### Carbonylation of Nitrobenzene in Methanol with Palladium Bidentate Phosphane Complexes: An Unexpectedly Complex Network of Catalytic Reactions, Centred around a Pd-imido Intermediate

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ed that several catalytic processes oper-

ate simultaneously, and are coupled via

common catalytic intermediates. Start-

ing from a P<sub>2</sub>Pd<sup>0</sup> compound formed in

situ, oxidation to a palladium imido

compound P<sub>2</sub>Pd<sup>II</sup>=NPh, can be ach-

ieved by de-oxygenation of nitroben-

zene 1) with two molecules of CO,

2) with two molecules of CO and the

acidic protons of two methanol mole-

cules, or 3) with all four hydrogen

Keywords: carbonylation • homo-

geneous catalysis · palladium · P li-

gands • reaction mechanisms

Abstract: The reactivity of palladium complexes of bidentate diaryl phosphane ligands  $(P_2)$  was studied in the reaction of nitrobenzene with CO in methanol. Careful analysis of the reaction mixtures revealed that, besides the frequently reported reduction products of nitrobenzene [methyl phenyl carbamate (MPC), N,N'-diphenylurea (DPU), aniline, azobenzene (Azo) and azoxybenzene (Azoxy)], large quantities of oxidation products of methanol were co-produced (dimethyl carbonate (DMC), dimethyl oxalate (DMO), methyl formate (MF),  $H_2O$ , and CO). From these observations, it is conclud-

### Introduction

Replacing wasteful and dangerous industrial processes by more environmentally friendly and safer ones is one of the challenges in current-day catalysis. For example, large-scale reduction of aromatic nitro compounds to their corresponding carbamates, ureas, or isocyanates is of great significance to society. Carbamates and ureas are used on a large scale as pesticides, fertilizers and dyes.<sup>[1]</sup> Aromatic isocyanates are used in the preparation of (flame-retarding) foams,<sup>[2,3]</sup> (biodegradable) plastics,<sup>[4,5]</sup> pesticides,<sup>[6,7]</sup> adhesives<sup>[8-10]</sup> and coatings.<sup>[6,11,12]</sup> In particular the polymer precursors MDI and TDI<sup>[13,14]</sup> are of great importance, and are annually produced on the megaton scale.<sup>[15]</sup>

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201100923. It contains full (analytical) details of catalytic experiments (gas-phase and H<sub>2</sub>O analysis), analysis of the possible reaction stoichiometries and simulation of the experimental results.

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atoms of one methanol molecule. Reduction of  $P_2Pd^{II}$ =NPh to  $P_2Pd^0$  makes the overall process catalytic, while at the same time forming Azo(xy), MPC, DPU and aniline. It is proposed that the Pd–imido species is the central key intermediate that can link together all reduction products of nitrobenzene and all oxidation products of methanol in one unified mechanistic scheme. The relative occurrence of the various catalytic processes is shown to be dependent on the characteristics of the catalysts, as imposed by the ligand structure.



Starting from nitroarenes, the synthesis of both MDI and TDI involves an excess of the highly toxic<sup>[16,17]</sup> phosgene, and produces two moles of hydrochloric acid per mole of product.<sup>[18,19]</sup> The most viable alternative for these processes to emerge so far is catalytic reductive carbonylation of nitroarenes.<sup>[20]</sup> In the presence of an alcohol or an amine, a carbamate or urea is formed [Eqs. (1a) and (1c)]. Both compounds can be pyrolyzed to yield the isocyanate with recovery of the alcohol or amine employed [Eqs. (1b) and (1d)].

$$\frac{\text{PhNO}_2 + \text{CH}_3\text{OH} + 3\text{CO} \rightarrow}{\text{PhNH}(\text{CO})\text{OCH}_3 + 2\text{CO}_2}$$
(1a)

 $PhNH(CO)OCH_3 + \Delta T \rightarrow PhNCO + CH_3OH$  (1b)

$$PhNO_2 + PhNH_2 + 3CO \rightarrow$$

$$PhNH(CO)NHPh + 2CO_{2}$$
(1c)

$$PhNH(CO)NHPh + \Delta T \rightarrow PhNCO + PhNH_2$$
(1d)

In the 1980s it was discovered that palladium supported by bidentate N or P ligands afforded catalysts for this reaction in methanol (ca. 500 turnovers).<sup>[21–23]</sup> In particular, the

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use of the ligand 1,10-phenanthroline (phen), in the presence of an acid co-catalyst, proved to result in quite active catalysts (turnover numbers on the order of 10<sup>3</sup>). Thus far, most scientific endeavours have concentrated on the [Pd-(phen)<sub>2</sub>]X<sub>2</sub>/H<sup>+</sup>catalytic system in methanol,<sup>[24-35]</sup> leaving the Pd–phosphorus-based systems virtually unstudied.<sup>[21,31,36-38]</sup> However, since it is commonly accepted that Pd<sup>0</sup> species function as intermediates in the catalytic cycle,<sup>[20,32,39-41]</sup> it was envisaged that catalysts with bidentate P ligands could well perform differently from those with N-based ligands; their  $\pi$ -backbonding capability could give improved stabilization of the Pd<sup>0</sup> intermediates.

We therefore studied palladium-catalyzed carbonylation of nitrobenzene in methanol, with bidentate diaryl phosphane ligands. By careful quantitative analysis of the reaction mixtures, we found that a number of reactions must be operating simultaneously. The aim of the present study was therefore to explore which reactions take place and to propose a reaction network comprising them.

#### Results

**General considerations**: In catalytic carbonylation reactions the catalyst precursor complexes were formed in situ from Pd(OAc)<sub>2</sub> and 1.5 equivalents of ligand, as we have shown that palladium–ligand complex formation in methanol is instantaneous with the bidentate ligands used in this study.<sup>[42]</sup> As a control, the activity of several preformed precursor complexes was also tested, and identical results were obtained. Care was taken that the carbonylation experiments were carried out under strictly anhydrous conditions (<100 ppm H<sub>2</sub>O) with pre-dried reagents (see the Supporting Information, Section 2).

The products observed in our carbonylation experiments are collected in Scheme 1. The commonly observed products of nitrobenzene carbonylation are methyl phenyl carbamate (MPC) and *N*,*N*'-diphenylurea (DPU) with methanol and aniline as the nucleophilic reagent, respectively. Commonly reported side products are azobenzene (Azo), azoxybenzene (Azoxy) and aniline.<sup>[20]</sup> Formation of aniline (and the related DPU) is usually attributed to the presence of water, either in the reagents or formed in situ, for example, by acid-catalyzed etherification of methanol. Unexpectedly, analysis of our carefully prepared water-free reaction system (see Section 2 of the Supporting Information) revealed that with most of the palladium–diphosphane catalyst systems signifi-

cant amounts of dimethyl carbonate (DMC), dimethyl oxalate (DMO) and, to a lesser extent, methyl formate (MF) were also produced. Even more surprisingly, significant amounts of water appeared to be formed as a reaction product (see Section 3 of the Supporting Information). However, neither dimethyl ether (DME) nor dimethoxymethane (DMM) was observed as a reaction product; this excludes methanol self-etherification or etherification with any possibly formed free formaldehyde under reaction conditions as a source of water. It is noteworthy that DMM is commonly observed in cationic palladium-catalyzed olefin hydrocarbonylation experiments involving methanol as the hydrogendonor substrate.<sup>[43]</sup>

In the initial screening studies a large number of diphosphane ligands were used, with variations in the length and flexibility of the backbone spacer as well as in the substituents on the phenyl rings. It appeared that not only the activity, but in particular the selectivity of the catalysts for the formation of the various products, was highly dependent on the ligand structure. The observed trends in reactivities and selectivities are illustrated with the ligands shown in Scheme 2. These bidentate phosphane ligands have a rigid



Scheme 2. Overview of the ligands used in this study.

 $C_3$  (L3X) or a rigid  $C_4$  backbone (L4X), while the aryl rings can be functionalized with methoxyl moieties in the *ortho* position (oMeOL3X and oMeOL4X). These ligands readily form stable complexes with Pd(OAc)<sub>2</sub> in methanol.<sup>[42]</sup> The results of the catalytic nitrobenzene carbonylation experiments using these complexes are summarized in Table 1. Results obtained with a more extended range of ligands will be the subject of a future publication.<sup>[44]</sup>

Ligand effects on the reduction products of nitrobenzene: Analysis of the reaction mixtures was carried out using GLC techniques; most products were quantified by using calibration lines made with authentic samples with decane as internal standard and are reported in Table 1. The appropriateness in time of the calibration lines was ensured by



Scheme 1. Reaction products found in the catalytic carbonylation of nitrobenzene in methanol with palladium-diphosphane catalysts.

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regular analysis of known quantities of analytes. Solid DPU was isolated and its quantity determined by weight.

The high accuracy of the quantitative analysis of the phenyl-containing products is demonstrated by the observed conservation of aryl rings (Table 1, column  $\Sigma_{0}$ ). The activities of the palladium catalysts with the four different ligands are good to high, with conversions of PhNO<sub>2</sub> varying between 50 and 100% (Table 1, column PhNO<sub>2</sub>). With L3X as supporting ligand a reasonably active catalyst is obtained; 67% conversion of nitrobenzene was reached in 4 h (Table 1, entry 1). The main reaction product is aniline,

$$2CH_3OH + n CO \rightarrow H_3CO(CO)_n OCH_3 + "2H"$$
(2a)

$$2CH_3OH \rightarrow HC(O)OCH_3 + ''4H'' \tag{2b}$$

$$PhNO_2 + 2CO + "2H" \rightarrow PhNH_2 + 2CO_2$$
(2c)

This implies that nitrobenzene is reduced while functioning as the oxidant for the oxidative carbonylation and oxidative dehydrogenation of methanol. Interestingly, the presence of *o*-MeO moieties on the ligands influences the relative amounts of DMC, DMO and MF formed in the reac-

Table 1. Results of the catalytic reaction of nitrobenzene in methanol with palladium-diphosphane catalysts.<sup>[a]</sup>

Entry	Ligand	$PhNO_2$	$PhNH_2$	DPU <sup>[b]</sup>	MPC	Azo	Azoxy	Σø	DMC	DMO	MF	$H_2O^{[c]}$
1	L3X	8.1	8.3	0.8	5.3	0.1	0.4	24.3	4.2	3.1	0.2	3.4
2	oMeOL3X	0.6	5.7	3.1	11.6	0.1	0.1	24.5	0.4	0.4	1.1	0.7
3	L4X	11.8	1.9	0.5	0.5	0.1	4.5	24.4	2.3	5.9	0.2	10.0
4	oMeOL4X	2.4	10.5	1.9	5.6	0.5	0.6	24.5	2.1	7.3	0.6	8.7

[a] Reaction conditions: Pd(OAc)<sub>2</sub>:ligand:nitrobenzene=0.05:0.075:24.4 mmol in 25 mL methanol. Reaction mixtures were heated for four hours at 110 °C under a CO atmosphere of 50 bar (initial pressure). Quantities are reported in millimoles. See also Table S1 of the Supporting Information. [b] Quantified by weight. [c] Quantified by reaction with trimethyl orthoformate (see Supporting Information, Sections 2 and 3).

while selectivity to MPC is only 33%. The catalyst with ligand L4X showed slightly lower activity, but drastically different selectivity; the major product is azoxybenzene (Table 1, entry 3). The highest activity is obtained with catalysts containing *ortho*-methoxy-substituted ligands (Table 1, entries 2 and 4) with greater than 90% nitrobenzene conversion. The use of these ligands also results in significantly higher selectivity for the product MPC; considerably smaller amounts of the coupling products azo- and azoxybenzene are produced.

Ligand effects on the oxidation products of methanol and the hydrogen mass balance: Although the mass conservation of phenyl rings appeared to be excellent for the products derived from nitrobenzene, a closer look at the hydrogen-atom conservation revealed that the products aniline and DPU contain hydrogen atoms that can only be derived from methanol. Indeed, quantitative analysis of all reaction products detectable by GLC in the liquid phase showed that in all experiments significant amounts of the methanol-derived oxidation products dimethyl carbonate (DMC) and dimethyl oxalate (DMO) are formed, products which are known to be formed from methanol in the presence of CO and an oxidant.<sup>[45-48]</sup> Methyl formate (MF) is also produced, albeit to a lesser extent. Clearly, these products are formed from a hydrogen-donating methanol carbonylation process (DMC, DMO) liberating two "hydrogen atoms" or an oxidative dehydrogenation process (MF) liberating four "hydrogen atoms" [Eqs. (2a) and (2b); n=1 or 2].<sup>[49]</sup> The produced hydrogen atoms are transferred to nitrobenzene by a mechanism postulated below, forming aniline, and thereby also DPU, as secondary product [Eq. (2c)].<sup>[50]</sup>

tions; the catalysts with unsubstituted ligands L3X or L4X produce more DMC and DMO, whereas the catalysts with the methoxy-substituted ligands oMeOL3X or oMeOL4X produce larger amounts of MF.

Hydrogen-atom conservation of all products requires that the sum of the hydrogenreleasing compounds (DMC+ DMO+2MF) equal that of the hydrogen-consuming products

(PhNH<sub>2</sub>+DPU). Although the hydrogen mass balance is partly restored when taking the formation of DMC, DMO and MF into account, the hydrogen balance still appeared to be significantly uneven. Further investigations revealed that water is co-produced (see Section 3 of the Supporting Information for the experimental procedure for determination of the quantity of water), and this suggests that the reactions described by Equations (3a) and (3b) may also play an important role.

 $PhNO_2 + CO + "4H" \rightarrow PhNH_2 + CO_2 + H_2O$ (3a)

$$PhNO_2 + "6H" \rightarrow PhNH_2 + 2H_2O \tag{3b}$$

However, the hydrogen balance appears even more uneven when  $H_2O$  production is taken into account (i.e.,  $DMC+DMO+2MF=PhNH_2+DPU+H_2O$ ). Interestingly, when using the ligands with a  $C_4$  backbone (Table 1, entries 2 and 4), large amounts of water were detected, whereas for ligands with a  $C_3$  backbone (Table 1, entries 1 and 2), relatively small amounts of water were detected. This could be due to concurrent production and consumption of water. Note, however, that consumption of water should not affect the hydrogen mass balance, as the hydrogen atoms would end up in PhNH<sub>2</sub> or DPU.

Hydrogen mass balance; complete dehydrogenation of methanol: The hydrogen mass balance involving all of the products detected in the liquid phase of the reaction mixture is shown schematically in Figure 1. For each of the catalysts significantly more "hydrogen-consuming" products (H<sub>2</sub>O, PhNH<sub>2</sub>, and DPU) than "hydrogen-releasing" compounds (DMC, DMO, and MF) are observed. This suggests that

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Figure 1. Visualization of the hydrogen mass-balance for the products reported in Table 2, 2(DMC+DMO+2MF) ( $\blacksquare$ ) and  $2(H_2O+PhNH_2+DPU)$  ( $\Box$ ).

there must be an as yet unknown additional source of hydrogen atoms. Because the CO used was more than 99% pure, the option was considered that the hydrogen atoms originate from impurities (H<sub>2</sub>O/H<sub>2</sub>) in this reactant. However, traces of water (20 vpm according to the manufactur $er)^{[51]}$  could account only for a maximum of about 6  $\mu mol$  of hydrogen atoms. Similarly, even if it is assumed that the CO contains 1% H<sub>2</sub> and this, as an unlikely event, would be totally consumed as reductant for nitrobenzene, the maximum amount of hydrogen atoms from this source can be only 4 mmol (2 mmol H<sub>2</sub>), whereas for the ligand oMeOL4X 21 mmol too many hydrogen atoms are observed. This leaves as a surprising conclusion that methanol itself is the only plausible source of hydrogen atoms, that is, methanol can also be fully dehydrogenated to CO. Apparently, in addition to the production of DMC/DMO [Eq. (2a)] or MF [Eq. (2b)], CO production can liberate four "hydrogen atoms" [Eq. (4)].

$$CH_3OH \rightarrow CO + "4H"$$
 (4)

To verify this possible reaction, the gas phase of an autoclave experiment in which a catalytic reaction was conducted in the presence of methanol containing 4% <sup>13</sup>CH<sub>3</sub>OH (v/v) and using only 5 bar CO was analyzed by mass spectroscopy (see Table S2 of the Supporting Information for details). A catalyst system with oMeOL3X as supporting ligand was chosen, as with this catalyst hydrogen mass conservation is significantly violated. This resulted in a significant increase of 15% of <sup>13</sup>C-enriched CO, which must originate from full methanol dehydrogenation.<sup>[52]</sup> Moreover, it appeared to be possible to even out the hydrogen mass balance for this experiment, as the amount of fully dehydrogenated methanol can be estimated.<sup>[53]</sup> When this experiment was repeated under an argon atmosphere (in the absence of CO) CO<sub>2</sub> was produced (see Figure S3, Supporting Information) with co-production of some nitrobenzene reduction products. This also proves that methanol must have been fully stripped of hydrogen atoms to function as the reductant of nitrobenzene.

**Methanol as transfer-hydrogenation reagent**: As the above observations imply that methanol can act as a transfer-hydrogenation reagent, we tested whether a better transfer-hydrogenation donor, that is, 2-propanol, would give similar

results. Indeed, with Pd<sup>II</sup>(oMeOL3X)(OAc)<sub>2</sub> as catalyst precursor, a reaction of nitrobenzene in 2-propanol with 50 bar CO resulted almost exclusively in the formation of aniline, with co-production of a large quantity of acetone. In contrast with acetone as stable transfer-hydrogenation end product, palladium-bound formaldehyde (formed after the first dehydrogenation of CH<sub>3</sub>OH) can be further stripped of hydrogen atoms under reaction conditions to give CO. To further test whether formaldehyde could indeed be an intermediate, 0.30 g of *para*-formaldehyde (about 9 mmol (O= CH<sub>2</sub>)<sub>n</sub>, assuming that 10% of the weight consists of water "end groups") was suspended in methanol/nitrobenzene and allowed to react for four hours at 110°C in the presence of an active catalyst (Table 2, entry 1). Surprisingly, in this re-

Table 2. Reactivity of *para*-formaldehyde with methanol and aniline in the presence or absence of an active catalyst. Quantities are reported in millimoles.<sup>[a]</sup>

Entry	Catalyst	$P_{\rm CO}$	Additives	MF	DMM	MBA
1	yes	50	$\approx 9 (H_2 CO)_n$ 24.4 PhNO <sub>2</sub>	7.8	trace	trace
2	no	50	$\approx 9 (H_2 CO)_n$	trace	3.7	-
3 <sup>[b]</sup>	yes	5	$\approx 9 (H_2 CO)_n$ 10 PhNH <sub>2</sub> 4.9 PhNO <sub>2</sub>	3.0	-	1.6

[a] Reaction mixtures were heated for four hours at 110°C in 25 mL methanol. The catalyst was Pd(oMeOL3X)(OAc)<sub>2</sub>, synthesized in situ from 0.05 mmol Pd(OAc)<sub>2</sub> and 0.075 mmol oMeOL3X. See also Table S1 of the Supporting Information for full analysis of the reaction mixtures.
[b] CO pressure and nitrobenzene concentration were lowered to suppress the carbonylation reaction.

action MF was formed almost exclusively. When this experiment was repeated in the absence of a catalyst and nitrobenzene (Table 2, entry 2) dimethoxymethane (DMM) was, as expected, exclusively formed instead. When aniline was also present in the reaction mixture (Table 2, entry 3), formaldehyde was again converted to MF, but now also a significant amount of N-methylenebenzenamine (PhN=CH<sub>2</sub>, MBA) was formed. MBA can be seen as a condensation product of formaldehyde and aniline and is sometimes also detected in small amounts after a normal catalytic experiment. This confirms that in the presence of the catalyst, formaldehyde can react to form MF and to MBA rather than DMM. Thus, when methanol dehydrogenation proceeds via a Pd-formaldehyde intermediate, this suggests that the formaldehyde molecule does not dissociate from the catalyst, as otherwise DMM would be produced instead.

Ligand effects in the consumption of water: As for some catalysts large amounts of water were detected (Table 1) and almost no water was observed for other catalysts, we investigated whether perhaps water could also be consumed during the reaction. Thus, the reactions listed in Table 1 were repeated, but now water was deliberately added to the system (Table 3, see also Section 4 of the Supporting Infor-

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Table 3. Catalytic carbonylation reactions with in situ synthesized Pd-(ligand)(OAc)<sub>2</sub> catalyst precursors with and without added water.<sup>[a]</sup>

Entry	Ligand	$H_2O$ added <sup>[b]</sup>	$\begin{array}{l} H_2O\\ detected^{[c]} \end{array}$	DMC+ DMO	MPC+ DPU	PhNH <sub>2</sub> + DPU
1-1	L3X	_	3.4	7.3	6.1	9.1
1-2	L3X	12	7.4	3.5	4.0	11.1
		cons:[d]	8.0	$\Delta^{[e]}\!=\!-3.8$	$\Delta\!=\!-2.1$	$\Delta = 2.0$
2-1	L4X	_	10.0	8.2	1.0	2.4
2-2	L4X	12	22.3	7.8	0.9	2.3
		cons:	-0.3	$\Delta = -0.4$	$\Delta\!=\!-0.1$	$\Delta\!=\!-0.2$
3-1	oMeOL3X	_	0.7	0.8	14.7	8.8
3-2	oMeOL3X	12	1.9	0.2	9.3	14.0
		cons:	10.8	$\Delta\!=\!-0.6$	$\Delta\!=\!-5.4$	$\Delta = 5.2$
4-1	oMeOL4X	_	8.7	9.4	7.5	12.4
4-2	oMeOL4X	12	18.8	9.6	6.6	13.3
		cons:	1.9	$\Delta = 0.2$	$\Delta\!=\!-0.9$	$\Delta = 0.9$

[a] Reaction conditions:  $Pd(OAc)_2$ :ligand:nitrobenzene = 0.05:0.075: 24.4 mmol in 25 mL methanol. Reaction mixtures were heated for four hours at 110 °C under a CO atmosphere of 50 bar (initial pressure). Quantities are reported in millimoles. See also Table S1 of the Supporting Information. [b] Before the catalytic reaction. [c] After the catalytic reaction. [d] mmol water consumed, as calculated by (12+entry x-1)-(entry x-2). [e] Difference (entry x-2)-(entry x-1). See also Section 4 of the Supporting Information.

mation for experimental details). When employing catalysts containing the ligands with a C<sub>3</sub> backbone (Table 3, entries 1 and 3), it appears that water is largely consumed during the reaction; some residual water was only detected when 12 mmol water was added prior to the catalytic run (Table 3, entries 1-2 and 3-2). However, when using ligands with a  $C_4$ backbone, large amounts of water were already detected after a normal catalytic experiment (Table 3, entries 2-1 and 4-1). When 12 mmol water was added prior to a catalytic run (Table 3, entries 2-2 and 4-2), this amount is found again after the experiment, in addition to the amount formed during the reaction. It thus appears that water is formed but only partly consumed when using catalysts containing the ligands L4X and oMeOL4X, but added water appears to be largely consumed when using catalysts with the ligands L3X and oMeOL3X.

Water may be consumed by replacing methanol as reagent in Equation (1a), the combination of (2a) + (2c), or the combination of  $(4) + 2 \times (2c)$ .

$$PhNO_2 + CH_3OH + 3CO \rightarrow MPC + 2CO_2$$
(1a)

 $\begin{array}{l} PhNO_2+2CH_3OH+3CO\rightarrow\\ PhNH_2+DMC+2CO_2 \end{array} \tag{2a+2c}$ 

$$\frac{2\text{PhNO}_2 + \text{CH}_3\text{OH} + 4\text{CO} \rightarrow}{2\text{PhNH}_2 + 4\text{CO}_2} \qquad (4 + 2 \times 2\text{c})$$

When water replaces methanol in the formation of MPC [Eq. (1a)], phenylcarbamic acid (PhNHC(O)OH) will be formed, which decomposes into aniline and  $CO_2$ , and thus leads to the stoichiometry shown in Equation (1a\*). When

water replaces one methanol molecule in the formation of DMC [Eq. (2a)], methyl hydrogen carbonate (CH<sub>3</sub>OC(O)OH) will be formed, which will readily decompose into methanol and CO<sub>2</sub>. This will lead to the stoichiometry given by Equation (2a<sup>\*</sup>), which is effectively the watergas shift reaction. When Equation (2a<sup>\*</sup>) is combined with Equation (2c) (aniline formation), the net overall stoichiometry also amounts to Equation (1a<sup>\*</sup>). Similarly, stoichiometry (1a<sup>\*</sup>) results when (two) water molecules replace methanol in Equation (4), and this reaction is combined with the production of aniline [2×Eq. (2c)].

$$PhNO_2 + H_2O + 3CO \rightarrow PhNH_2 + 3CO_2$$
 (1a\*)

$$H_2O+CO \rightarrow CO_2 + ''2H'' \tag{2a*}$$

From the above it follows that, when water is consumed, either the amount of MPC (or DPU) must decrease while increasing the amount of aniline accordingly, or the amount of DMC (or DMO) must decrease while keeping the amount of aniline constant. This is indeed reflected in the change in product distributions for the reactions with and without added water, as can be seen in Table 3.<sup>[54]</sup>

**In situ trapping experiments:** As the formation of all observed products may very well be explained by postulating a palladium imido species "Pd=NPh" as key intermediate (see below), we sought evidence for its existence under reaction conditions. Attempts were thus made to trap this species by adding cyclohexene<sup>[55]</sup> during a catalytic experiment (Scheme 3). When 25 mmol cyclohexene was added during a catalytic run formation of the corresponding aziridine was indeed observed when employing Pd<sup>2+</sup>(L4X) or Pd<sup>2+</sup> (oMeOL3X) as catalyst precursor. Figure 2 shows the mass and fragmentation pattern of the peak in the GLC-MS spec-

$$Ph \rightarrow P_2Pd=N' \rightarrow N-Ph + P_2Pd^0$$

Scheme 3. Proposed trapping reaction of an imido complex with cyclohexene.



Figure 2. Mass spectrum of a compound detected by GLC-MS analysis of a reaction mixture to which cyclohexene was added.

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trum that was assigned to this trapping product; both are consistent with the structure of 7-phenyl-7-aza-bicyclo-[4.1.0]heptane.

#### Discussion

**Coupling oxidation of methanol with reduction of nitrobenzene**: In the studies on the carbonylation of nitrobenzene in methanol to form methyl phenyl carbamate, the usually reported side products only comprise the phenyl-containing compounds aniline, DPU, Azo and Azoxy, depending on the reaction conditions and additives.<sup>[20]</sup> In general, the mechanistic proposals (Scheme 4) for the reaction catalyzed by



Scheme 4. Generally accepted mechanistic proposal for the reductive carbonylation of nitrobenzene, wherein the bidentate ligand  $(L_2)$  is 1,10-phenanthroline.

Pd–1,10-phenanthroline systems start with oxidative coupling of CO and PhNO<sub>2</sub> at an (in situ generated) Pd<sup>0</sup> species to form a Pd<sup>II</sup> species.<sup>[20,32,56]</sup> During the proposed catalytic cycle the catalyst remains in the Pd<sup>II</sup> oxidation state; in the final MPC-generating step, Pd<sup>0</sup> is regenerated from a palladacyclic intermediate such as that shown in Scheme 4.<sup>[28,39]</sup>

The most remarkable observation when applying bidentate diaryl phosphanes as ligands in the catalyst is the formation, under mild reaction conditions, of substantial amounts of products that are derived from oxidative reactions involving methanol as well as products derived from reduction of nitrobenzene. Clearly, carbonylation of methanol to DMC (or DMO) must be accompanied by reduction of Pd<sup>II</sup> to Pd<sup>0</sup>; conversely, the oxidant nitrobenzene will oxidize Pd<sup>0</sup> to Pd<sup>II</sup> while being reduced to aniline, DPU, MPC and Azo(xy). These elementary process steps must form the basis for product formation shown in Table 1. Dictated by the hydrogen mass balance, transfer of "hydrogen atoms" from methanol [Eqs. (2a), (2b) and (4)] to nitrobenzene [Eqs. (2c), (3a) and (3b)] must play an important role in these reactions. A palladacyclic intermediate such as that shown in Scheme 4 cannot be used to rationalize formation of oxidation products of methanol, nor the hydrogen transfer from methanol to nitrobenzene. Therefore, an alternative catalytic intermediate must be proposed that can link the reduction of nitrobenzene with the oxidation of methanol.

Reduction of nitrobenzene; a palladium imido complex as key intermediate: Central to understanding the Pd-phosphine catalysts systems is our hypothesis that the PhNO<sub>2</sub> reduction process is modified in the sense that a Pd–imido intermediate is formed (see further details below).<sup>[32,56,57]</sup> Such a species will allow a catalytic connection to be made between the reductive processes involving nitrobenzene and oxidative processes involving methanol. Thus, with Pd–phosphine systems, we propose a nitrobenzene reduction reaction with CO as the reductant [Eq. (5a)].

$$P_2Pd^0 + PhNO_2 + 2CO \rightarrow P_2Pd^{II} = NPh + 2CO_2$$
(5a)

However, as clearly evidenced by significant formation of  $H_2O$  with some of the catalysts, "hydrogen atoms" from methanol obviously also act as a direct reductant for nitrobenzene, to eventually form the same Pd-imido intermediate. A reasonable way to achieve this is via reaction (5b), wherein the acidic hydrogen atoms of two methanol molecules and two CO molecules act as reductant for nitrobenzene. Note that the second molecule of CO is not directly used to de-oxygenate nitrobenzene, but is merely used to form DMC.

$$P_{2}Pd^{0}+PhNO_{2}+2CO+2CH_{3}OH \rightarrow P_{2}Pd^{II}=NPh+DMC+H_{2}O+CO_{2}$$
(5b)

Furthermore, as evidenced by the gas-phase enrichment of  $^{13}$ CO from  $^{13}$ CH<sub>3</sub>OH, it must be concluded that methanol can be fully stripped of hydrogen atoms, for example, via reaction (5c).

$$P_2Pd^0 + PhNO_2 + CH_3OH \rightarrow P_2Pd^{II} = NPh + 2H_2O + CO$$
(5c)

In this reaction, CO could also act as a co-reductant together with two instead of four hydrogen atoms of methanol to form H<sub>2</sub>C=O. However, formaldehyde was never detected, and nor was its methanol condensation product DMM. On the other hand, MF was always detected, which may be seen as resulting from a modified version of Equation (5c), wherein two molecules of methanol react to give MF instead of CO [see also Eq. (2b)].

The proposed Pd–imido intermediate can thus be formed in three ways: de-oxygenation of nitrobenzene with two equivalents of CO only [Eq. (5a)], with the acidic protons of two molecules of CH<sub>3</sub>OH and with two CO [Eq. (5b)] and with all four hydrogen atoms of one CH<sub>3</sub>OH [Eq. (5c)].

A palladium imido complex as key intermediate; mechanistic considerations: The reductive cyclization of (*ortho*) functionalized aromatic nitro compounds has been proposed to proceed via a palladium imido compound.<sup>[58]</sup> Additionally, by using deuterium labelling experiments the intermediacy of a palladium imido species was demonstrated in the reductive N-heterocyclization of various 2-nitrostyrene and *N*-(2nitrobenzylidene)amine derivatives to the corresponding indole and 2*H*-indazole derivatives.<sup>[59]</sup> A Pd–imido com-

pound has never been reported and only once claimed to be spectroscopically (IR) detected.<sup>[60]</sup> However, a series of bidentate phosphane stabilized Ni imido complexes has been isolated. Upon reaction with CO these complexes formed phenyl isocyanate, and upon reaction with ethene the corresponding aziridine could be obtained.<sup>[61-63]</sup> Inspired by these reports, we added cyclohexene during a catalytic run with the aim to trap the nitrene ligand of the possible  $P_2Pd^{II}$ = NPh intermediate. GLC-MS analysis after these runs indeed revealed the presence of the corresponding aziridine. These observations lend credibility to the postulation of a Pdimido complex as important intermediate for the reduction reactions of nitrobenzene.<sup>[32,56,57]</sup> Our synthetic efforts aimed at formation and spectroscopic characterization of diphosphane Pd-imido complexes give further evidence of their existence; the synthesis and reactivity of these complexes will be reported elsewhere.<sup>[64]</sup>

At this stage, experimentally proven, direct evidence for intermediacy of a palladium imido species in the above-proposed reactions [Eqs. (5a)–(5c)] cannot yet be given. However, we consider it useful to further elaborate on the molecular mechanistic basis underlying these proposed reactions. Such a consideration will provide us with the appropriate framework to rationalize how the nitrobenzene reduction process is linked with the oxidation of methanol. Also, the experimentally observed product compositions can then be related to the P<sub>2</sub>Pd<sup>II</sup> complexes in terms of their structural and electronic properties (vide supra).

The commonly proposed pathway to reduce nitrobenzene with CO alone is shown at the top of Scheme 5. Oxidative coupling of CO and nitrobenzene at Pd<sup>0</sup> involves formal oxi-



Scheme 5. Mechanistic proposals for nitrobenzene reduction with CO as only reductant [top, forming  $P_2Pd^{II}$ =NPh via Eq. (5a)] and the initial steps with CH<sub>3</sub>OH as reductant (bottom).

dation of  $P_2Pd^0$  (C1) to give the palladacyclic species C2a. This can be followed by further de-oxygenation by successive CO<sub>2</sub> extrusion/carbonylation/CO<sub>2</sub> extrusion (via C3a and C4a) to give the palladium imido intermediate. This sequence would account for the stoichiometry given in Equation (5a). Note that CO insertion into the Pd–N bond of C4a can also occur; this would afford the palladacycle generally proposed and observed for Pd–1,10-phenanthroline nitrobenzene reduction systems.<sup>[28,39]</sup>

Alternatively, reduction of nitrobenzene must be achieved by hydrogen atoms from methanol eventually leading to Equations (5b) and (5c). This transfer-hydrogenation process most likely involves palladium hydride chemistry, without involvement of "free" H<sub>2</sub>, as methanol dehydrogenation to  $H_2$  and DMC, MF or CO is endothermic by about +21, +48 and +44 kcalmol<sup>-1</sup>, respectively.<sup>[65-67]</sup> First, Pd-hydride formation might take place by oxidative addition of methanol to  $P_2Pd^0$  to give **C2b/c**, as shown at the bottom of Scheme 5. Displacement of a CH<sub>3</sub>O<sup>-</sup> anion by nitrobenzene gives cationic Pd hydride C3b/c. Migration of the hydride to the coordinated nitrobenzene then yields C4b/c, in which the nitrobenzene fragment has become anionic, that is, [ON(Ph)OH]<sup>-</sup>. Nucleophilic attack of the anionic [ON(Ph)OH]<sup>-</sup> fragment on the acidic proton of methanol in C4b/c forms palladium-bound nitrosobenzene (C5b/c) and liberates H<sub>2</sub>O, thus completing the first reduction step.<sup>[68]</sup>

As is shown in Scheme 6, it is thought that the different pathways to the reactions given in Equation (5b) or (5c) are determined in complex **C5b/c**. Thus, CO insertion (top) into the Pd–OCH<sub>3</sub> bond of **C5b/c** affords **C6b**, from which DMC can be formed, thus yielding Pd<sup>0</sup> nitrosobenzene complex **C3a** (nitrosobenzene was indeed experimentally observed in trace amounts). From here, just as in the "CO-only" reduction route (top of Scheme 5), the Pd–imido complex can be formed by carbonylation/CO<sub>2</sub> extrusion, thus leading to the overall stoichiometry given by Equation (5b).



Scheme 6. Mechanistic proposals for nitrobenzene reduction to  $P_2Pd^{II}$ = NPh with either CH<sub>3</sub>OH/CO as co-reductants [top, using only the OH proton of methanol, Eq. (5b)] or with only CH<sub>3</sub>OH as reductant [bottom, also using the CH<sub>3</sub> protons of methanol, Eq. (5c)].

Alternatively (Scheme 5, bottom), nucleophilic attack of the uncoordinated  $CH_3O^-$  anion in **C5b/c** on an hydrogen atom of the coordinated  $CH_3O^-$  anion (i.e., a net  $\beta$ -hydrogen abstraction) will liberate methanol and form zero-valent palladium formaldehyde/nitrosobenzene complex **C6c**. In a subsequent reaction involving intramolecular hydrogen transfer (presumably via the Pd centre) from formaldehyde to nitrosobenzene, palladium can be oxidized to **C7c**. This clearly is a hypothetical reaction, but may be viewed as bearing resemblance to oxidative coupling of CO with nitrobenzene at Pd<sup>0</sup> in the formation of a palladacycle (**C2a**, Scheme 5). The last hydrogen atom can then be transferred by nucleophilic attack of the [N(Ph)OH]<sup>-</sup> anion on the PdC(O)H proton, forming the Pd–imido complex, H<sub>2</sub>O and

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CO. This results in the overall stoichiometry given by Equation (5c). Note that reaction of (C7c) with methanol could also lead to MF, water and the imido intermediate (not shown in Scheme 6).

While there is no a priori way to estimate the respective contributions of nitrobenzene reduction by two CO [Eq. (5a)], two CH<sub>3</sub>OH and two CO [Eq. (5b)] or one  $CH_3OH$  alone [Eq. (5c)], the above mechanistic basis provides a rationale for the generation of H<sub>2</sub>O, DMC/DMO, CO and MF by oxidative dehydrogenation of methanol with nitrobenzene as oxidant. All these proposed reactions result in the same P<sub>2</sub>Pd<sup>II</sup>=NPh intermediate (as summarized in Scheme 7) as a centrally important intermediate species in a complex network of catalytic cycles that links all oxidation products of methanol with all reduction products of nitrobenzene, as is discussed below.



Scheme 7. Three competing pathways for reduction of nitrobenzene to a Pd<sup>II</sup> imido intermediate, with two CO (top), one CO and the acidic protons of two methanol (centre) or all H atoms of one methanol (bottom) as de-oxygenating agent.

**Protonation of the palladium imido complex; formation of aniline**: To sustain coupled catalytic cycles for production of both the methanol oxidation and nitrobenzene reduction products, a product-releasing species of one cycle must be an initiating intermediate species in the complementary product catalytic cycle. Thus, it is appropriate to consider how the palladium imido species could account for formation of the aryl-containing products while being reduced to Pd<sup>0</sup> to sustain such reactions catalytically.

Because the imido nitrogen atom is formally dianionic and thus expected to be basic, protonation by methanol may readily occur. This will generate aniline and a dimethoxide species,  $P_2Pd^{II}(OCH_3)_2$ , as shown in Equation (6).

$$P_2Pd^{II} = NPh + 2HOCH_3 \rightarrow PhNH_2 + P_2Pd^{II}(OCH_3)_2$$
(6)

Once this dimethoxido  $Pd^{II}$  complex is formed, carbonylation can reduce  $Pd^{II}$  to  $Pd^0$  and generate DMC or DMO [Eqs. (7a) and (7b)].

$$P_2Pd^{II}(OCH_3)_2 + CO \rightarrow OC(OCH_3)_2 + P_2Pd^0 \tag{7a}$$

$$P_2Pd^{II}(OCH_3)_2 + 2CO \rightarrow (OC)_2(OCH_3)_2 + P_2Pd^0 \eqno(7b)$$

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Carbonylation reactions (7) are thought to proceed by displacement of the anionic CH<sub>3</sub>O<sup>-</sup> moiety by CO coordination and subsequent nucleophilic attack of methoxide on coordinated CO forming  $P_2Pd(C(O)OCH_3)(OCH_3)$  (I); reductive elimination of DMC then regenerates the P<sub>2</sub>Pd<sup>0</sup> compound. When CO displaces the CH<sub>3</sub>O<sup>-</sup> moiety in I, subsequent nucleophilic attack of CH3O- on coordinated CO gives the dicarbomethoxide compound  $P_2Pd(C(O)OCH_3)_2$ (II) which again gives  $P_2Pd^0$  upon reductive elimination of DMO. It is thus thought that DMC and DMO are formed in related elementary reaction steps. Their respective yields will depend on the relative abundance of species I and II, which is determined by the competition between CO and  $CH_3O^-$  for a coordination site at the palladium centre in **I**. Further details of this methanol carbonylation process and factors that influence the rate and selectivity of these reactions will be subject of a separate publication.<sup>[64]</sup> As far as the present discussion concerns, it suffices to note that DMC and DMO can be regarded as one product, providing two hydrogen atoms.

Thus, catalytic coupling can be established between two sets of half reactions: one set [Eqs. (5a)–(5c)] wherein nitrobenzene is reduced while  $P_2Pd^0$  is oxidized to a  $P_2Pd^{II}=NPh$ intermediate (producing CO<sub>2</sub>/H<sub>2</sub>O/DMC/DMO/CO/MF); and one complementary series of reactions [Eqs. (6), (7a) and (7b)] wherein the  $P_2Pd^{II}=NPh$  intermediate is reduced to  $P_2Pd^0$  via the  $P_2Pd^{II}(OCH_3)_2$  complex, thereby producing PhNH<sub>2</sub>, but also DMC/DMO.

"Disproportionation" of nitrobenzene with the palladium imido complex; formation of azo(xy)benzene: When P<sub>2</sub>Pd-(L4X) was used as catalyst, significant amounts of azoxybenzene were produced, apparently at the expense of aniline and MPC (Table 1). It seems likely that, when employing  $P_2Pd(L4X)$ , the Pd-imido intermediate is also formed, but this species then does not react with methanol to produce DMC/DMO and aniline [Eq. (6)], but instead undergoes attack by nitrobenzene giving a "disproportionation"-type reaction to form azoxybenzene and formally a "P2Pd=O" complex [Eq. (8a)]. The possible existence of such a compound has been proposed before in the form of "(Ph<sub>3</sub>P)<sub>2</sub>PdO".<sup>[69]</sup> Furthermore, (*t*Bu<sub>3</sub>P)<sub>2</sub>Pd has been reported to react with dioxygen to give a deep red compound analyzed as  $[(tBu_3P)PdO]_n$ . The IR spectrum of this compound did not show the v(O-O) band that is expected for side-on O2 coordination.<sup>[70]</sup> Our hypothetical "P2Pd=O" species will be readily de-oxygenated by CO to form CO<sub>2</sub>, thus regenerating the zero-valent palladium species [Eq. (8b)]. Alternatively, the "P<sub>2</sub>Pd=O" complex can be protonated with methanol to form water and  $P_2Pd^{II}(OCH_3)_2$  [Eq. (8c)], which can also regenerate  $P_2Pd^0$  [Eq. (7)]. This sequence couples azoxybenzene formation to catalytic nitrobenzene reduction, either directly via P<sub>2</sub>Pd<sup>0</sup> [Eq. (8b)], or indirectly via P<sub>2</sub>Pd- $(OCH_3)_2$  [Eq. (8c)]. The considerably less pronounced formation of azobenzene can be seen as a similar process involving attack of nitrosobenzene (as intermediate product in nitrobenzene de-oxygenation, Scheme 5) on the same Pd-

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imido intermediate [Eq. (8d)]. Indeed, trace amounts of nitrosobenzene were sometimes observed.

$$P_2Pd^{II}=NPh + PhNO_2 \rightarrow PhN(O)NPh + "P_2Pd^{II}=O"$$
 (8a)

$$"P_2Pd^{II} = O" + CO \rightarrow CO_2 + P_2Pd^0$$
(8b)

$$"P_2Pd^{II} = O" + 2 \text{ HOCH}_3 \rightarrow H_2O + P_2Pd^{II}(OCH_3)_2$$
(8c)

 $P_2Pd^{II} {=} NPh + PhNO \rightarrow PhNNPh + "P_2Pd^{II} {=} O" \tag{8d}$ 

It thus appears that the formation of reductive self-coupling products of nitrobenzene (to give azoxy- and azobenzene) can also be linked into the network of  $P_2Pd^{II}/P_2Pd^0$ catalytic cycles centred around the Pd–imido intermediate [Eqs. (5)–(8)].

**Carbonylation of nitrobenzene**—**MPC, DPU and CO**<sub>2</sub>: The nitrobenzene carbonylation products MPC and DPU can also be linked to the imido intermediate. Mono-protonation of  $P_2Pd^{II}$ =NPh [Eq. (9a)] by methanol, followed by CO insertion [Eq. (9b)] and reductive elimination [Eq. (9c)], leads to MPC while regenerating  $P_2Pd^0$ . When in this sequence of reactions methanol is replaced by aniline, DPU will be formed instead of MPC. Likewise, when water replaces methanol, phenyl carbamic acid will be produced. MPC and DPU can interconvert with each other under reaction conditions by trans-esterification, and can thus be considered as essentially the same nitrobenzene carbonylation product. Phenylcarbamic acid will decompose [Eq. (9d)] into aniline and CO<sub>2</sub>, which is formally also a carbonylation product of nitrobenzene.

 $P_2Pd^{II} = NPh + HOCH_3 \rightarrow P_2Pd^{II}(OCH_3)NHPh$  (9a)

 $P_2Pd^{II}(OCH_3)NHPh + CO \rightarrow Pd^{II}C(O)OCH_3(NHPh)$  (9b)

 $Pd^{II}C(O)OCH_3(NHPh) \rightarrow P_2Pd^0 + MPC$  (9c)

### $PhNHC(O)OH \rightarrow PhNH_2 + CO_2 \tag{9d}$

Such a sequence of reactions bears strong mechanistic resemblance to those of olefin carbonylation reactions catalyzed by similar  $P_2Pd^{II}$  catalysts; in the presence of methanol, aniline or water, esters, amides or carboxylic acids are produced respectively.<sup>[71]</sup>

Alternatively, CO coordination and migration of the imido moiety towards coordinated CO could yield  $P_2Pd^0$  and phenyl isocyanate, which can be trapped by methanol, aniline or water to produce MPC, DPU or aniline and CO<sub>2</sub> (phenylcarbamic acid). Note, however, that both pathways involve complete de-oxygenation of nitrobenzene, followed by (methoxy)carbonylation of the Pd-imido intermediate. Thus, the combination of both sets of half-reactions, represented by Equations (5) and (9), naturally leads to the full catalytic cycles for reductive carbonylation of nitroaromatics to products like carbamates and ureas.

An attractive feature of the above proposed nitrobenzene carbonylation mechanism is that even this carbonylation cycle involves—and competes for—the Pd-imido intermediate. This Pd-imido complex thus not only rationalizes the observed catalytic connection between nitrobenzene reduction and methanol oxidation, but also provides a link with reductive carbonylation of nitrobenzene as well as with reductive self-coupling of nitrobenzene. The connection between nitrobenzene carbonylation, azo(xy)benzene formation and methanol carbonylation is schematically depicted in Scheme 8.



Scheme 8. Competing reactions for the Pd–imido intermediate with methanol and CO (top) or nitrobenzene and CO (bottom). Both pathways can also lead to  $P_2Pd(OCH_3)_2$  by reaction with methanol (centre). In all cases,  $P_2Pd^0$  is formed.

A complex network of catalytic cycles, centred around the Pd-imido complex: It seems that when palladium-diphosphane catalysts are used for the carbonylation of nitroben-



Scheme 9. Working hypothesis of the interrelated catalytic cycles operating in the  $P_2Pd$ -catalyzed reaction of nitrobenzene with CO in methanol, rationalizing all the products observed.

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zene in methanol, several catalytic reactions are simultaneously operative in an unexpectedly complex network. Our prime hypothesis is that these reactions encompass competing processes for conversion of  $P_2Pd^0$  to the  $P_2Pd^{II}$  imido complex, as well as competing processes for transformation of the  $P_2Pd^{II}$  imido complex into  $P_2Pd^0$ . A hypothetical catalytic scheme that links together all these processes is shown in Scheme 9, which has the  $P_2Pd^{II}$ =NPh complex as central intermediate.

The  $P_2Pd^0$  complex in situ formed can be seen as entry point for all catalytic processes (Scheme 9, left). The first competing processes are net oxidation of  $P_2Pd^0$  to the  $P_2Pd^{II}$ imido complex with two CO [Scheme 9, top left, Eq. (5a)], two CH<sub>3</sub>OH and two CO [Scheme 9, centre left, Eq. (5b)] or one CH<sub>3</sub>OH [Scheme 9, bottom left, Eq. (5c)] as de-oxygenating reagents for nitrobenzene.

Formation of the imido intermediate can be followed (right) by protonation to form  $P_2Pd^{II}(OCH_3)NHPh$ [Scheme 9, top right, Eq. (9a)] or "disproportionation" to form Azo(xy) and "P<sub>2</sub>Pd=O" [Scheme 9, bottom right, Eq. (8a)]. Both intermediates can be carbonylated to form, respectively, MPC [Scheme 9, top right, Eq. (9b/c)] or CO<sub>2</sub> [Scheme 9, bottom right, Eq. (8b)] and reform the initial P<sub>2</sub>Pd<sup>0</sup> species to make these reactions catalytic. Alternatively, both intermediates can be protonated to form P<sub>2</sub>Pd<sup>II</sup>-(OCH<sub>3</sub>)<sub>2</sub> and aniline [Scheme 9, top right, Eq. (6)] or water [Scheme 9, bottom right, Eq. (8c)]. Carbonylation of this P<sub>2</sub>Pd<sup>II</sup>(OCH<sub>3</sub>)<sub>2</sub> complex will produce DMC/DMO and regenerate P<sub>2</sub>Pd<sup>0</sup> [Scheme 9, centre right, Eq. (7)], which allows these reactions to proceed catalytically as well.

**Simulation of reaction stoichiometries**: From the complex network of reactions unfolded above, it follows that a combination of the half-reactions that oxidize  $P_2Pd^0$  to  $P_2Pd^{II}$ = NPh with the half-reactions that reduce  $P_2Pd^{II}$ =NPh to  $P_2Pd^0$  will result in all possible overall reactions being catalytic in both  $P_2Pd^0$  and  $P_2Pd$ =NPh. The exercise to derive all possible catalytic stoichiometries is shown in the Supporting Information (Section 5, see especially Scheme S1). For simplification, DMO is counted as DMC, MF is counted as CO, and DPU is counted both as aniline and as MPC. Also, the very small amount of azobenzene is taken with azoxybenzene as "Azoxy".

Thus, the possible overall stoichiometries are given by Equations (10)–(18), all of which are highly exothermic  $(\Delta H_f^{\circ})$  varies from -95 to -175 kcalmol<sup>-1</sup>, see Table S5 of the Supporting Information for details). In Equations (10)–(12), CO is the only de-oxygenating agent, while for Equations (13)–(15) two CO and two acidic hydrogen atoms from methanol function as de-oxygenating reagents. In Equations (16)–(18), all four hydrogen atoms from methanol are used to de-oxygenate one nitrobenzene. The equations marked with an asterisk are reactions wherein one methanol molecule is substituted for a water molecule (see Supporting Information for details).

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$PhNO_2 + CH_3OH + 3CO \rightarrow MPC + 2CO_2$	(10)
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$$PhNO_2 + 2CH_3OH + 3CO \rightarrow PhNH_2 + 2CO_2 + DMC$$
 (11)

$$2PhNO_2 + 3CO \rightarrow Azoxy + 3CO_2 \tag{12}$$

$$PhNO_{2}+3CH_{3}OH + 3CO \rightarrow$$

$$MPC + CO_{2} + H_{2}O + DMC$$
(13)

$$PhNO_{2}+4CH_{3}OH + 3CO \rightarrow PhNH_{2} + CO_{2} + H_{2}O + 2DMC$$
(14)

$$\begin{array}{l} 2PhNO_2+2CH_3OH+3CO\rightarrow\\ Azoxy+2CO_2+H_2O+DMC \end{array} \tag{15}$$

$$PhNO_2 + 2CH_3OH \rightarrow MPC + 2H_2O \tag{16}$$

 $PhNO_2 + 3CH_3OH \rightarrow PhNH_2 + 2H_2O + DMC$ (17)

$$2PhNO_2 + CH_3OH \rightarrow Azoxy + 2H_2O + CO_2$$
(18)

 $PhNO_2 + H_2O + 3CO \rightarrow PhNH_2 + 3CO_2 \qquad (10/11*)$ 

$$\begin{array}{l} PhNO_2 + 2CH_3OH + 3CO \rightarrow \\ PhNH_2 + 2CO_2 + DMC \end{array} \tag{13/14*}$$

$$PhNO_2 + CH_3OH \rightarrow PhNH_2 + CO_2 + H_2O \qquad (16/17*)$$

The sum of weighted contributions of each of these catalytic reactions will ultimately determine the experimentally observed product composition in the liquid phase (note: the gaseous product  $CO_2$  was not quantitatively determined).

The experimental parameters obtainable from the observed product compositions, that is, hydrogen-atom balance, aryl product distribution, product ratios, water production and the effect of water addition on product composition, were used to extract the weighted contribution of the various possible reactions given in Equations (10)-(18) and (10/11\*)-(16/17\*), and thus to simulate the product compositions as a function of the catalyst (see Supporting Information). The results of this simulation are summarized in Table 4. By grouping reactions together according to their underlying nitrobenzene de-oxygenation pathway, it can be seen that the actual reaction pathways catalyzed by a specific catalyst appear to depend strongly on its structure, which is primarily determined by the supporting ligand. For the catalysts tested, all three de-oxygenation pathways contribute, but significant differences exist between catalysts. Remarkably, de-oxygenation by full methanol dehydrogenation (column " $CH_3OH$ ") is less dependent on the catalyst structure, while the DMC (DMO)-producing "2CO/2CH<sub>3</sub>OH" de-oxygenation pathway is strongly suppressed by o-meth-

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	Product distribution						"Water	De-oxygenation pathway [%]		
Ligand	Data	"MPC"	"PhNH <sub>2</sub> "	"Azoxy"	"DMC"	$H_2O$	cons. [%]" <sup>[a]</sup>	CO <sup>[b]</sup>	$2CO/2CH_3OH^{[c]}$	$CH_3OH^{[d]}$
L3X	exptl	6.1	9.1	0.5	7.3	3.4	100	37	46	17
	sim	6.1	9.1	0.5	7.2	3.5				
o-MeO-L3X	exptl	14.7	8.8	0.2	0.8	0.7	100	78	3	18
	sim	14.7	8.8	0.2	0.8	0.7				
L4X	exptl	1.0	2.4	4.6	8.2	10.0	24	9	66	24
	sim	1.0	2.4	4.6	8.6	9.6				
o-MeO-L4X	exptl	7.5	12.4	1.1	9.4	8.7	24	72	0	28
	sim	7.5	12.4	1.1	9.4	8.7				

[a] Sum of weighted contributions of the three "water-consuming" reactions given in Equations (10/11\*), (13/14\*) and (16/17\*) as fraction of the total sum of weighted contributions of the reaction given by Equations (10), (11), (13), (14), (16), (17), and (10/11\*), (13/14\*), (16/17\*). [b] Sum of weighted contributions for Equations (10)–(12). [c] Sum of weighted contributions for Equations (13)–(15). [d] Sum of weighted contributions for Equations (16–(18). See Supporting Information for more details. "MPC"=MPC+DPU, "Azoxy"=Azoxy+Azo, "PhNH"=PhNH<sub>2</sub>+DPU and "DMC"=DMC+DMO.

oxy substitution of the aryl groups in the diphosphane ligand. In contrast, the "CO" de-oxygenation pathway appears to be enhanced by this substitution.

A longer backbone of the diphosphane ligand (L4X vs. L3X), which affects the ligand's bite-angle, leads to a larger contribution (from 46 to 66%) of the " $2CO/2CH_3OH$ " de-oxygenation pathway. Remarkably, when *o*-methoxy substitution in the L4X ligand is introduced, the situation completely changes toward a strong contribution of the "CO" de-oxygenation pathway (9% for L4X and 72% for oMeOL4X).

Finally, a noteworthy difference between catalysts with  $C_3$ - and  $C_4$ -backbone ligands is their reactivity towards water as nucleophilic reagent (column "water cons."): whereas the Pd<sup>II</sup>(L3X) catalysts are very reactive towards water, the Pd<sup>II</sup>(L4X) catalysts appear to be much less sensitive to water (see also Table 3).

Complete rationalization of the catalyst performance as judged from its product slate, in terms of molecular details of these catalysts is, of course, not easily achieved. To come to a fully detailed molecular rationalization of catalyst performance will require further in-depth organometallic studies on possible catalytic intermediates. One such a study, involving the synthesis and study of the reactivity patterns of P<sub>2</sub>Pd<sup>II</sup> imido complexes, is currently underway.<sup>[44]</sup> Nevertheless, we consider it worthwhile as a first attempt to discuss some of the most prominent observations from the product simulations in terms of the molecular characteristics of proposed catalytic Pd intermediates. We hope such a discussion may provide some guidance for future (organometallic) mechanistic studies.

**Ligand effects—2CO versus 2CO/2CH<sub>3</sub>OH versus CH<sub>3</sub>OH de-oxygenation**: The first remarkable observation from the product simulations shown in Table 4 is the significant effect of *o*-MeO substituents of the ligands (oMeOL3X and oMeOL4X) on the nitrobenzene de-oxygenation pathway. The relative contribution of the reactions in which CO is the only reductant ["CO"; Eqs. (10)-(12)] is largest for catalysts bearing the o-MeO-functionalized ligands (ca. 75%). For catalysts with the unfunctionalized ligands L3X and L4X on the other hand, the reactions in which two CO and the acidic hydrogen atoms of methanol ("2CO/2CH<sub>3</sub>OH") function as co-reductant [Eqs. (13)-(15)] are dominant (ca. 50-70%). The catalyst structure is of less importance for the reactions wherein full methanol dehydrogenation (" $CH_3OH$ ") drives nitrobenzene de-oxygenation [Eqs. (16)-(18)]. The contribution of Equations (16)-(18) hardly alters when the ligands bear o-MeO groups and only slightly (7-10%) when the longer butylene backbone is employed. The modest increase of the " $CH_3OH$ " de-oxygenation pathway due to o-MeO substituents in the ligands might seem somewhat surprising. One would expect the electron-donating o-MeO substituents to enhance the basicity of the palladium centre in  $P_2Pd^0$ , thereby facilitating oxidative addition of methanol to  $P_2Pd^0$  (i.e., protonation at the basic metal centre) and rendering the "2CO/2CH<sub>3</sub>OH" and "CH<sub>3</sub>OH" pathways (Scheme 5 and Scheme 6) more probable. This suggests that electronic effects are counteracted by steric effects of the o-MeO substituents. On the other hand, the data also suggest that in the competition between oxidative addition of methanol and oxidative coupling of CO and nitrobenzene on  $P_2Pd^0$  (Scheme 5), a more basic metal catalyst (o-MeO groups) is more involved in the oxidative CO coupling reaction with nitrobenzene. This is in line with the general notion that when the even more basic N-donor ligand 1,10phenanthroline is used as supporting ligand, CO reduction is the only de-oxygenation pathway.<sup>[20-35]</sup> Our observations with various Pd-phenanthroline catalyst systems confirm this as well. A comprehensive performance comparison under various conditions between N2Pd and P2Pd catalyst systems will be published shortly.<sup>[64]</sup>

For the nitrobenzene de-oxygenation pathways that start with oxidative addition of methanol ("2CO/2CH<sub>3</sub>OH" and "CH<sub>3</sub>OH") to P<sub>2</sub>Pd<sup>0</sup> (Scheme 5), the *o*-MeO-functionalized catalysts are much more selective (ca. 85–100%) via the full

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dehydrogenation pathway of methanol (" $CH_3OH$ ") relative to the "2CO/2CH<sub>3</sub>OH" de-oxygenation pathway. This can be understood by the steric hindrance that the *o*-MeO-substituents impose on the axial positions of the Pd centre in the catalyst, effectively shielding the d<sub>z<sup>2</sup></sub> orbitals of palladium.<sup>[42,72,73]</sup>

Thus, after formation of **C5b/c** (see Schemes 5 and 6), coordination of CO at the axial position is sterically hampered, as is also (temporarily) associative displacement of a nitroso ligand required for formation of **C6b** (Scheme 10, left), and



Scheme 10. Mechanistic scheme rationalizing the selectivity that the o-MeO group induces in de-oxygenation with one CO and two CH<sub>3</sub>OH (left) versus one CH<sub>3</sub>OH (right).

thus also the "2CO/2CH<sub>3</sub>O*H*" de-oxygenating pathway. Instead, the CH<sub>3</sub>O<sup>-</sup> anion present outside the first coordination sphere of the P<sub>2</sub>Pd<sup>II</sup> centre in **C5b/c** will deprotonate the coordinated CH<sub>3</sub>O<sup>-</sup> to form methanol and palladiumbound formaldehyde (Scheme 10, right), eventually leading to full dehydrogenation of methanol (Scheme 6).

Ligand effects—DMC/DMO versus MPC/DPU versus PhNH<sub>2</sub>/CO<sub>2</sub>: Another important observation from the product simulation is that for L3X and oMeOL3X it appears that all aniline produced can be formed via the "water-consuming reactions" given by Equations (10/11\*), (13/14\*) and (16/17\*). For the catalysts containing the ligands with a butylene backbone, these reactions only contribute about 25% (see column "Water cons." in Table 4). This is in line with our findings that, especially with Pd<sup>II</sup>(L3X) and Pd<sup>II</sup>(oMeOL3X), added water could quite effectively replace methanol as reactant to give aniline instead of MPC (or DPU) and DMC (or DMO). Also remarkable is the observation that the *o*-methoxy substituents make the catalyst more selective towards MPC (DPU), clearly at the expense of DMC/DMO formation.

These observations can be rationalized schematically as illustrated in Scheme 11. First, the imido nitrogen atom of the  $P_2Pd^{II}$ =NPh intermediate can be protonated by a CH<sub>3</sub>OH molecule (Scheme 11, top) that approaches the Pd centre from the (less sterically crowded) equatorial positions, forming  $P_2Pd^{II}$ NHPh(OCH<sub>3</sub>). As this species is sterically more crowded in the equatorial positions, a second CH<sub>3</sub>OH molecule will first associate with the Pd centre through its axial positions, with formation of aniline and a  $P_2Pd^{II}$ (OCH<sub>3</sub>)<sub>2</sub> complex. As the *o*-MeO-substituents on the ligands shield the axial positions of Pd,<sup>[42,72,73]</sup> these *o*-MeO groups will hamper this second protonation step, and thus also DMC formation. Instead, MPC is then formed by the sequence: associative displacement of CH<sub>3</sub>O<sup>-</sup> by the smaller and neu-



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Scheme 11. Mechanistic scheme showing the related production of MPC, DMC, and aniline/CO<sub>2</sub>.

tral CO molecule, followed by nucleophilic attack by  $CH_3O^-$  at the coordinated CO molecule and reductive elimination of MPC (Scheme 11, upper pathway).

Alternatively, water can replace methanol in the first protonation step (bottom of Scheme 11, although formally also in a later stage) to open up two analogous reaction pathways that result in the formation of aniline instead of MPC (top) or DMC (bottom). It appears from the data (Tables 3 and 4) that the amount of aniline (DPU) formed in such "water-consuming" reactions is not so large when using catalysts with a ligand having a C<sub>4</sub> backbone (weighted contribution 24%), but when the supporting ligand has a C<sub>3</sub> backbone, all aniline is formed in this way. This is counterintuitive from a steric point of view, because water is smaller than methanol and because a C<sub>4</sub> backbone could induce more steric constraint in the equatorial coordination positions of the catalyst (larger bite angle). The effect must therefore be of combined electronic and steric origin.

Indeed,  $P_2Pd^{II}$  complexes in which the ligand has a  $C_3$  backbone typically have a P-Pd-P angle close to the ideal 90°, whereas the steric constraints imposed by a longer  $C_4$  backbone result in a P-Pd-P angle of typically 96°.<sup>[74]</sup> As a result, orbital overlap will be less, thus hampering electron flow from the aryl rings to palladium, resulting in a less basic palladium centre (e.g., in  $P_2Pd^{II}$ =NPh).

**Ligand effects—Azoxy versus PhNH<sub>2</sub>/MPC**: Interestingly, from our working hypothesis shown in Scheme 9, it can be predicted that the phenyl moiety in the imido intermediate can end up either in Azoxy [disproportionation, bottom right in Scheme 9, Eq. (8a)] or in aniline/MPC [protonation, top right in Scheme 9, Eqs. (6) and (9b/c)]. From the catalytic data shown in Table 2, it appears that when using Pd<sup>II</sup>-(L4X), the disproportionation route dominates (4.6 mmol Azo(xy) and 3.4 mmol "PhNH<sub>2</sub>"/"MPC"), but for Pd<sup>II</sup>(L3X) the protonation route becomes dominant (0.5 mmol Azo(xy) and 15.6 mmol "PhNH<sub>2</sub>"/"PhNCO").

This difference in selectivity must be related to the different ligand bite angle,<sup>[75]</sup> which is about 90° in L3X and 96° in L4X.<sup>[74]</sup> As is illustrated in Scheme 12, one N-O bond in nitrobenzene is formally completely polarized, whereas the O-H bond in methanol is charge-neutral. As a result, and because the imido complex is also polarized, nitrobenzene is thought to associate more strongly with the Pd=N bond than methanol.



Scheme 12. Competition for association with the Pd-imido intermediate between nitrobenzene and methanol.

This effect may be similar in catalysts with either ligand L3X or L4X. However, as the bite angle is larger in L4X, this might well enforce a kind of disproportionation reaction between the imido intermediate and nitrobenzene by forcing them together and thus lowering the activation barrier for this reaction. It is indeed well-known that reaction between cis-coordinated fragments (e.g., reductive elimination) opposite to a bidentate phosphane ligand is expedited by enlarging the bite angle of the ligand.<sup>[75-79]</sup> What is more, the observation that azoxybenzene formation can be suppressed by equipping the ligand with o-MeO-phenyl rings is in line with such a mechanistic proposal; the electron-donating methoxyl groups can render the imido intermediate more basic, and thus allow easier reaction with the (abundantly present) methanol. The o-MeO groups might also (concurrently) prevent approach of the larger nitrobenzene to the axial positions of Pd, in favour of the smaller methanol.

Ligand effects; activity versus o-MeO-groups: The overall activity is significantly higher with o-MeO-functionalized ligands: conversion increases from 67% with L3X to 98% with oMeOL3X, and from 52% with L4X to 90% with oMeOL4X. This probably implies that the methanol carbonylation cycle to DMC (DMO) is rate-determining in the combined nitrobenzene reduction/methanol carbonylation cycle. With o-MeO-modified ligands, the overall catalytic cycle can take a short-cut to MPC formation, which results in an overall higher rate of reductive carbonylation. It is furthermore likely that the "CO" de-oxygenation route is faster than the two de-oxygenation routes involving methanol. As the o-MeO-functionalized catalysts are mostly involved in this "CO" de-oxygenation pathway (ca. 75%), these catalysts thus can lead to higher nitrobenzene conversion rates.

### Conclusion

We have shown that a number of unexpected products is formed when carbonylation of nitrobenzene in methanol is

performed with P<sub>2</sub>Pd-based catalysts. We postulated that nitrobenzene can oxidize  $P_2Pd^0$  to the imido species " $P_2Pd^{II}$ = NPh". In this process nitrobenzene is reduced; this can be done not only by two CO molecules, but also by two CO in combination with the acidic protons of two methanol molecules, or by using all four hydrogen atoms of one molecule of methanol. During these processes, CO2, H2O, DMC/ DMO, CO and MF are formed. Starting from the  $P_2Pd^{II}$ = NPh intermediate, the formation of Azo(xy), MPC/DPU and aniline is accompanied by regeneration of  $P_2Pd^0$ , making these reactions catalytic.

Although many of the (organometallic) details of the catalytic pathways are still largely unknown, our first aim was to unravel all catalytic organic reactions that proceed in the palladium-diphosphane-catalyzed carbonylation of nitrobenzene in methanol. A network of coupled catalytic cycles containing common intermediate catalytic species has been developed, which all point towards a P2PdII=NPh complex as the key intermediate species. Indeed, by using this imido intermediate it is possible to connect a complex network of catalytic reactions, both for the oxidation of methanol as well as for the reduction of nitrobenzene. What is more, when cyclohexene was added during a catalytic run, the corresponding aziridine was observed, which strongly suggests the presence of a P<sub>2</sub>Pd<sup>II</sup>=NPh intermediate. Based on our analysis of the observed product distribution in combination with the possible reactions involving the hypothetical  $P_2Pd^{II}$ =NPh key intermediate species, we could accurately simulate the relative weights of the reactions taking place and-to some extent-relate the performance of the catalysts with structural parameters of the catalyst complexes.

Regarding the original aim of selective reductive carbonylation of nitrobenzene, it was found that P<sub>2</sub>Pd<sup>II</sup>(oMeOL3X) is the most active (98% conversion) and selective (62% carbonylation) of the catalysts tested. The catalytic carbonylation of methanol to DMC and DMO can have important technological implications, as both DMC and DMO are industrially important compounds. DMC has been proposed to replace phosgene as carbonylating agent,<sup>[80-84]</sup> while DMO can serve as intermediate in a syngas-based route to monoethylene glycol (MEG).<sup>[85]</sup> The catalysts described her that catalytically produce DMC or DMO are worth investigating further in this respect.

The present work provides a basis for two-pronged further development of optimal catalyst systems for either effective and selective reductive carbonylation of nitro aromatics to give carbamate esters or ureas, or to optimal catalysts systems for selective oxidative carbonylation of alcohols to give difunctional esters such as carbonates or oxalates, in which nitro aromatics can serve as the oxidant, thus co-producing aromatic amines. Further catalytic and organometallic research into the reductive carbonylation of nitro aromatics as well as the oxidative carbonylation of alcohols thus is imminent.

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### **Experimental Section**

**General remarks**: All ligands were generously provided by Shell Global Solutions Amsterdam B.V., where they were synthesized according to literature procedures.<sup>[86-94]</sup> All other solids were purchased from Acros organics and used as received. Methanol, nitrobenzene and aniline were all of analytical-reagent purity, and were distilled under an argon atmosphere over the appropriate drying agent.<sup>[95]</sup> After distillation, they were saturated with argon. It was ensured that no water was present by using an analytical reaction with trimethyl orthoformate according to a modified literature procedure<sup>[96]</sup> (see below and also the Supporting Information). Carbon monoxide (>99 % pure)<sup>[51]</sup> was purchased from Linde gas Benelux B.V. and used as received.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DPX300 (300 MHz) or a Bruker DMX400 (400 MHZ) machine. High-pressure catalysis experiments were conducted in stainless steel autoclaves (100 mL) equipped with two inlet/outlet valves, a burst disc, a pressure sensor and a thermocouple. The autoclaves were heated by a Hel polyBLOCK electrical heating system. Temperatures and pressures where measured with probes connected to a computer interface making it possible to record these parameters throughout the course of the reaction. GLC-MS measurements were performed on a Hewlett Packard series 2 type 5890 gas chromatograph equipped with a Hewlett Packard 5971 mass-selective detector. Depending on the analyte, a polar or an apolar column was used. Technical details and settings are identical to those used for the quantitative GLC-FID measurements (see below). Mass spectra of the gas phase were recorded with a Spectra MicroVision plus 24 VDC series K64764, coupled to a computer for digital readout. Data points were collected with a resolution of m/z 0.25 in the range of m/z 3–50.

Catalytic/high-pressure reactions: In a typical catalytic experiment, 0.05 mmol Pd(OAc)<sub>2</sub> and 0.075 mmol ligand (and, if relevant, another additive) were weighed and transferred into an autoclave, together with a magnetic stirring rod. The autoclave was tightly closed and subsequently filled with argon by using a Schlenk system that was connected to one of the valves of the autoclave. Through the other valve 2.50 mL (24.4 mmol) dried and degassed nitrobenzene was added under a continuous flow of argon. In a similar fashion, 25.0 mL dried and degassed methanol was then added. This reaction mixture was allowed to stir at 500 rpm for about 15 min to ensure that complex formation was complete.<sup>[42]</sup> The autoclave was then inserted into the heating block and pressurized with 50 bar CO gas. The reaction mixture was heated to 110°C (within 30 min) under stirring at 500 rpm. After standing for four hours at this temperature, the autoclave was cooled to room temperature over about one hour. The autoclave was then slowly vented to atmospheric pressure and the reaction mixture was analyzed as described below. To check reproducibility, all catalytic reactions were performed in quadruplet; the relative standard deviation was always less than 5% for all products.

**Trapping experiments with cyclohexane**: Cyclohexene (passed through an alumina column and saturated with argon; 2.7 mL, 25 mmol) was transferred to a piece of stainless steel tubing (5 mL) that was closed on both sides by two valves. This piece of tubing was mounted on one of the gas inlet/outlet valves of an autoclave that was prepared for a normal high-pressure catalytic reaction (see above). The catalytic reaction was then started as normal. After the decline in pressure inside the autoclave was about half of what is usually observed when using a specific catalyst, cyclohexene was added to the reaction mixture with a small overpressure of CO. The reaction was then allowed to continue for the usual total of four hours. After cooling and venting, the reaction mixture was analyzed by GLC-FID and GLC-MS.

**Quantitative GLC-FID analysis of reaction mixtures**: Prior to the workup of N,N'-diphenylurea (see below), a sample (0.5 mL, diluted with 1.0 mL methanol) was taken to quantify the other analytes by GLC-FID analysis with an apolar and a polar column, and decane as internal standard.

For the apolar column, a Hewlett Packard 6890 series gas chromatograph equipped with an auto sampler was used. An AT-1 column (length: 30 m; diameter: 0.25 mm; film thickness: 1.00 µm) was used as stationary phase

with helium as mobile phase. The injector and detector were operated at 250 °C. An injection volume of 1  $\mu$ L was taken with a split ratio of 10:1. After injection, the column was heated at 120 °C for five minutes, whereafter it was heated to 175 °C (10 °Cmin<sup>-1</sup>) and then to 325 °C (50 °Cmin<sup>-1</sup>) for four minutes. This method was used to quantify the following products ( $t_R$  in minutes): dimethyl carbonate (4.1), dimethyl oxalate (5.9), nitrosobenzene (7.8), aniline (8.5), decane (9.7), methylenebenzenamine (10.2) nitrobenzene (11.0), methyl phenylcarbamate (13.4), azobenzene (14.8), and azoxybenzene (15.7).

For the polar column, a Varian star 3400 CX gas chromatograph equipped with a Shimadzu integrator was used. A Varian WCOT fused silica CP-wax 58 (FFAP) column (length: 25 m; diameter: 0.32 mm; film thickness: 1.20  $\mu$ m) was used as stationary phase with helium as mobile phase. The injector and detector were operated at 250 °C. An injection volume of 0.5  $\mu$ L was taken with a split ratio of 10:1. The temperature of the column was maintained at 40 °C throughout the 10 min elution time. This method was used to quantify the products ( $t_R$  in minutes): dimethoxymethane (1.5), methyl formate (1.9), acetone (2.4), decane (6.4), and trimethyl orthoformate (7.3). Water was analyzed by adding an amount of freshly prepared 0.55  $\mu$  p-toluenesulfonic acid in trimethyl orthoformate to the reaction mixture, heating to 70 °C for 120 min followed by cooling to laboratory temperature and thereafter analyzing the amount of methyl formate that is formed. See the Supporting Information for more details.<sup>[96]</sup>

**Quantification of** *N*,*N*'-diphenylurea: Because *N*,*N*'-diphenylurea (DPU) is a solid and poorly soluble in methanol, this compound was quantitatively analyzed by isolation and determination of its weight. First, a sample was taken for GLC-FID analysis (see above). Then, 10 mL *n*-hexane was added to the reaction mixture to ensure that all DPU precipitated. The reaction mixture was then stirred and carefully filtered by using a weighed paper filter and a Büchner funnel. The resulting solid was washed five times with 2 mL portions of *n*-hexane and dried overnight in a vacuum oven at 50 °C. The amount of DPU could then be determined by weight. For each isolated batch, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic analysis was used to verify the purity of DPU.

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- [53] For the initial 15.1 mmol CO (5 bar, ca. 75 mL) to become enriched from 1.27% to 1.46% <sup>13</sup>CO by <sup>13</sup>CH<sub>3</sub>OH (4% v/v) dehydrogenation, about 0.72 mmol methanol could have been dehydrogenated to CO [15.1 mmol×(0.0146–0.0127)×(100/4)]. This should result in 2.9 mmol hydrogen atoms. In the liquid phase of this experiment, 1.3 mmol MF was found, that is, the total amount of hydrogen atoms produced should be 8.1 mmol (4×1.3+2.9). Also in the liquid phase, 1.8 mmol aniline and 2.1 mmol H<sub>2</sub>O were detected, which correspond to 7.8 mmol hydrogen atoms. Thus, the hydrogen atoms should have been produced by CO and MF formation from methanol, and 7.8 mmol hydrogen atoms were measured in the form of PhNH<sub>2</sub> and H<sub>2</sub>O: a difference well within the experimental error of about 5%.
- [54] For Pd<sup>II</sup>(L3X), 8.0 mmol H<sub>2</sub>O has replaced CH<sub>3</sub>OH in some way as hydrogen-donating agent. The amount of MPC+DPU decreased by 2.1 mmol, accompanied by a corresponding increase in  $PhNH_2+$ DPU of 2.0 mmol, while at the same time the amount of DMC+ DMO decreased to 3.8 mmol. Taken together, this amounts to 2.1+ 3.8 = 5.9 mmol of combined products from reactions in which water has replaced methanol as H donor. The remaining 8.0-5.9= 2.1 mmol water must then have (at least partially) replaced methanol in reactions that otherwise, in the absence of water, would involve complete stripping of H atoms from methanol [to give CO, analogous to Eq. (4)]. Likewise, for Pd<sup>II</sup>(oMeOL3X), the 10.8 mmol water consumed replaced methanol in the production of MPC (5.4 mmol), DMC (0.6 mmol) and CO (10.8-0.6-5.4 = 4.8 mmol). For Pd<sup>II</sup>(L4X), hardly any water was consumed, which is also reflected in the unchanged product distribution. For PdII(oMeOL4X) a mere 1.9 mmol of water was consumed, which apparently replaced methanol in the formation of MPC (0.9 mmol), DMC (0.2 mmol) and CO (1.9-0.2-0.9=0.8 mmol).
- [55] Cyclohexene was chosen because it is easy to handle and because a P<sub>2</sub>Ni=NR complex can react stoichiometrically with double bonds (see reference [62]).
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  [68] Note that complexes C3b/c through C5b/c are denoted as cationic palladium complexes. Of course, the methoxide anion generally cannot be regarded as non-coordinating anion to a P<sub>2</sub>Pd<sup>II</sup> centre. However, in methanol as solvent the methoxide anion can be comfortably accommodated by solvent methanol molecules around the

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palladium centre by spreading its negative charge over several methanol molecules by means of a (dynamic) hydrogen-bonding network.

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- [85] For example, following the sequence: Ox. (an oxidant in general; in our case, nitrobenzene)+ $2CO+2CH_3OH \rightarrow "H_2Ox."+H_3CO-(CO)_2OCH_3$  (DMO); DMO+ $4H_2 \rightarrow HO(CH_2)_2OH$  (MEG)+ $2CH_3OH$ . This amounts to the net stoichiometry: Ox.+ $2CO + 4H_2 \rightarrow "H_2Ox."+HO(CH_2)_2OH$  (MEG).
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