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Mechanistic Study of the Oxidative Carbonylation of Methanol Catalyzed by Palladium Diphosphane Complexes with Nitrobenzene as Oxidant

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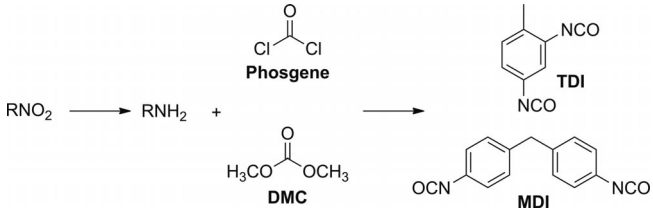
The reactivity of Pd complexes having bidentate diarylphosphane ligands was studied in the oxidative carbonylation of CH_3OH to dimethyl carbonate/oxalate (DMC/O) with $PhNO_2$ as the oxidant. Different ligands were employed with variation in backbone length and aryl ring substituent, and the acidity, CO pressure, or the partial pressure of H_2 was varied. At two different stages in the catalytic cycle, one equivalent of DMC/O may evolve for every equivalent of $PhNO_2$ reduced, which means that the efficiency with which nitrobenzene can function as the oxidant for the oxidative carbonylation of methanol (E_{OC}) can potentially be 200 % relative to nitrobenzene conversion. The selectivity for DMC relative to DMO is thought to be determined by a species of the type $[P_2PdC(O)OCH_3(R)]$; the DMO/DMC ratio can be increased by increasing the CO pressure, by addition of an acid, or by using a ligand with a relatively large bite angle. On the basis of the collected results, we conclude that an ideal catalyst for oxidative carbonylation would have a relatively acidic palladium center and be sterically undemanding in the axial positions but sterically demanding in the equatorial positions of palladium. The Pd complex of bis(diphenylphosphanyl)ferrocene meets these criteria and was found to function most efficiently with $PhNO_2$ as oxidant for the oxidative carbonylation of methanol among the series of compounds studied, that is, with about 50 % of the theoretical maximum efficiency E_{OC}.

Introduction

One of the challenges in current day catalysis is to replace wasteful and dangerous industrial processes by more environmentally friendly and safer ones. An example of such a challenge is to replace the highly toxic and corrosive phosgene,[1,2] which is often used as carbonylating agent. For example, in the synthesis of aromatic isocyanates[3,4] such as TDI and MDI,[5,6] phosgene is employed on the megaton scale[7] to carbonylate a reduced nitroaromatic compound (Scheme 1).



Scheme 1. Two industrially important aromatic isocyanates (MDI, TDI) and two carbonylating reagents (phosgene, DMC).

Dimethyl carbonate (DMC),[8–12] and to a lesser extent dimethyl oxalate (DMO),[13] have been proposed to replace phosgene as carbonylating agent (Scheme 1), which, by transesterification with an aromatic amine, will liberate methanol to form a carbamate, which in turn can be pyrolyzed to the isocyanate (e.g. TDI or MDI). Such (aliphatic but also aromatic) carbonates and oxalates can be prepared by a palladium-catalyzed oxidative carbonylation of the alcohol (e.g. methanol to DMC and DMO).[14–31] The terminal oxidant is usually O_2, but a metal co-catalyst such as Cu^{2+}/Cu^{+}[24,26] or Pb^{4+}/Pb^{2+}[25] is often necessary to reoxidize palladium, which is difficult to oxidize with molecular oxygen. Notably, alkyl nitrites (RON=O) have been used to replace O_2 as the oxidant in the synthesis of DMC.[27]

Working with strong oxidants such as O_2 and RON=O is not too problematic when the palladium catalyst is stabilized by N- or O-donor ligands, but nitrogen and oxygen are generally poor ligands for palladium, since they cannot be involved in π back-bonding. P-donor ligands, on the other hand, are very good ligands for palladium for that very reason, but they easily react with strong oxidants such as O_2 and RON=O to form phosphane oxides leading to catalyst degradation. It is therefore not surprising that carbonate and oxalate syntheses employing P-donor ligands are mainly stoichiometric with regard to palladium.[14,15,20,22,23] For this reaction to be catalytic in palladium, milder oxidants have been considered, such as 1,4-benzoquinone[24–26,28,32] and $NaNO_2/NaNO_3$,[32] but the co-products that are then obtained stoichiometrically on the carbonate/oxalate cannot easily be utilized on a large scale.

Notably, for the oxidative carbonylation of phenols to diphenyl carbonate (DPC), nitrobenzene was proposed as the oxidant. Demonstrated yields, however, were less than

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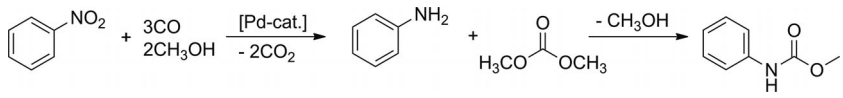


Scheme 2. A new synthetic route to prepare aromatic isocyanates (in the carbamate form) from dimethyl carbonate and aniline, formed by the oxidative carbonylation of methanol using nitrobenzene as the terminal oxidant.

stoichiometric on palladium.[33] To the best of our knowledge, nitrobenzene has never before been used or proposed as oxidant for the preparation of DMC or DMO. Furthermore, nitrobenzene may be reduced to aniline by the hydrogen atoms liberated by the formation of DMC/DMO, thus establishing a catalytic coupling between methanol oxidation and nitrobenzene hydrogenation chemistry. This potentially unlocks a new procedure to prepare the reactants aniline and DMC, which can be used to make aromatic isocyanates via methyl phenyl carbamate (Scheme 2). Furthermore, the product DMO is an industrially interesting intermediate for the sustainable production of monoethylene glycol (MEG) solely from synthesis gas as feedstock, which can be produced from practically any carbon source, including coal, gas, bio-waste or even CO_2.

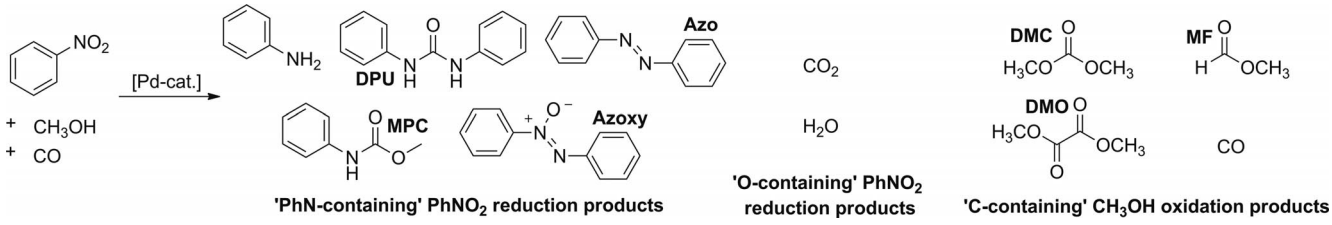
The reductive carbonylation of nitrobenzene in methanol forming methyl phenyl carbamate is a reported alternative for the industrial preparation of aromatic isocyanates such as TDI and MDI, which we are actively studying with palladium–diphosphane catalytic systems. In these studies, we found that, for some diphosphane-supported palladium catalysts, apart from the desired nitrobenzene carbonylation product large amounts of DMC, DMO, and aniline were formed.[34,35] It became clear that in our catalytic system nitrobenzene reduction is catalytically coupled with methanol oxidation,[34] and we have focused on the mechanism of formation of the nitrobenzene reduction products elsewhere.[35]

The focus of this paper is on the genesis of methanol oxidation products, in particular the useful oxidative carbonylation products DMC and DMO, and how the production of and selectivity for these products depends on the structure of the catalyst and on reaction conditions.

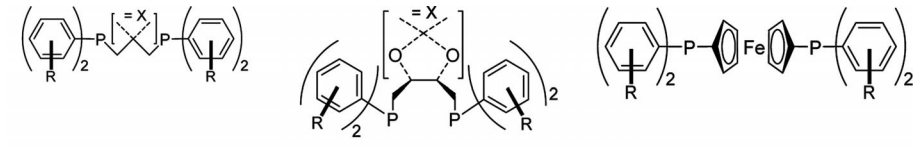
Results

General Considerations

In the catalytic reactions for the oxidation of methanol and the concomitant reduction of nitrobenzene, the catalyst was formed in situ from $Pd(OAc)_2$ and a bidentate phosphane ligand (1:1.5). Complex formation is instantaneous in methanol with the ligands used in this study,[36] and identical results were obtained when the activity of selected preformed complexes was tested. It was ensured that methanol and nitrobenzene were anhydrous by thoroughly drying these liquids. In the initial screening studies, a large variety of diarylphosphane ligands have been used, with variations in the substituents on the phenyl rings as well as in the length and flexibility of the backbone spacer.



Scheme 3. Overview of the different products that are formed in the palladium-catalyzed reaction of nitrobenzene with CO in methanol.



L3	(R = H)	**L4**	(R = H)	**L5Fc**	(R = H)
L3X	(R = H)	**L4X**	(R = H)	***o*MeO–L5Fc**	(R = *o*-MeO)
oMeO–L3	(R = *o*-MeO)	**oMeO–L4X**	(R = *o*-MeO)		
oMeO–L3X	(R = *o*-MeO)	**pMeO–L4**	(R = *p*-MeO)		
pMeO–L3	(R = *p*-MeO)				

Figure 1. Overview of the ligands used in this study.

In the carbonylation of nitrobenzene with diphosphanylpalladium catalyst systems, the products of the oxidative carbonylation of methanol, DMC and DMO, as well as those of methanol oxidation, methyl formate (MF) and carbon monoxide (CO), are formed (Scheme 3). We could experimentally establish the generation of gaseous CO in an estimated amount that satisfied the overall hydrogen mass balance between methanol oxidation ("H-liberating") and nitrobenzene reduction ("H-consuming") products.[34]

The "PhN-containing" reduction products of nitrobenzene are methyl phenyl carbamate (MPC), *N*,*N*′-diphenylurea (DPU), aniline, azobenzene (Azo), and azoxybenzene (Azoxy). Other reduction products of nitrobenzene are CO_2 and H_2O, both containing one oxygen atom from $PhNO_2$. H_2O, aniline, and DPU are derived from methanol oxidation, as the (OH, NH) hydrogen atoms in these molecules originate from methanol.[34]

The selectivity of the catalysts for the various products is highly dependent on the structure of the ligand. The trends in reactivity and selectivity will be discussed by using the ligands shown in Figure 1. These ligands have either a propylene (L3), butylene (L4), or ferrocene (L5Fc) backbone, which in some cases is made more rigid by substitution (indicated by X). The aryl rings of the ligands can be functionalized with methoxy moieties in the *ortho* or *para* position (*o*-MeO– or *p*-MeO–) to allow discrimination of steric from electronic effects.

Ligand Effects in the Oxidation of Methanol

General Comments

The quantities (in mmol) of the C-containing oxidation products of methanol and H-containing reduction products of nitrobenzene formed in nitrobenzene carbonylation experiments are given in Table 1. A full analysis of the reaction mixtures was always performed, however, and the data for the other reaction products are available in Table S1. The table also gives the conversion of nitrobenzene, the amount of nitrobenzene that is reduced to a "PhN-containing" fragment (column $\Sigma PhNO_2$), and the efficiency with which a certain catalytic system can use nitrobenzene as oxidant for the oxidative carbonylation of methanol to DMC and DMO (column E_{OC}, see discussion for details).

The data reported in this table have been used to generate the bar diagrams shown in this paper. The mechanism of formation of all phenyl-containing reduction products of nitrobenzene is discussed in a separate publication.[35]

Note that DMC, DMO, and MF can be easily quantified by using GLC analysis, but the amount of CO produced had to be deduced from the hydrogen mass balance.[34]

Oxidative Carbonylation of Methanol to DMC or DMO

A comparison of the amount of DMC/DMO produced by the various catalysts bearing the ligands L3, L4X, and L5Fc with the available *ortho*-methoxy and *para*-methoxy analogues is shown in Figure 2. The amount of DMC and DMO produced is highest when employing the unsubstituted ligands L3, L4X, and L5Fc (left). When the *o*-MeO analogues of these ligands were employed, the production of DMC and DMO was significantly suppressed (middle). Although this effect does not seem to hold when comparing the oMeO–L4X and L4X systems, it must be noted that twice as much nitrobenzene is converted when using oMeO–L4X (90%) as opposed to L4X (52%) as supporting ligand. The suppression of DMC and DMO production is considerably less pronounced when employing ligands with *para*-methoxyphenyl rings (right), indicating that the effect must be predominantly steric in nature. For example, the catalytic systems employing L4 and pMeO–L4 produce 8.0 and 5.4 mmol of DMC plus DMO at a nitrobenzene conversion of 60 and 40%, respectively.

The selectivity for either DMC or DMO appeared to vary significantly as a function of the bite angle (β) of the ligand used, as indicated by the increasing DMO/DMC ra-

Table 1. Results of the reactions of nitrobenzene with CO in methanol, catalyzed by a variety of in situ formed Pd^{II}(ligand) complexes.[a]

Entry	Ligand	Conv. $PhNO_2$ (%)	"C-containing" oxidation products (mmol)			"H-containing" reduction products (mmol)			$\Sigma PhNO_2$ reduced (mmol)	E_{OC}[b] (%)
			MF	DMC	DMO	H_2O	$PhNH_2$	DPU		
1	L3	67	0.1	3.6	3.3	3.0	5.1	1.7	15.4	45
2	L3X	67	0.2	4.2	3.1	3.4	8.3	0.8	16.2	45
3	oMeO–L3	53	0.6	0.6	0.5	n.d.	4.1	0.9	12.9	10
4	oMeO–L3X	98	1.1	0.4	0.4	0.7	5.7	3.1	23.9	5
5	pMeO–L3	54	0.1	2.2	2.1	n.d.	3.9	1.9	12.9	30
6	L4	60	0.3	2.4	5.6	3.9	5.4	0.8	14.6	55
7	L4X	52	0.2	2.3	5.9	10.0	1.9	0.5	12.6	65
8	oMeO–L4X	90	0.6	2.1	7.3	8.7	10.5	1.9	22.1	45
9	pMeO–L4	40	0.2	1.7	3.7	n.d.	5.9	0.0	9.1	60
10	L5Fc	70	0.4	4.3	13.7	n.d.	7.2	0.2	17.4	105
11	oMeO–L5Fc	100	1.8	2.5	8.0	n.d.	11.2	2.6	24.4	45

[a] Reaction mixtures were heated for four hours at 110 °C in 25.0 mL of dry and degassed methanol under 50 bar CO pressure. The catalyst was always generated in situ from 0.05 mmol $Pd(OAc)_2$. Mole ratios are: $Pd(OAc)_2$/Ligand/nitrobenzene = 1:1.5:488. Quantities are reported in mmol and "n.d." stands for "not determined". [b] E_{OC}: estimated efficiency of the oxidative carbonylation of methanol in percentages based on nitrobenzene conversion: E_{OC} = (DMC + DMO)/($PhNO_2$) fully reduced = $PhNH_2$ + MPC + 2[DPU + Azo(xy)] × 100%.

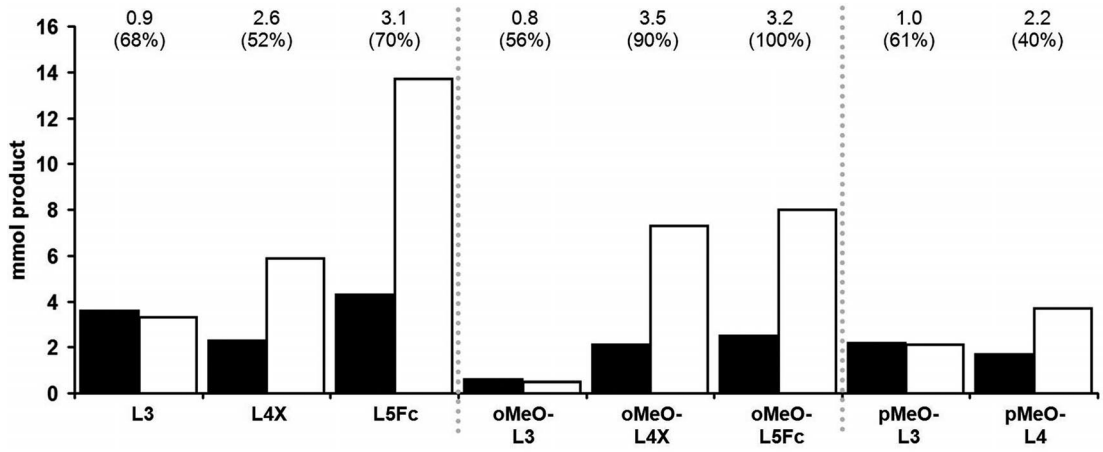


Figure 2. The influence of selected ligands on the selectivity and productivity of the catalysts for DMC (■) and DMO (□). The DMO/DMC ratio is given at the top; the conversion of nitrobenzene is given in parentheses.

tio from approximately 0.75 to about 2.5–3.1 when using the ligands L3X ($\beta \approx 90°$) and L4X/L5Fc ($\beta \approx 96°$), respectively. The DMO/DMC ratio does not significantly change when the supporting ligand in the catalyst is functionalized with electron-donating methoxy groups in either the *ortho* or *para* position.

The Effects of Reactants and Additives in the Oxidation of Methanol

Effect of the Acidity of the Reaction Medium

To investigate the effect of acidity on the product formation, a series of experiments was conducted wherein 5 equiv. (on Pd) of 2,4,6-trimethylbenzoic acid (TMBA) or 10 equiv. of Proton-sponge [1,8-bis(dimethylamino)naphthalene, DMAN] were added. The catalyst of choice for these experiments is Pd^{II}(L3), as this catalyst proved to be relatively active for the formation of the products of the carbonylation of methanol (DMC + DMO ≈ 7 mmol), but rather non-preferential with respect to the DMO/DMC ratio (ca. 1). For comparison, the *o*-MeO-functionalized catalyst Pd^{II}(oMeO–L3X) was used. The results are shown in Figure 3.

Upon addition of 5 equiv. (on Pd) of TMBA to the catalytic system comprising L3, the production of DMC and DMO decreased from 6.9 to 2.6 mmol and the conversion of nitrobenzene also decreased (from 68 to 50%). For the system Pd^{II}(oMeO–L3X), the effect was similar, although less pronounced as a result of the rather low oxidative carbonylation activity. When adding 10 equiv. (on Pd) of the base DMAN, the opposite occurred: the production of DMC and DMO increased from 6.9 to 11.9 mmol and the nitrobenzene conversion increased from 68 to 91% for the catalytic system based on L3. Again, a similar but less pronounced effect was observed for Pd^{II}(oMeO–L3X). The DMO/DMC ratio decreased when going from the acidic to the basic system: from 1.2 to 0.8 when using Pd^{II}(L3) and from 1.0 to 0.7 when employing Pd^{II}(oMeO–L3X).

Effect of the Concentration of CO and H_2

The CO pressure was varied in a series of catalytic runs with the complexes Pd^{II}(L3) and Pd^{II}(L4). The results of these experiments are shown in Figure 4. When increasing the CO pressure from 25 to 50 to 100 bar, the DMO/DMC ratio increased from 0.3 to 0.9 to 2.0 when using Pd^{II}(L3)

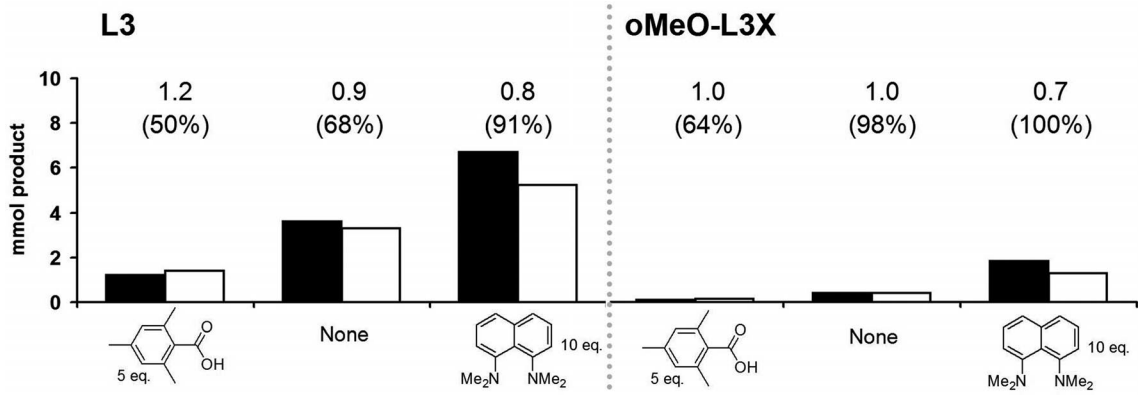


Figure 3. The selectivity and productivity for DMC (■) and DMO (□) as a function of the acidity (adding acid or base) for catalysts with the ligand L3 (left) and oMeO–L3X (right). The DMO/DMC ratio is shown at the top; the conversion of nitrobenzene is given in parentheses.

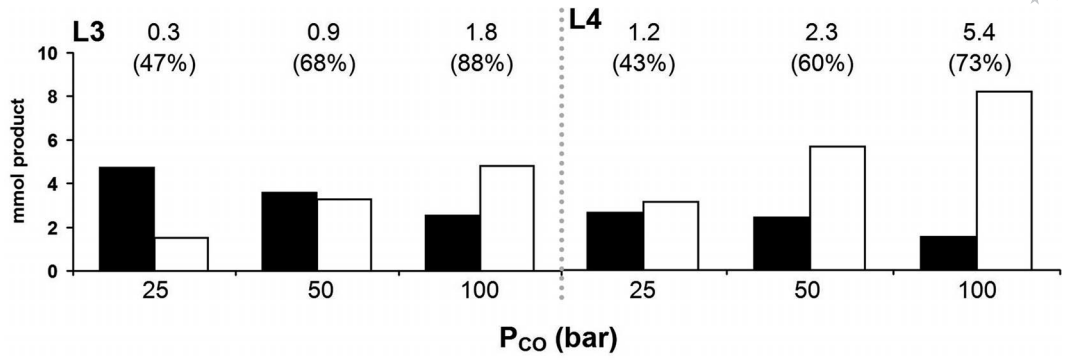


Figure 4. The selectivity and productivity of catalysts Pd^{II}(L3) and Pd^{II}(L4) for DMC (■) and DMO (□) as a function of CO pressure. The DMO/DMC ratio is given at the top; the conversion of nitrobenzene is given in parentheses.

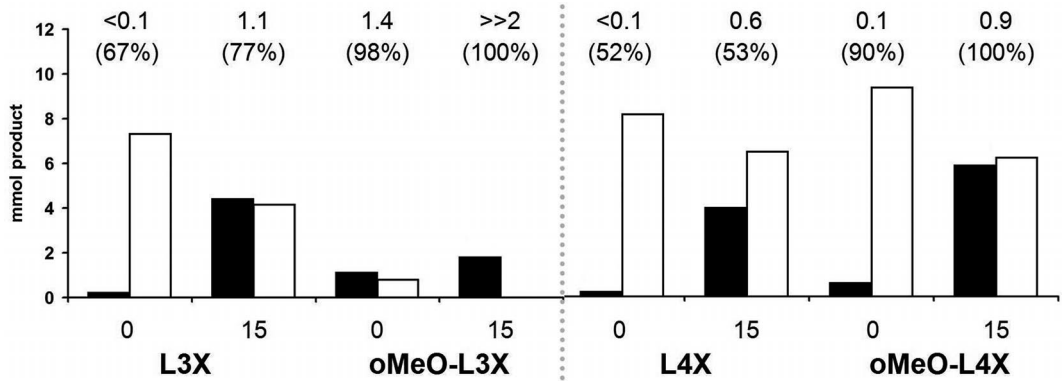


Figure 5. The selectivity and productivity for MF (■) and [DMC + DMO] (□) as a function of the partial pressure of H_2 (total = 50 bar) for catalysts comprising a ligand with a propylene backbone (left) or a butylene backbone (right). The MF/(DMC + DMO) ratio is given at the top; the nitrobenzene conversion is given in parentheses.

and from 1.2 to 2.5 to 5.0 when using Pd^{II}(L4). The conversion of nitrobenzene roughly doubled for both catalyst systems with increasing CO pressures (see also the Supporting Information).

When applying higher CO pressures, the total amount of DMC and DMO produced significantly increased when using L4 (5.7 vs. 9.6 mmol at 25 and 100 bar CO), in line with the increased nitrobenzene conversion. For L3, the effect of increasing the pressure on the amount of DMC and DMO produced is less significant; 6.2 vs. 7.4 mmol at 25 and 100 bar CO, whereas the nitrobenzene conversion is nearly doubled.

Several catalytic runs were performed under an atmosphere of H_2 and CO (15 and 35 bar, respectively; see Figure 5). As expected, the presence of hydrogen resulted in most cases in an increase in aniline formation. In particular, the catalyst supported with the ligand oMeO–L3X led to a high yield of aniline (22.6 mmol, 90% selectivity; see Supporting Information).

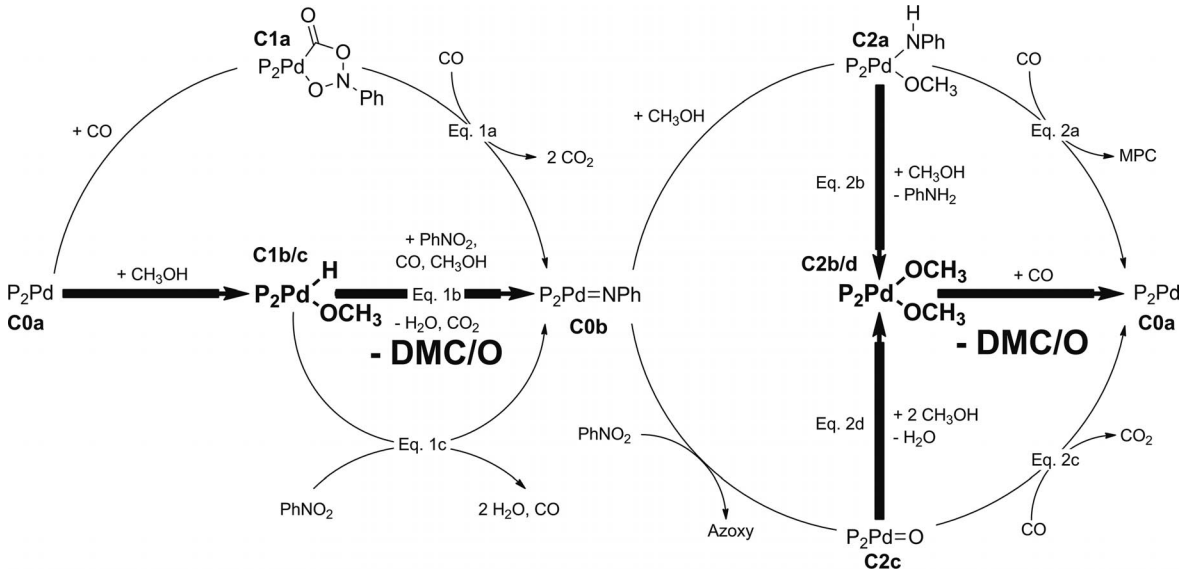
Whereas in the absence of H_2 all catalysts produce relatively small amounts of MF (0.2–1.1 mmol), under an atmosphere containing 15 bar H_2 significantly more MF is produced (1.8–5.9 mmol) at the expense of DMC and DMO production, as reflected by the higher MF/(DMC + DMO) ratios (Figure 5). The conversion of nitrobenzene is only slightly affected in all cases.

Discussion

Overall Mechanism of $PhNO_2$ Reduction and CH_3OH Oxidation with P_2Pd Catalysts

During our studies on the reductive carbonylation of nitrobenzene in methanol, we found that nitrobenzene reduction chemistry is catalytically linked with methanol oxidation chemistry by two sets of half-reactions.[34,35] One set of half-reactions describes the oxidation of Pd^0 to Pd^{II}=NPh [Equations (1a)–(1c)], while the complementary set describes the reduction of P_2Pd^{II}=NPh to Pd^0 [Equations (2a)–(2d)] in order to make the reactions catalytic (see Scheme 4; the exact stoichiometries are given in the Supporting Information). Combining the two sets of half-reactions leads to the overall possible stoichiometries and allows the construction of the relatively simple and unifying catalytic scheme shown in Scheme 4.

Note that in this scheme nitrobenzene is always the substrate, whereas nitrosobenzene (PhNO) may be produced as an intermediate and enter the reaction described by Equations (1a)–(1c). Traces of nitrosobenzene were indeed frequently observed after a catalytic experiment. It is unlikely that nitrosobenzene is deoxygenated by methanol by the reactions in Equations (1b) and (1c), as it is well-documented that the first deoxygenation (with CO) of nitrobenzene (to



Scheme 4. Proposed reaction scheme for the overall catalytic processes.

nitrosobenzene) is considerably slower and energetically less favorable compared to nitrosobenzene deoxygenation with CO.[37,38]

Two Pathways to Oxidative Carbonylation Products DMC and DMO

In this paper, the focus lies on the genesis of the oxidative carbonylation products of methanol, DMC and DMO. Scheme 4 is helpful for this purpose, as it shows that DMC and DMO can be produced at two stages (following the bold arrows in Scheme 4).

DMC/DMO production at the first stage starts with a P_2Pd^0 species with oxidation of methanol and concomitant reduction of nitrobenzene according to Equation (1b) to produce one equivalent of DMC/DMO on nitrobenzene. At the second stage, DMC/DMO is produced from a reaction of P_2Pd^{II}=NPh with either CO/CH_3OH [Equation (2b)] or $PhNO_2/CO/2CH_3OH$ [Equation (2d)] while the initial P_2Pd^0 species is regenerated. The sum of Equations (1b) and (2b) or (1b) and (2d) results in the overall stoichiometries given in Equations (3a) or (3b), respectively. The equations marked with an asterisk are similar to the unmarked equations, but they describe the formation of DMO instead of DMC.

$$PhNO_2 + 3CO + 4CH_3OH \rightarrow 2DMC + PhNH_2 + H_2O + CO_2 \quad (3a)$$

$$PhNO_2 + 5CO + 4CH_3OH \rightarrow 2DMO + PhNH_2 + H_2O + CO_2 \quad (3a)^*$$

$$2PhNO_2 + 3CO + 4CH_3OH \rightarrow 2DMC + Azoxy + 2H_2O + CO_2 \quad (3b)$$

$$2PhNO_2 + 5CO + 4CH_3OH \rightarrow 2DMO + Azoxy + 2H_2O + CO_2 \quad (3b)^*$$

We have defined the efficiency of oxidative carbonylation (E_{OC}) as the mol ratio of [DMC + DMO] produced to nitrobenzene converted {i.e. the sum of products containing nitrobenzene "PhN" fragments [MPC + $PhNH_2$ + 2Azo(xy) + 2DPU] × 100%}. It follows from the above that the maximum value for E_{OC} is 200%; that is, when the sequence of reactions in Equations (1b) and (2b) or (1b) and (2d) [which are equivalent to those in Equations (3a) or (3a)*] is exclusively taking place. Lower efficiencies indicate that the other reactions along the periphery of the cycles in Scheme 4 [Equations (1a), (1c), (2a), and (2c)] are also operative. One should note that the amounts of aniline and DMC/DMO produced are not necessarily linked only through Equation (3a)/(3a)*. Aniline can also be formed as a consecutive product [e.g. by replacing methanol with H_2O in Equation (2a)] from water that is produced by the reactions given in Equations (1b) or (1c).

The E_{OC} for catalytic systems based on ligands comprising unsubstituted aryl rings and a C_3 backbone is about 45% (Table 1). For catalytic systems based on similar ligands with a larger backbone (i.e. a larger bite angle), the E_{OC} is greater: 65% for L4X and even 105% for L5Fc. This means that some catalysts can use nitrobenzene more efficiently as an oxidant than other catalysts for the production of DMC/DMO.

To unlock potentially even more efficient or selective catalytic systems for DMC/DMO production, it will be necessary to comprehend the effects of the structural parameters of the catalyst on the efficiency of the catalysis and thereby gain insight into the mechanistic details underlying the reactions summarized in Scheme 4. We have discussed our understanding of some of the molecular details of nitrobenzene deoxygenation[34] and the formation of Azoxy and MPC elsewhere.[35,38] The complexity of the parallel reactions shown in Scheme 4, which together make up the overall efficiency with which nitrobenzene can act as the oxidant in methanol carbonylation, makes it impossible to

present a fully detailed molecular picture of the catalytic consequences of the variations in the catalyst structure. Instead, we will focus on some of the most remarkable catalytic observations relevant for the chemistry of the oxidative carbonylation of methanol, attempting to rationalize these.

Effects of Catalyst Structure

Effects of o-MeO– and p-MeO– Substituents

The most prominent effect on the yield of DMC/DMO is observed with the introduction of *o*-MeO– substituents in L3-type ligands (Table 1). The formation of DMC/DMO is strongly inhibited and its amount is decreased by almost an order of magnitude relative to that with the unsubstituted ligands. Irrespective of the stage at which DMC/DMO is produced [Scheme 4; Equations (1b) and (2b) or (1b) and (2d)], a serious inhibition of methanol carbonylation takes place. The significantly weaker effects observed with *p*-MeO substitution suggests that steric rather than electronic effects play a dominant role with *o*-MeO substitution.

In the first stage, the formation of DMC/DMO [Equation (1b)] is in competition with the reduction of nitrobenzene with CO only [Equation (1a)] and oxidative dehydrogenation of methanol [producing MF and CO, Equation (1c)]. The first product-determining step is thus the reaction of the palladium(0) center in **C0a** through oxidative coupling of CO and nitrobenzene (to **C1a**) or oxidative addition of methanol (to **C1b/c**) as shown in Scheme 4.

We have shown that oxidative coupling of CO with nitrobenzene is promoted with the use of more electron-donating ligands, resulting in higher electron density at the Pd center,[34,35] which thus partly explains the lower amount of DMC/DMO produced with the catalytic systems containing *ortho*- or *para*-methoxy-substituted ligands.

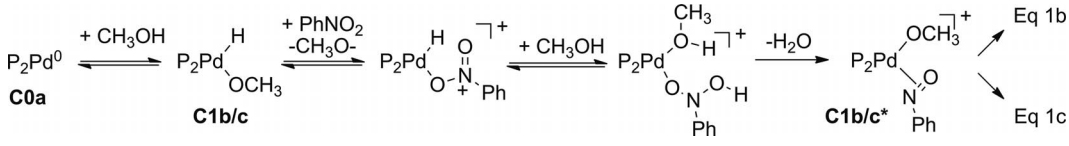
We have observed that more methanol is oxidatively dehydrogenated (to MF or CO) when the aryl rings in the ligand are functionalized with *o*-MeO groups or when the backbone spacer is enlarged from a C_3 to a C_4-type backbone.[34] Discrimination of the oxidative carbonylation of methanol to form DMC or DMO [Equation (1b)] over its oxidative dehydrogenation to form CO or MF [Equation (1c)] must occur after the first deoxygenation of nitrobenzene by methanol[34] through the different fates of the methoxide complex $[P_2Pd^{II}(OCH_3)(ONPh)]^+$ (**C1b/c***), as depicted in Scheme 5. Crucially important for the occurrence of oxidative *carbonylation* of methanol [Equation (1b)] relative to that of oxidative *dehydrogenation* of methanol [Equation (1c)] must be the effective displacement of the nitrosobenzene ligand in **C1b/c***.

This displacement likely involves an associative substitution of the nitrosobenzene ligand by CO or methoxide via a fifth coordination site at the Pd center of **C1b/c***. Such a process will be hampered by the presence of *o*-methoxy groups protecting the axial coordination sites of palladium, thus making the conversion to DMC/DMO precursors less likely.

Conversely, without a rapid displacement of nitrosobenzene from the palladium coordination site, the nitrosobenzene "ligand" becomes more likely involved in H-atom transfer at the Pd center from coordinated methoxide to nitrosobenzene,[34] ultimately leading to catalytic oxidative dehydrogenation of methanol to give CO (and H_2O).

We previously developed arguments for the competition at the second stage of the reaction forming DMC/DMO [Equations (2a) and (2b); Scheme 4].[34] At this stage, the presence of axially protective *o*-methoxy substituents prevents ready protonation and associative displacement of the phenylamido ($PhNH^-$) ligand in $[P_2Pd^{II}(OCH_3)(NHPh)]$ (**C2a**) by methanol to generate aniline and $[P_2Pd^{II}(OCH_3)_2]$ (**C2b/d**), a precursor species for the formation of DMC/DMO (Scheme 4). Instead, displacement of the methoxide anion in **C2a** by coordination of the smaller neutral CO can occur, thus leading to carbonylation of **C2a** and ultimately to the formation of MPC. This rationalizes the concomitant increase in MPC formation [Equation (2a)] with a decrease in DMC/DMO formation [Equation (2b)], as is schematically illustrated in Scheme 4. That a decrease in the amount of Azoxy is not observed with increasing amounts of DMC/DMO is because the formation of Azoxy can also be coupled with DMC/DMO production in the second stage [Equation (3b)] by the protonation of the intermediate P_2Pd^{II}=O species **C2c** to dimethoxide species **C2b/d** (Scheme 4).[34]

We may thus conclude that it is likely that in both possible stages of DMC/DMO production the introduction of *o*-MeO substituents in C_3-backbone bis(diphenylphosphanyl) ligands leads to a reduction of the efficiency of nitrobenzene as oxidant in the palladium-catalyzed oxidative carbonylation of methanol. Also with ligands L4X and L5Fc that have a larger bite angle, *o*-MeO substituents are expected to play a similar role in reducing the efficiency, although to a lesser extent, of nitrobenzene as the oxidant in the oxidative carbonylation of methanol. In addition, a significant decrease in the formation of Azoxy is observed with these ligands, when either *p*-methoxy or *o*-methoxy



Scheme 5. First reaction intermediates in the deoxygenation of nitrobenzene that are common for Equations (1b) and (1c).

substituents are present (Table S1). Apparently the attack on P_2Pd^{II}=NPh intermediates by nitrobenzene become less likely in comparison with protonation by methanol (eventually leading to relatively more aniline and DMC/DMO or MPC) for a more basic P_2Pd^{II}=NPh center.[38]

Effects of Ligand Bite Angle

The catalysts based on ligands with larger bite angles, such as L4, L4X, and L5Fc, systematically produce significantly larger amounts of the products of the oxidative carbonylation of methanol, DMC and DMO, than do the systems with the propylene-bridged ligands (Table 1). A most remarkable observation is, however, that the DMO/DMC *ratio* increases significantly with increasing bite angle of the ligand.

A higher efficiency of nitrobenzene as the oxidant for the oxidative carbonylation of methanol could again, in principle, occur at both possible DMC/DMO-generating stages 1 and 2 (Scheme 4). At stage 1, the restricted coordination space at the equatorial positions around Pd, such as that in L4(X) and L5Fc, could favor oxidative addition of methanol at Pd^0, ultimately leading to reactions in Equations (1b) and (1c), over the space-demanding oxidative coupling of CO and nitrobenzene [Equation (1a); top left in Scheme 4]. This hypothesis is in correspondence with the increased contribution of CH_3OH as (co-)reductant of nitrobenzene [both in Equations (1b) and (1c)], as suggested by quantitative product simulations comparing ligands L3X and L4X.[34] This may thus at least partly account for an increase in the formation of DMC/DMO when using ligands with a large bite angle, such as L4X and L5Fc.

In stage 2, one might expect that coordination of the bulky phenylamido ligand in the Pd^{II} complex **C2a** (Scheme 4) is less favorable at the restricted coordination space in L4(X) and L5Fc relative to L3(X) ligands. Therefore, coordination of a smaller CO or methoxide ligand becomes more likely, thus producing a DMC/DMO precursor complex (**C2b/d**) rather than the MPC precursor complex. This argument may thus rationalize the lower production of MPC with concomitantly higher DMC/DMO formation, as indeed observed with L4(X) and L5Fc catalysts.

The same concept of restriction in equatorial coordination space with ligands having a larger bite angle can also rationalize an increase in the DMO/DMC ratio observed with these ligands, as depicted in Scheme 6.

Thus, CO can displace methoxide from the first coordination sphere of Pd in **C1b-1** (**C2b/d** in Scheme 4), which results in Pd carbonyl complexes such as **C1b-3** and/or **C1b-4**. It is thought that a restricted coordination space at Pd, such as in the complexes of the L4- and L5-type ligands, will relatively favor coordination of the small neutral CO molecule over the larger-sized methoxide anion. The latter can be suitably accommodated by solvation and hydrogen bonding with methanol solvent molecules in close proximity of the Pd center.

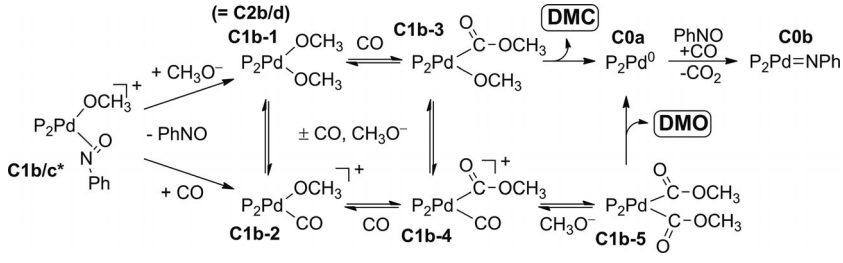
The competition between the formation of **C1b-3** and **C1b-4** (Scheme 6) follows the same steric rules. Thus, the small CO molecule will be more advantageous for coordination than methoxide in the acyl complexes, thus *relatively* favoring **C1b-4** over **C1b-3** when the coordination space is more restricted and hence shifting the equilibrium towards dimethoxycarbonyl complex **C1b-5**. This restricted coordination space argument thus clearly rationalizes the increase in DMO/DMC ratios (up to ca. 3 for L5Fc) when ligands with a large bite angle are applied instead of ligands with a smaller bite angle (e.g. a ratio of ca. 1 for L3).

Effects of Reaction Conditions

Addition of H_2 during the oxidative carbonylation of methanol results in the formation of more methyl formate at the expense of DMC/DMO. This can be rationalized by the existence of $[Pd^{II}C(O)OCH_3]^+$-type intermediate species for DMC/DMO formation, such as **C1b-3** and **C1b-4** (see Scheme 6). Such species are prone to undergo hydrogenolysis by a reaction with dihydrogen, thus forming MF at the expense of DMC and DMO.

The decreased DMO/DMC ratio upon addition of a base (and the reverse effect when an acid is added) can also be rationalized by the process summarized in Scheme 6; a higher methoxide concentration will favor rapid coordination of the methoxide anion to form **C1b-3**, as a result forming more DMC.

Likewise, the observed effect that increasing CO pressure leads to a higher DMO/DMC ratio can be easily rationalized. A higher CO concentration makes CO more successful, relative to methoxide, in the competition for the coordination site in the **C1b-3** ⇄ **C1b-4** equilibrium, producing more of complex **C1b-4** and as a result giving a higher DMO/DMC ratio.



Scheme 6. Proposed intermediates for DMC or DMO production in stage 1. Complexes **C1b-1** to **C1b-5** are also intermediates for DMC or DMO production in stage 2.

Summary and Conclusions

The catalytic reactivity of palladium complexes supported by bidentate diarylphosphane ligands has been studied in the oxidative carbonylation of methanol to dimethyl carbonate (DMC) and dimethyl oxalate (DMO) using nitrobenzene as terminal oxidant.

Insight into the molecular mechanism of the oxidative carbonylation process of methanol has been obtained from catalytic experiments employing a variety of bis(diarylphosphanyl) ligands with variations in the substituents on the phenyl rings as well as in the length of the backbone spacer, and from experiments in which the acidity or the CO pressure was varied, or in which an additional partial pressure of H_2 was applied.

It was found that two key intermediate stages exist at which the oxidative carbonylation process of methanol can be identified. Identification of these two stages for DMC/DMO production was shown to be helpful in rationalizing the observed influence that the structure of the catalyst and the reaction conditions can have on the oxidative carbonylation process.

On the basis of the mechanistic insights, it is concluded that an ideal P_2Pd catalyst for the oxidative carbonylation of methanol with nitrobenzene as the oxidant would need a relatively acidic palladium center, be sterically open in the axial coordination positions, but have restricted coordination space at the equatorial coordination positions of palladium. The palladium complex of the ligand 1,1′-bis(diphenylphosphanyl)ferrocene (L5Fc) meets these criteria and was found to use nitrobenzene as oxidant for the oxidative carbonylation of methanol most efficiently, with an E_{OC} of 105% of the 200% maximum theoretical efficiency possible.

In view of these initial results and the mechanistic information generated by the present work, even more active and/or selective catalytic systems may reasonably be anticipated for the oxidative carbonylation of methanol using nitrobenzene as oxidant.

Experimental Section

All ligands were generously provided by Shell Global Solutions Amsterdam B. V., where they were synthesized according to literature procedures.[39–47] All other solids were purchased from Acros organics and used as received. Methanol and nitrobenzene were of analytical reagent purity and were distilled under an argon atmosphere from the appropriate drying agent.[48] After distillation, these liquids were stored under argon. It was ensured that no water was present by using an analytical reaction with trimethyl orthoformate according to a literature procedure.[49] Carbon monoxide (> 99% pure)[50] was purchased from Linde gas Benelux B. V. and used as received.

^{1}H-, and ^{13}C-NMR spectra were recorded with a Bruker DPX300 (300 MHz) or a Bruker DMX400 (400 MHz) machine. High-pressure 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 were measured with probes connected to a computer interface, making it possible to record these parameters throughout the course of the reaction. Procedures for the catalytic experiments and analysis of the reaction mixtures are described elsewhere.[34] To ensure reproducibility, some catalytic reactions were performed in quadruple, and the relative standard deviation was always less than 5% for all products.

Supporting Information (see footnote on the first page of this article): A table with full analytical data of the experiments and a list of all half-reactions relevant for the redox chemistry discussed in the text.

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[1] *Registry of Toxic Effects of Chemical Substances (RTECS, online database)*, United States Department of Health and Human Services (National Toxicology Information, National Library of Medicine), Bethesda, MD, **1993**.
[2] R. C. Weast (Ed.), *Handbook of Chemistry and Physics*, D-110, 58th ed., CRC Press Inc., Cleveland, **1977–1978**.
[3] R. H. Richter, R. D. Priester in *Kirk-Othmer Encyclopedia of Chemical Technology* (Eds.: J. L. Kroschmitz, M. Howe-Grand), Wiley, New York, **1995**.
[4] H. Ulrich, *Ullmann's Encyclopedia of Industrial Chemistry*, VCH publishers, New York, **1989**.
[5] A. J. Ryan, J. L. Stanford in *Comprehensive Polymer Science* (Eds.: G. Allen, J. C. Bevington), Pergamon, New York, **1989**.
[6] K. Weisermel, H. J. Arpe, *Industrielle Organische Chemie*, VCH Verslagsgesellschaft GmbH, Weinheim, Germany, **1988**.
[7] www.gem-chem.net/capacity.html, December **2011**.
[8] Y. Ono, *Pure Appl. Chem.* **1996**, *68*, 367–375.
[9] Y. Ono, *Appl. Catal. A* **1997**, *155*, 133–166.
[10] Y. Ono, *Catal. Today* **1997**, *35*, 15–25.
[11] F. Rivetti, *CR Acad. Sci. II C* **2000**, *3*, 497–503.
[12] P. Tundo, M. Selva, *Acc. Chem. Res.* **2002**, *35*, 706–716.
[13] J. L. Gong, X. B. Ma, S. P. Wang, *Appl. Catal. A* **2007**, *316*, 1–21.
[14] R. Bertani, G. Cavinato, L. Toniolo, G. Vasapollo, *J. Mol. Catal.* **1993**, *84*, 165–176.
[15] T. W. Dekleva, D. Forster, *Adv. Catal.* **1986**, *34*, 81–130.
[16] D. Delledonne, F. Rivetti, U. Romano, *J. Organomet. Chem.* **1995**, *488*, C15–C19.
[17] P. Giannoccaro, *J. Organomet. Chem.* **1994**, *470*, 249–252.
[18] W. B. Kim, U. A. Joshi, J. S. Lee, *Ind. Eng. Chem. Res.* **2004**, *43*, 1897–1914.
[19] J. Muzart, *Tetrahedron* **2005**, *61*, 9423–9463.
[20] F. Rivetti, U. Romano, *J. Organomet. Chem.* **1978**, *154*, 323–326.
[21] D. M. Fenton, P. J. Steinwan, *J. Org. Chem.* **1974**, *39*, 701–704.
[22] F. Rivetti, U. Romano, *J. Organomet. Chem.* **1979**, *174*, 221–226.
[23] F. Rivetti, U. Romano, *Chim. Ind.* **1980**, *62*, 7–12.
[24] M. Goyal, R. Nagahata, J. Sugiyama, M. Asai, M. Ueda, K. Takeuchi, *Catal. Lett.* **1998**, *54*, 29–31.
[25] M. Takagi, H. Miyagi, T. Yoneyama, Y. Ohgomori, *J. Mol. Catal. A* **1998**, *129*, L1–L3.
[26] M. Goyal, R. Nagahata, J. Sugiyama, M. Asai, M. Ueda, K. Takeuchi, *J. Mol. Catal. A* **1999**, *137*, 147–154.

[27] S. Uchiumi, K. Ataka, T. Matsuzaki, *J. Organomet. Chem.* **1999**, *576*, 279–289.
[28] S. P. Current, *J. Org. Chem.* **1983**, *48*, 1779–1780.
[29] D. Delledonne, F. Rivetti, U. Romano, *Appl. Catal. A* **2001**, *221*, 241–251.
[30] H. Ishii, M. Goyal, M. Ueda, K. Takeuchi, M. Asai, *Appl. Catal. A* **2000**, *201*, 101–105.
[31] H. Yasuda, K. Watarai, J. C. Choi, T. Sakakura, *J. Mol. Catal. A* **2005**, *236*, 149–155.
[32] E. Amadio, G. Cavinato, A. Dolmella, L. Toniolo, *Inorg. Chem.* **2010**, *49*, 3721–3729.
[33] I. I. Moiseev, M. N. Vargaftik, T. V. Chernysheva, T. A. Stromnova, A. E. Gekhman, G. A. Tsirkov, A. M. Makhlina, *J. Mol. Catal. A* **1996**, *108*, 77–85.
[34] T. J. Mooibroek, L. Schoon, E. Bouwman, E. Drent, *Chem. Eur. J.* **2011**, *17*, 13318–13333.
[35] T. J. Mooibroek, W. Smit, E. Bouwman, E. Drent, **2012**, to be submitted.
[36] T. J. Mooibroek, E. Bouwman, M. Lutz, A. L. Spek, E. Drent, *Eur. J. Inorg. Chem.* **2010**, *2*, 298–310.
[37] H. Lund in *Organic Electrochemistry. An Introduction and a Guide*, (Eds.: H. Lund, M. M. Baizer), Marcel Dekker, New York, 3rd ed., **1991**, p. 411.
[38] T. J. Mooibroek, E. Bouwman, E. Drent, *Organometallics* **2011**, submitted.
[39] F. Bickelhaupt, US 4874897, **1989**.
[40] W. Eilenberg, EU 364046, **1991**.
[41] J. A. van Doorn, US 4994592, **1991**.
[42] R. van Ginkel, US 6548708, **2003**.
[43] E. Drent, US 5091587, **1992**.
[44] C. F. Hobbs, US 4120901, **1987**.
[45] P. W. Clark, B. J. Mulraney, *J. Organomet. Chem.* **1981**, *217*, 51–59.
[46] J. M. Brown, B. A. Murrer, *Tetrahedron Lett.* **1980**, *21*, 581–584.
[47] R. L. Wife, A. B. van Oort, J. A. van Doorn, P. W. N. M. van Leeuwen, *Synthesis* **1983**, *1*, 71–73.
[48] W. L. F. Armarego, C. L. L. Chai, *Purification of Laboratory Chemicals*, 5th ed., Elsevier, Amsterdam, **2003**.
[49] J. Chen, J. S. Fritz, *Anal. Chem.* **1991**, *63*, 2016–2020.
[50] customer.linde.com/FIRSTspiritWeb/linde/LGNL/media/datasheets/NL-PIB-0024.pdf, December **2011**.

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