P)], together with the carbonylation procedures]. See DOI: 10.1039/b000000x/
‡This precursor is the cationic aquo complex *cis*–[Pd(OTs)(H$_2$O)(dppf)](TsO).

1 G. Kiss, *Chem. Rev.,* 2001, **101**, 3435.

2 a) E. Drent, P. H. M. Budzelaar, *Chem. Rev.,* 1996, **96**, 663. b) E. Drent, R. van Dijk, R. van Ginkel, B. van Ort, R. I. Pugh, *Chem. Commun.,* 2002, 964. c) A. Nakamura, T. M. J. Anselment, J. Claverie, B. Goodall, R. J. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. van Leeuwen, K. Nozaki, *Acc. Chem. Res.,* 2013, **46**, 1438.

3 a) A. Klausener, J. D. Jentsch, "Oxidative Carbonylation" in *"Applied Homogeneous Catalysis with Organometallic Compounds"* (Eds. B. Cornils, W. A. Herrmann), Wiley–VCH, 1996. b) V. R. Khabibulin, A. V. Kulik, I. V. Oshanina, L. G. Bruk, O. N. Temkin, V. M. Nosova, Y. A. Ustynyuk, V. K. Belskii, A. I. Stash, K. A. Lysenko, M. Y. Antipin, *Kinetics and Catalysis,* 2007, **48**, 228.

4 S. D. Friis, T. Skrydstrup, S. L. Buchwald, *Org. Lett.,* 2014, **16**, 4296.

5 a) J. A. Gillespie, L. D. Debora, P. C. J. Kamer, *Dalton. Trans.*, 2010, **39**, 2751. b) J. A. Gillespie, E. Zuidema, P. W. N. M. van Leeuwen, P. C. J. Kamer, "Phosphorus Ligand Effects in Homogeneous Catalysis and Rational Catalyst Design" in *Phosphorus(III) Ligands in Homogeneous Catalysis: Design and Synthesis* (Eds P. C. J. Kamer, P. W. N. M. van Leeuwen), John Wiley & Sons, 2012.

6 G. Cavinato, L. Toniolo, *Molecules,* 2014, **19**, 15116.

7 A. Sen, "Catalytic Synthesis of Alkene–Carbon Monoxide Copolymers and Cooligomers", (Ed. A. Sen), Kluwer Academic Publishers: Dordrecht, 2003.

8 a)Y. Ono, Pure Appl. Chem., 1996, **68**, 367. b) D. Delledonne, F. Rivetti, U. Romano, *Appl. Cat. A–Gen.*, 2001, **221**, 241. c) P. Tundo, M. Selva, *Acc. Chem. Res.*, 2002, **35**, 706. d) J. L. Gong, X. B. Ma, S. P. Wang, *Appl. Catal. A*, 2007, **316**,1.

9 S. Uchiumi, K. Ataka, T. Matsuzaki, *J. Organomet. Chem.*, 1999, **576**, 279.

10 D. M. Fenton, P. J. Steinwand, *J. Org. Chem.*, 1974, **39**, 701.

11 a) S. P. Current, *J. Org. Chem.,* 1983, **48**, 1779. b) L. N. Zhir–Lebed, O. N. Temkin, *Kinet. Katal. (Engl. Transl.),* 1984, **25**, 255. c) L. N. Zhir–Lebed, O. N. Temkin, *Kinet. Katal. (Engl. Transl.),* 1984, **25**, 263. d) R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, *J. Mol. Catal.,* 1993, **84**, 165. e) D. Delledonne, F. Rivetti, U. Romano, *J. Organomet. Chem.,* 1995, **488**, C15. f) P. Giannoccaro, *J. Organomet. Chem.,* 1994, **470**, 249. g) S. Uchiumi, K. Ataka, T. Matsuzaki, *J. Organomet. Chem.,* 1999, **576**, 279. h) C. S. Chin, D. Shin, G. Won, J. Ryu, H. S. Kim, B. G. Lee, *J. Mol. Catal. A Chem.*, 2000, **160**, 315.

12 a) F. Rivetti, U. Romano, *J. Organomet. Chem.,* 1978, **154**, 323. b) F. Rivetti, U. Romano, *J. Organomet. Chem.,* 1979, **174**, 221. c) F. Rivetti, U. Romano, *Chim. Ind.,* 1980, **62**, 7. d) L. Toniolo, *J. Organomet. Chem.* 1993, **444**, C65. e) E. Amadio, G. Cavinato, A. Dolmella, L. Toniolo, *Inorg. Chem.,* 2010, **49**, 3721. f) G. Cavinato, S. Facchetti, L. Toniolo, *J. Mol. Catal. A. Chem.,* 2012, **352**, 63. g) J. M. Tiddo, E. Bouwman, E. Drent, *Eur. J. Inorg. Chem.,* 2012, 1403. h) E. Amadio, L. Toniolo, *J. Organomet. Chem.*, 2014, **750**, 74. i) E. Amadio, L. Toniolo, *J. Organomet. Chem*., 2014, **767**, 72.

13 M. N. Birkholz, Z. Freixa, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.,* 2009, **38**, 1099.

14 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.

15 P. W. N. M. van Leeuwen, M. A. Zuideveld, B. H. G. Swennenhuis, Z. Freixa, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Luitz, A. L. Spek, *J. Am. Chem. Soc.,* 2003, **125**, 5523.

16 a) M. Kranenburg, P. C. J. Kamer, P. W. N. M. van Leeuwen, D. Vogt, W. Keim, *J. Chem. Soc., Chem. Commun.* 1995, 2177. b) M. Kranenburg, J. P. C. Kamer, P. W. N. M. van Leeuwen, *Eur. J. Inorg. Chem*. 1998, 155.

17 Z. Freixa, M. S. Beentjes, G. D. Batema, C. B. Dieleman, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, J. Fraanje, K. Goubitz, P. W. N. M. van Leeuwen, *Angew. Chem. Int. Ed*., 2003, **42**, 1284.

18 Z. Freixa, P. W. N. M. van Leeuwen, *Dalton Trans.,* 2003, 1980.

19 J. E. Marcone, K. J. Moloy, *J. Am. Chem. Soc*. 1998, **120**, 8527.

20 M. Zuideveld, B. H. G. Swennenhuis, M. D. K. Boele, Y. Guari, G. P. F. van Strijdonck, J. N. H. Reek, P. C. J. Kamer, K. Goubitz, J. Fraanje, M. Lutz, L. Spek, L.; P. W. N. M. van Leeuwen, *J. Chem. Soc. Dalton Trans.,* 2002, 2308.

21 C. Jimenez–Rodriguez, F. X. Roca, C. Bo, J. Benet–Buchholz, E. C. Escudero–Adan, Z. Freixa, P. W. N. M. van Leeuwen, *Dalton Trans*., 2006, 268.

22 C. A.Tolman, *Chem. Rev*., 1977, **77**, 313.

23 T. Bartik, T. Himmler, H. Schulte, K. J. Seevogel, *J. Organomet. Chem.* 1984, **272**, 29.

24 E. Negishi, T. Takahashi, K. Akiyoshi, *J. Organomet. Chem.*, 1987, **334**, 181.

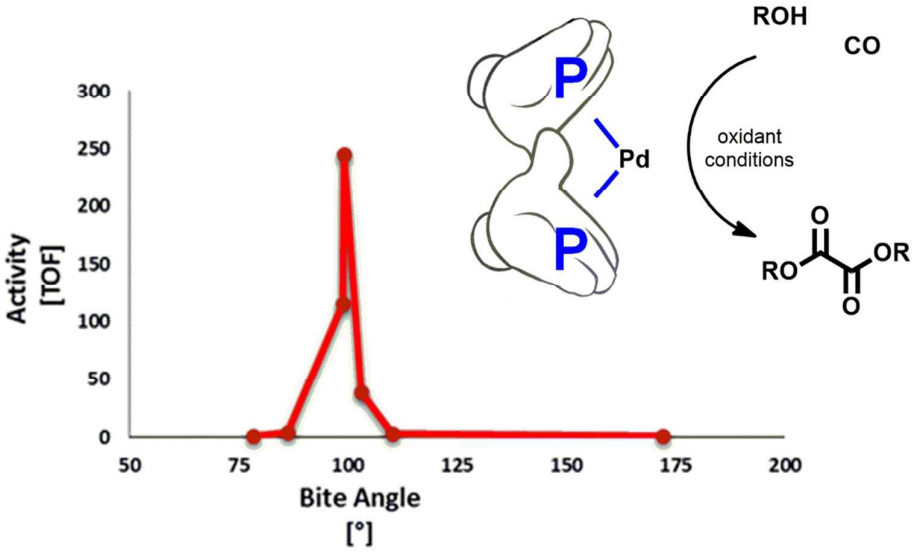
25 a) C. Bianchini, A. Meli, W. Oberhauser, S. Parisel, E. Passaglia, F. Ciardelli, O. V. Gusev, A. M. Kal'si, N. Vologdin, *Organometallics,* 2005, **24**, 1018. b) M. A. Zuideveld, B. H. G. Swennenhuis, P. C. J. Kamer, P. W. N. M. van Leeuwen, *J. Organomet. Chem.,* 2001, **637–639**, 805.

26 a) R. Santi, A. M. Romano, R. Garrone, R. Millini, *J. Organomet. Chem.,* 1998, **566**, 37. b) P. Giannoccaro, N. Ravasio, M. Aresta, *J. Organomet. Chem*., 1993, **451**, 243. c) G. D. Smith, B. E. Hanson, J. S. Merola, F. Waller, *Organometallics,* 1993, **12**, 568.

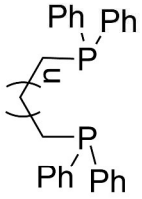
27 a) T. Ukai, H. Kawazura, Y. Ishii, J. J. Bonnet, J. A. Ibers, J. Organomet. Chem., 1974, 65, 253. b) M. Hiramatsu, K. Shiozaki, T. Fujinami, S. Sakai, J. Organomet. Chem. 1983, 246, 203.

28 a) A. V. Kulik, L. G. Bruk, O. N. Temkin, V. R. Kabibulin, V. K. Belsky, V. E. Zavodnik, *Mendeleev Commun.* 2002, **12**, 47. b) O. N. Temkin, L. G. Bruk, *Kinetics and Catalysis*, 2003, **44**, 601.

29 E. Zuidema, P. W. N. M. van Leeuwen, C. Bo, *Organometallics*., 2005, **24**, 3703.



Best catalytic performance using Lewis Base P∩P with a relatively wide bite angle capable of maintaining *cis*–geometry

P∩P			β_n [a] [º]
	n = 0	dppe	78.1
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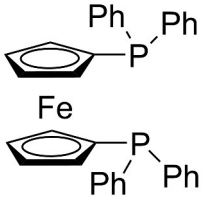
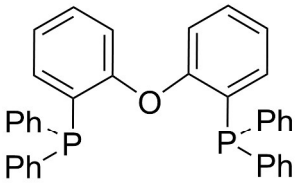
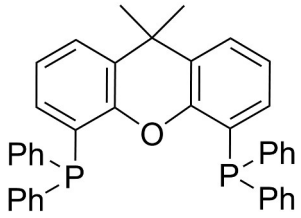
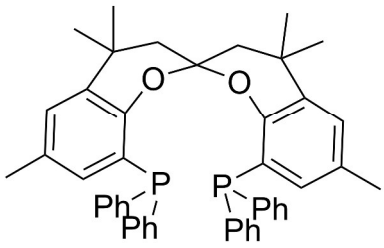
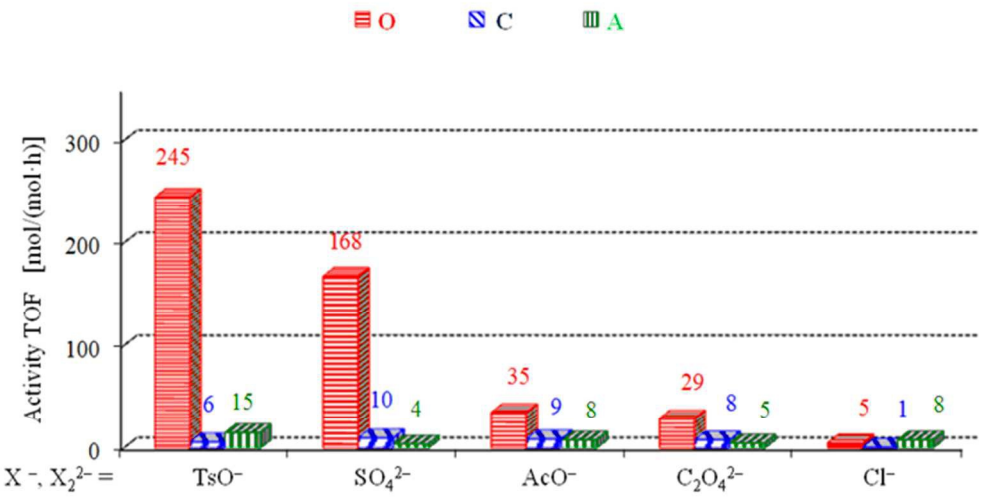
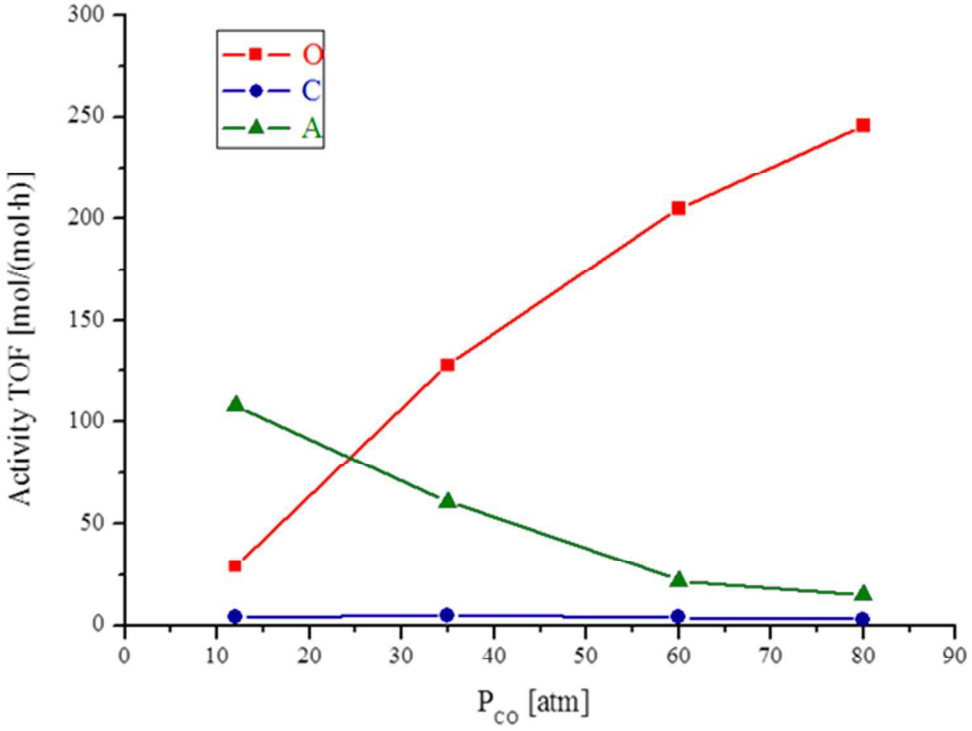
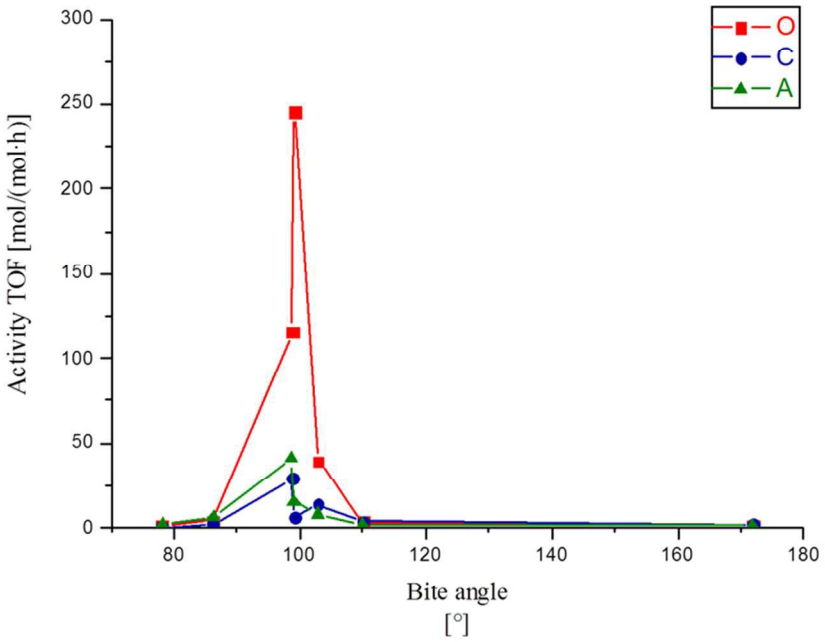
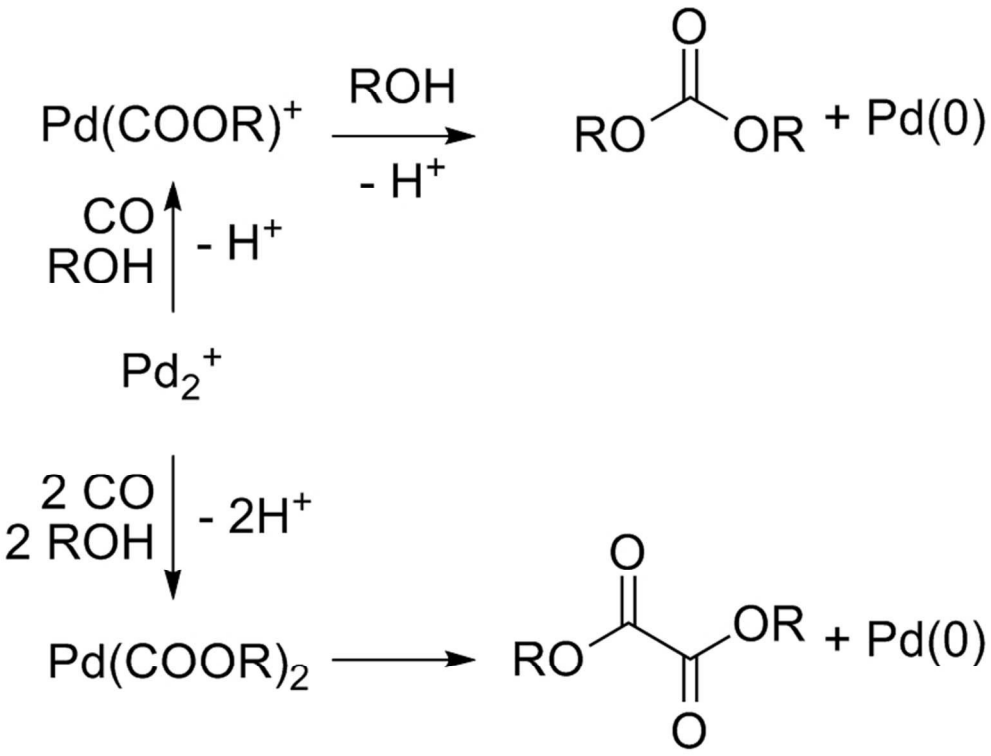
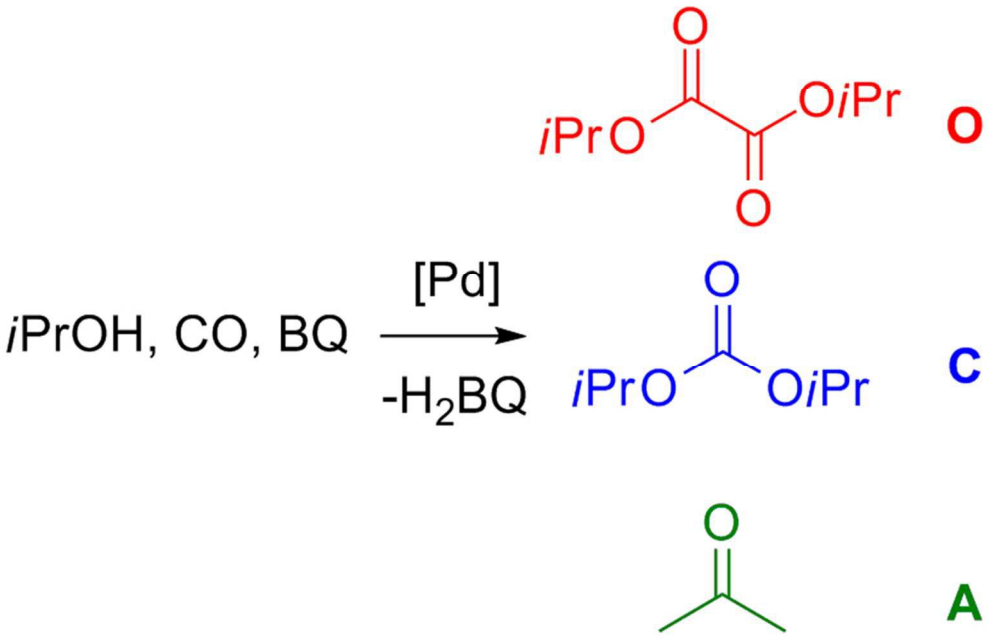
		dppf	99.1
		DPEphos	102.9
		Xantphos	110.0
		SPANphos	171.9 [b]

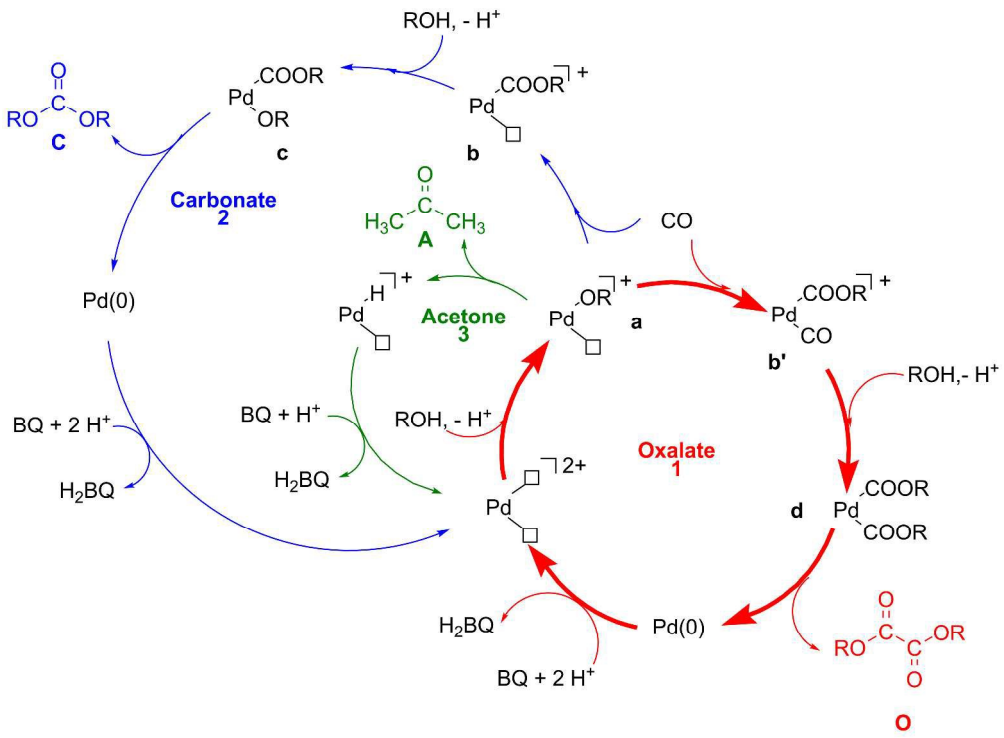


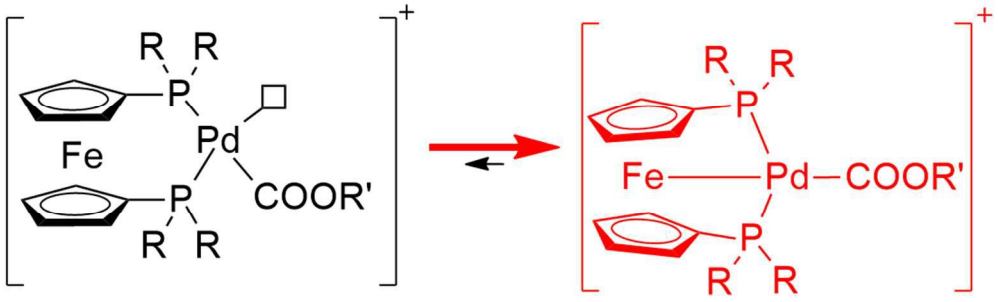












reactive
cis complex
k2-P,P

stable, less reactive
trans complex
k3-P,P,Fe