Influence of various P/N and P/P ligands on the palladium-catalysed reductive carbonylation of nitrobenzene

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Abstract

A series of bidentate phosphorus–nitrogen ligands was synthesised for the palladium-catalysed reductive carbonylation of nitrobenzene in order to combine the favourable influence of the phosphorus atom on the stability of the catalyst complex with the stimulating effect of the nitrogen atom on the catalytic activity.

The nitrogen atom of the P/N ligand was either incorporated in an imine function, yielding the N-(2'-diphenylphosphinobenzylidene)–R–amine ligands (R = phenyl, 4-chlorophenyl, 2,4-dimethoxyphenyl, 2,4-dimethylphenyl, tert-butyl), or in a heteroaromatic ring system which gave 2-(2'-(diphenylphosphino)ethyl)pyridine and 8-(diphenylphosphino)quinoline. Complexes of the type Pd(ligand)$_2$(BF$_4$)$_2$ were prepared for these ligands. Additionally, a series of bidentate phosphorus ligands was tested: dppm, dppe, dppp, dppb, dppf, 1,2-bis(diphenylphosphino)benzene, 1,8-bis(diphenylphosphino)naphthalene, bis(2-diphenylphosphinophenyl)ether, and 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene.

The P/N ligands containing the imine function did not yield any conversion of the nitrobenzene in combination with Pd. On the use of the second type of P/N ligand, moderately active palladium catalysts were obtained. This different behaviour is ascribed to the relatively low π*-level of the imine-containing ligands.

Oxidation of the phosphorus donor atom by the nitro substrate inactivated the catalysts derived from the P/N ligands as well as from a series of P/P ligands.

For the bidentate phosphorus ligands the bite angle and flexibility of the ligand turned out to be of crucial influence due to the different geometries required for the Pd(II) and Pd(0) intermediates of the catalytic cycle. © 1997 Elsevier Science S.A.
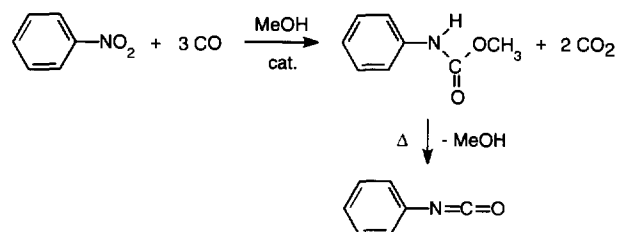
1. Introduction

Traditionally, aromatic isocyanates and carbamates are prepared on a commercial scale from aromatic nitro compounds, which are first catalytically hydrogenated to the corresponding amine. A subsequent reaction with phosgene yields the desired aromatic isocyanates. A reaction between the isocyanate and an alcohol finally affords the aromatic carbamate [1,2]. The isocyanates, especially the diisocyanates, are industrially important products for the preparation of polyurethanes, which are primarily applied as soft foams [3]. Carbamates, on the other hand, are used in the pharmaceutical industry and as agrochemicals [1,2].

The use of the extremely toxic phosgene and the production of large amounts of HCl in the step from the amine to the isocyanate are major disadvantages of this traditional production process [1,2]. Therefore, ever since 1962, research has been done on an alternative route in the form of the reductive carbonylation of the aromatic nitro compounds. In this one-step process the nitro function reacts directly with CO under the influence of a catalyst. If the reaction is performed in an alcohol, like methanol, the carbamate is formed as the main product. This carbamate can be thermally degraded into the isocyanate if desired (Scheme 1).

The first catalyst systems for this reaction were heterogeneous systems, using Rh as active metal [4]. The use of Group 8–10 metals in homogeneous catalyst systems for the reductive carbonylation of aromatic

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Scheme 1. General scheme for the reductive carbonylation of nitrobenzene.

2. Results and discussion

2.1. Synthesis of the ligands

In general, two types of bidentate phosphorus–nitrogen ligand can be distinguished among the P/N ligands we have used in the palladium-catalysed reductive carbonylation of nitrobenzene (Scheme 2). For the phosphorus donor atom a diphenylphosphino unit has been incorporated in both types of P/N ligand. As a result the phosphorus ligands are all electronically similar and have similar ^{31}P NMR shifts (P/N-1, −12.8; P/N-2, −12.5; P/N-3, −13.7; P/N-4, −13.0; P/N-5, −11.7; P/N-6, −14.8; P/N-7, −11.4).

The nitrogen donor atom is either present in an imine function (the N-(2′-diphenylphosphino-benzylidene)–R–amine ligands (P/N-1-5)) or in a heteroaromatic ring (2-(2′-(diphenylphosphino)ethyl)pyridine (P/N-6) and 8-(diphenylphosphino)quinoline (P/N-7)). Therefore a significant difference between the σ-donating capacity and π*-levels of both types of ligand could be

nitro compounds has developed rapidly the last 15 years, especially for the synthesis of carbamates. The addition of bidentate nitrogen or phosphorus donor ligands, in particular 1,10-phenanthroline (phen) or 1,3-bis(diphenylphosphino)propane (dppp), to palladium salts or metal meant an important breakthrough in the use of homogeneous catalyst systems [5–9]. Mechanistic insight into the catalytic reductive carbonylation of aromatic nitro compounds has mainly been gained with ruthenium systems as active, homogeneous catalysts [10]. Whereas the Ru catalyst systems mostly comprise $Ru_3(CO)_{12}$ in combination with a phosphine ligand [11] or a $Ru(dppe)(CO)_3$ complex (dppe = 1,2-bis(diphenylphosphino)ethane) [10], the Pd catalyst systems mostly contain a bidentate nitrogen ligand [6,12,13]. Yet, also several Pd–phosphine systems are known as active catalysts for the reductive carbonylation of aromatic nitro compounds [5,9,14]. For example, Alper and coworkers have applied a $Pd(dppp)Cl_2$–K_2CO_3 catalyst system for the conversion of nitrobenzene with a turnover frequency of $2\,mol\,(mol\,h)^{-1}$ and a selectivity towards the desired carbamate of 58% [14]. The system by Drent, consisting of $Pd(acetate)_2$, dppp, and 2,4,6-trimethylbenzoic acid, yields a higher activity $(t.o.f. = 500\,mol\,(mol\,h)^{-1})$ and better selectivity (95%), but still these figures remain far behind the results that were obtained with $Pd(OAc)_2$, phen, and p-toluenesulfonic acid $(t.o.f. > 1600\,mol\,(mol\,h)^{-1}$; selectivity 96%) [9].

Though the catalytic activities found for the Pd–P/P systems are much lower than those observed for the Pd–N/N systems, the P/P ligands have the advantage that the phosphorus atoms are intrinsically better coordinating atoms for Pd than the nitrogen atoms. This might have a positive influence on the stability of the catalytic intermediates, since Pd–bipyridyl systems easily form Pd black during the reductive carbonylation of nitrobenzene [12].
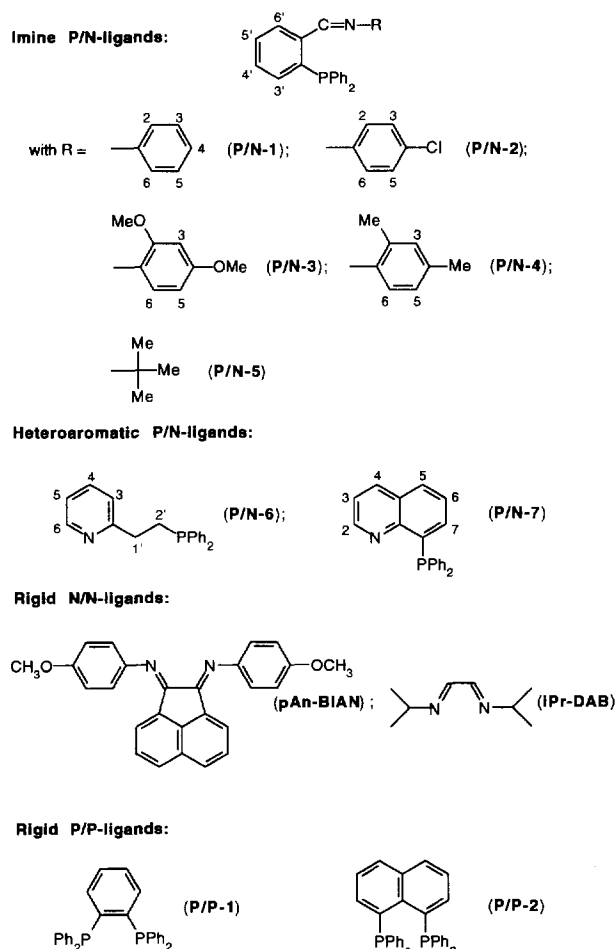
We applied phosphorus–nitrogen (P/N) ligands in the palladium-catalysed reductive carbonylation of nitrobenzene. The nitrogen atom is incorporated either in an imine function or in a heteroaromatic ring system. A more detailed study on the reason for the lower catalytic activities with phosphine ligands will also be presented.

Scheme 2. P/N-ligands with numbering schemes, rigid N/N- and P/P-ligands.

expected. α-Diimine ligands are known as good σ-donors and very good π-acceptors because of their relatively low π^*-levels [15]. Incorporation of an imine function in the P/N ligands was thus expected to enhance π-accepting abilities of these kinds of ligand as well [16,17], which could be of importance for the catalytic performance of the corresponding Pd complexes.

The imine-containing P/N ligands were all prepared from 2-diphenylphosphino-benzaldehyde, the synthesis of which has been described by Rauchfuss and coworkers [18]. Related N-(2'-diphenylphosphino-benzylidene)–R–amine ligands have been prepared by Rauchfuss with $R = p\text{-}C_6H_4OCH_3$, $CH_2\text{-}CH=CH_2$, $CH_2\text{-}2\text{-}C_5H_4N$, and $CH_2CH_2SCH_3$ [19].

The ^1H NMR spectra of all imine-containing P/N ligands (P/N-1–5) show a phosphorus coupling constant in the range of 5–5.5 Hz on the imine proton. This formally ^4J-coupling is thought to be a through-space coupling [16,17]. Such a through-space coupling has been observed before for a related, terdentate PNN ligand that is also based on the N-(2'-diphenylphosphinobenzylidene)amine moiety (N-(2'-diphenylphosphinobenzylidene)-2-(2-pyridyl)ethylamine, J(P–H) = 4.7 Hz) [16,17]. The through-space coupling indicates that the conformation of the ligands in solution is such that the imine-proton is directed towards the phosphorus lone-pair [17]. Phosphorus couplings could also be observed on the protons $H_{3'}$ and $H_{5'}$ of the benzylidene ring, resulting in double doublets and triplets, respectively (J(P–$H_{3'}$) $\approx$ 3.8 Hz, J(P–$H_{5'}$) $\approx$ 4.5 Hz; this is in good agreement with the coupling constants found for the PNN ligand [17]).

Similar to the phosphorus couplings observed on $H_{3'}$ and $H_{5'}$ of P/N-1–5, a phosphorus coupling constant of 3.3 Hz was found on H_7 of 8-(diphenylphosphino)-quinoline (P/N-7). The expected coupling on H_5, however, was absent. For the 2-(2'-(diphenylphosphino)-ethyl)pyridine ligand (P/N-6) a large phosphorus coupling constant was measured on $H_{2'}$, the protons neighbouring the phosphorus atom on the ethyl substituent. In none of these cases could phosphorus couplings on the protons of the phenyl rings attached to the phosphorus atom be determined because the resonance signals of these protons were not sufficiently well resolved.

2.2. Synthesis of the complexes

All Pd(bidentate ligand)$_2$(BF$_4$)$_2$ complexes (ligand = bis(*p*-anisylimino)acenaphthene (pAn-BIAN), N-(2'-diphenylphosphinobenzylidene)-*tert*-butylamine (P/N-5), 2-(2'-(diphenylphosphino)ethyl)pyridine (P/N-6), and 8-(diphenylphosphino)quinoline (P/N-7)) were prepared from Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ [16,20]. In the ^{31}P NMR

spectra of the P/N ligands a large downfield shift of 53–62 ppm could be observed for their phosphorus signal upon coordination of the ligands to Pd(BF$_4$)$_2$. A ^{31}P NMR spectrum of the Pd(N-(2'-diphenylphosphinobenzylidene)-*tert*-butylamine (P / N-5))$_2$(BF$_4$)$_2$ complex measured immediately after the addition of the Pd(CH$_3$CN)$_4$(BF$_4$)$_2$ precursor to the ligand revealed the presence of cis and trans conformers in a ratio of 1:0.45. The complex rearranged to the cis conformer completely, which is thermodynamically the most stable conformer due to the larger trans-influence of the phosphine with respect to the imine moiety [21]. The initial formation of the trans-isomer is the result of the trans-effect of the phosphine moiety of the first added ligand.

This cis conformation of the final Pd(P/N-5)$_2$(BF$_4$)$_2$ complex is confirmed by its ^1H NMR spectrum. A phosphorus coupling constant of 12.8 Hz is found for the signal of the imine-proton. Due to the coordination to the metal centre the intra-ligand through-space coupling vanishes. This has been observed for Mo(CO)$_4$(P/N) complexes by Rauchfuss (R = p-C$_6$H$_4$OCH$_3$, CH$_2$-CH=CH$_2$, CH$_2$-2-C$_5$H$_4$N, and CH$_2$CH$_2$SCH$_3$) [19] and for Pd(PNN)(CH$_3$)(X) (X = Cl, OTf) complexes of the related terdentate N-(2'-diphenylphosphino-benzylidene)-2-(2-pyridyl)ethylamine (PNN) ligand [16,17]. In the ^1H NMR spectra of these complexes a singlet was found for the signal of the imine proton. The doublet that was observed for the Pd(P/N-5)$_2$(BF$_4$)$_2$ complex should therefore originate from a P–H coupling through the palladium metal involving two ligand molecules. In the case of a trans complex a triplet for the signal of the imine proton in the ^1H NMR spectrum of the complex would be expected. Since a doublet is observed for the imine proton it is concluded that the complex has the cis conformation.

A similar trans coupling constant through the metal of 10.7 Hz (doublet) between the phosphorus atom and H_2 of the second 8-(diphenylphosphino)quinoline ligand (P/N-7) was observed in the ^1H NMR spectrum of the Pd(8-(diphenylphosphino)quinoline)$_2$(BF$_4$)$_2$ complex. This indicates that the thermodynamically most stable complex of the 8-(diphenylphosphino)quinoline ligand (P/N-7) has also adopted the cis conformation.

For the palladium complex of the 2-(2'-(diphenylphosphino)ethyl)pyridine ligand (P/N-6) the bidentate coordination is confirmed by the ^1H NMR signals of $H_{1'}$ and $H_{2'}$ of the ethyl bridge. In the ^1H NMR spectrum of the free ligand a sharp double triplet and a sharp triplet could be observed for $H_{2'}$ and $H_{1'}$ respectively. These signals changed to broadened multiplets upon coordination, which is probably caused by a slow conformational exchange of the non-planar six-membered ring structure that is formed by the Pd-pyridyl-ethylphosphine moiety, in which all four hydrogens $H_{2'}$ and $H_{1'}$ have become inequivalent [22].

2.3. Catalysis

To study the influence of the various P/N ligands on the catalytic activity and selectivity in the palladium-catalysed reductive carbonylation of aromatic nitro compounds, nitrobenzene has been used as a model substrate. The reactions have been performed in methanol, resulting in methyl N-phenylcarbamate as the desired product in all cases. The common side products that could be observed are N,N'-diphenylurea, aniline, and azoxybenzene [20]. The experiments have all been conducted at least in duplicate and the average turnover frequencies will be used to compare the activities of the various catalyst systems. Two different types of catalyst system have been used to test the various P/N ligands.

(I) Presynthesised $Pd(P/N)_2(BF_4)_2$ complexes with 3 equiv. of free ligand with respect to Pd. Because of the rapid formation of the desired complexes from the $Pd(CH_3CN)_4(BF_4)_2$ precursor, especially at elevated temperature, the catalyst complexes could also be prepared in situ from $Pd(CH_3CN)_4(BF_4)_2$ and the ligand. The tests with the BF_4 systems were all carried out over a reaction period of 2 h at a palladium concentration of 2 mM and a nitrobenzene:Pd ratio of 365 [12].

(II) In situ generated catalyst systems from $Pd(acetate)_2$, a ligand, and 2,4,6-trimethylbenzoic acid (TMBA). A higher Pd-concentration and ligand:Pd ratio were used in catalyst system II ([Pd] = 2.5 mM, ligand:Pd = 10). Because the amount of substrate was doubled compared to the $Pd–BF_4$ catalyst systems (nitrobenzene:Pd = 584) the reaction time was prolonged to 3 h. TMBA had to be added as cocatalyst (TMBA:Pd = 25) in order to replace the firmly coordinating acetate anions by more weakly coordinating 2,4,6-trimethylbenzoate anions [9]. The conditions of system I are based on previously performed experiments with several Pd–bipyridine systems [12], whereas the conditions for system II have been derived from literature experiments with bidentate phosphorus ligands [9].

To be able to compare the catalytic results obtained with the P/N ligands to those obtained with other ligand systems, several bidentate nitrogen ligands have been tested under the conditions described for catalyst system I. A series of bidentate phosphorus ligands have been studied under the conditions of catalyst system II.

2.4. Influence of various P / N ligands in catalyst system I

The two types of P/N ligand differ from one another by a significant distinction in their σ-donating capacity and their π^*-levels due to the fact that the nitrogen donor atom is either incorporated in an imine function or in a heteroaromatic ring system. Cyclic voltammetric measurements on a series of $Pd(R_2–phen)_2(OTf)_2$ complexes (R_2-phen = 4,7-disubstituted-1,10-

phenanthroline with R = Cl, H, Me, and MeO) have shown that the Pd^{II}/Pd^0 redox couple is influenced by the ligand [20]. This might be one of the reasons why the ligands exert a pronounced effect on the catalytic activity and selectivity as the Pd^{II}/Pd^0 redox couple probably plays an important role in the reductive carbonylation of aromatic nitro compounds [23].

Both types of P/N ligand have first been tried as $Pd(P/N)_2(BF_4)_2$ complexes in catalytic experiments of type I. None of the P/N ligands, however, yielded any catalytic activity under these conditions. This inactivity cannot be ascribed to decomposition of the catalyst system as only traces of Pd black could be detected. To exclude the possibility that the palladium centre is completely blocked for the substrate by a ligand that is coordinating too strongly, the ligand:Pd ratio was gradually decreased for 2-(2'-(diphenylphosphino)-ethyl)pyridine (P/N-6). Yet, at a ligand:Pd ratio of 2 or 1 still no conversion was found, while the experiment with the ratio of 1 afforded a large amount of Pd black, indicative of a large degree of catalyst decomposition. On the basis of these results it does not seem likely that the Pd–(P/N) catalyst systems are poisoned by too strong a coordination of the P/N ligands.

To study the effect of the σ-donating capacity and the π^*-level of the ligands, two α-diimine ligands having low-lying π^*-orbitals have been tried as well. The bis(p-anisylimino)acenaphthene ligand (pAn-BIAN) [24] is a rigid α-diimine ligand, whereas 1,4-di-isopropyl-1,4-diaza-1,3-butadiene (iPr-DAB) [25] is a more flexible compound. In view of the results obtained with bpy and phen [12,20] a higher catalytic activity would be expected for pAn-BIAN than for iPr-DAB, due to the higher flexibility of the latter. This trend could indeed be observed. The flexible iPr-DAB ligand yielded no conversion at all but with the more rigid pAn-BIAN ligand a low but distinct activity could be measured. A turnover frequency of $4 \, mol(mol \, h)^{-1}$ was reached, which is about eight times as low as the t.o.f. for bpy under the same conditions (t.o.f. = $31 \, mol(mol \, h)^{-1}$). The selectivity towards the desired carbamate was even slightly higher for the pAn-BIAN ligand than for bpy (pAn-BIAN: 74% carbamate, 26% aniline; bpy: 66% carbamate, 34% azoxybenzene). An active catalyst system can be obtained using a diimine ligand, though the combination of the σ-donating capacity and the relatively low π^*-level of such a ligand is clearly not preferable. This is in good agreement with the cyclic voltammetric study on the $Pd(R_2–phen)_2(OTf)_2$ systems [20] that has shown that the catalytic activity decreases if the reduction potential of the catalyst complex becomes more positive. The reduction potential of the $Pd(pAn-BIAN)_2(BF_4)_2$ complex ($E_{p,c} = -0.96 \, V$ vs. $E_{1/2}$ of Fc/Fc^+ [20])is far more positive than the highest value obtained for the $Pd(R_2–phen)_2(OTf)_2$ complexes (R = Cl; $E_{p,c} = -1.17 \, V$, R =

MeO; $E_{p,c}$ = -1.30 V vs. $E_{1/2}$ of Fc/Fc$^+$ [20]) indicating that for the **pAn-BIAN** ligand the Pd^{II}/Pd^0 redox potential is far from optimal for an efficient catalysis.

2.5. Influence of various P / N ligands in catalyst system II

The results of the experiments of type II with Pd(OAc)$_2$ and TMBA are collected in Table 1. The P/N ligands in which the nitrogen donor atom is incorporated in a heteroaromatic ring (**P/N-6** and **P/N-7**) did now lead to conversion of a small amount of the nitro substrate, resulting in very moderate turnover frequencies. Again the more rigid 8-(diphenylphosphino)quinoline ligand (**P/N-7**) (t.o.f. = 17 mol(mol h)$^{-1}$) turned out to give higher catalytic activity than its more flexible counterpart, the 2-(2'-(diphenylphosphino)ethyl)pyridine ligand (**P / N-6**) (t.o.f. = 8 mol(mol h)$^{-1}$). Like in the case of the bidentate nitrogen ligands, the better chelating properties of a rigid ligand appear to have a positive effect on the catalytic activity induced by a P/N ligand as well. Compared to the α-diimine ligand (**pAn-BIAN**; catalyst system I) these two P/N ligands yield more active catalyst systems under their own optimal reaction conditions (catalyst system II), but their activity is still much lower than the highest activity that could be reached with bpy (t.o.f. = 31 mol(mol h)$^{-1}$; catalyst system I).

Table 1
Results of the reductive carbonylation of nitrobenzene in methanol with Pd(OAc)$_2$, a P/N or P/P ligand, and TMBA [a]

Ligand	T.o.f. (mol(mol h^{-1}))	Product distribution (%) [b]			
		CA	UR	AN	AZOX
P/N-1	0	—	—	—	—
P/N-5	0	—	—	—	—
P/N-6	8	65	0	20	15
P/N-7	17	66	1	18	15
Dppm	0	—	—	—	—
Dppe	26	74	0	23	4
Dppp	68	78	6	13	3
Dppb	23	83	0	14	3
Dppf	35	61	1	36	2
P/P-1	29	71	2	18	9
P/P-2	23	50	4	42	4
DPEphos [c]	15	0	0	0	100
Xantphos [c]	33	28	0	0	72
Dppp [d]	72	73	6	18	3
Preoxidised dppp [d]	27	56	6	37	5
None [d]	30	60	1	33	6

[a] See Section 2.3 for the precise conditions.
[b] CA = methyl *N*-phenylcarbamate; UR = *N,N'*-diphenylurea; AN = aniline; AZOX = azoxybenzene.
[c] DPEphos = bis(2-diphenylphosphino-phenyl)ether; Xantphos = 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene; vide infra.
[d] Reductive carbonylation of nitrobenzene in methanol with presynthesised Pd(dppp)(OAc)$_2$.

The ligands **P/N-1** and **P/N-5** afford completely inactive catalysts even in the presence of the weakly coordinating 2,4,6-trimethylbenzoate anions (catalyst system II). This is probably caused by the negative influence of the relatively low π*-level of these ligands due to the imine function, as was already observed for the **pAn-BIAN** ligand in comparison to bpy or phen. It should be remarked that the imine functions of the P/N ligands appear to remain intact during the catalytic experiments, indicating that the deactivation of the catalyst is not caused by decomposition of the C=N function.

Apparently, the better coordinating properties of a phosphorus atom with respect to the nitrogen atom do not induce a higher catalytic activity or selectivity in the palladium-catalysed reductive carbonylation of nitrobenzene. This could be the result of oxidation of the phosphorus atoms of the P/N ligands by the nitro substrate. Nitrobenzene is a fairly powerful oxidising agent that might lead to the formation of the phosphine-oxide under reaction conditions. To gain more insight into this phenomenon a series of bidentate phosphorus ligands have been studied in more detail.

2.6. Influence of various P / P ligands (catalyst system II)

A series of bidentate Ph$_2$P-(CH$_2$)$_n$-PPh$_2$ ligands ($_n$ = 1–4) with increasing chain length between the two coordinating phosphine moieties have been tested in the palladium-catalysed reductive carbonylation of nitrobenzene. 1,1'-Bis(diphenylphosphino)ferrocene (dppf) was tried as well. Additionally, two rigid P/P ligands were prepared and tested, viz. 1,2-bis(diphenylphosphino)benzene (**P / P-1**) and 1,8-bis(diphenylphosphino)naphthalene (**P/P-2**) (Scheme 2). Though there is a distinct variation in the backbones interconnecting the coordinating phosphorus atoms in these ligands they are all known as cis chelating ligands [26]. Only for dppb is the coordination behaviour somewhat more complicated, as it can also act as a bridging ligand between two Pd centres [27,28]. According to the possible catalytic intermediates isolated by Osborn and coworkers [13], a cis chelating ligand probably is a prerequisite for an active catalyst system.

The various P/P ligands are electronically very similar. Though they can be divided into alkyl-(diphenyl)phosphine ligands and aryl(diphenyl)-phosphine ligands, the electronic differences are only very small.

The results obtained with the Pd(OAc)$_2$, a P/P ligand, and TMBA (catalyst system II) are given in Table 1. Under the influence of the smallest P/P ligand in the series, dppm, absolutely no conversion was found. At the end of the catalytic runs a large amount of Pd black could be observed, indicating decomposition of the catalyst system to a large extent. All other P/P

ligands did yield catalytic activity in combination with Pd(OAc)$_2$ and TMBA, with an apparent optimum for dppp.

The difference in catalytic behaviour induced by the various P/P ligands can be largely explained by steric reasoning, assuming that the stabilisation of the Pd(0) intermediates and the reoxidation to Pd(II) are crucial points in the catalytic cycle. Whereas Pd(II) is known to distinctly favour a square planar configuration over any other geometry, Pd(0) prefers a Y-shaped or tetrahedral rearrangement [29]. The ideal bite angle in a square planar rearrangement has a value of 90°, while the tetrahedral configuration requires a larger angle of 109.5°. Theoretical calculations on the energy levels of the molecular orbitals in various Pd^0(PPh$_3$)$_2$(Y) complexes (Y = π-ligands like O$_2$, C$_2$H$_2$, and C$_2$H$_4$) have shown that the lowest energies for these Y-shaped compounds are obtained at P–Pd–P angles between 94 and 102° [30]. For complexes of the type Pd(P/P)(X)$_2$ (X = Cl, SCN, NCS) containing the P/P ligands that were tested in the catalysis, the P–Pd–P angle and averaged Pd–P distance measured in X-ray analyses are shown in Table 2 [31–34].

The bite angles of dppm and dppe are too small to yield highly stable Pd(0) species. This was evidenced by the fair amount of Pd black that was found at the end of the catalytic runs. With dppp, however, the conversion of Pd(II) into Pd(0) and vice versa appears to proceed smoothly, yielding the highest catalytic activity and no formation of Pd black. The chain length of the alkyl bridge in this ligand might be just long enough to give reasonably stable Pd(0) species, as is depicted in Scheme 3. Larger ligands like dppb and dppf become more suitable for Pd(0) complexes than for the Pd(II) counterparts. Apparently, the bridges of these ligands have now become too long to give rise to efficient catalysis, presumably because the reoxidation of the Pd(0) intermediates is severely hampered. These features appear to be in disagreement with the results obtained by Lee et al. who used a Pd(OAc)$_2$/Ph$_2$P–
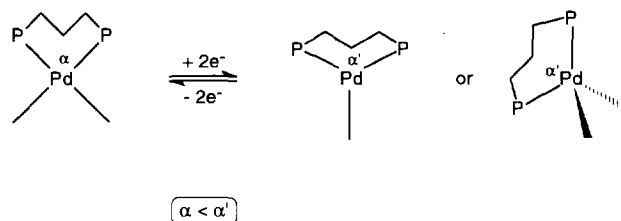
Scheme 3. Different coordination modes of dppp to Pd(II) and Pd(0).

(CH$_2$)$_n$–PPh$_2$/NEt$_4$Cl ($n = 1$–6) catalyst system for the production of N,N'-diphenylurea from nitrobenzene, aniline, and CO [35]. They found a maximum catalytic activity with dppb ($n = 4$) instead of dppp ($n = 3$). Yet, a different mechanism is suggested for this reaction in the presence of a large amount of aniline which might proceed through several trigonal-bipyramidal transition states [35]. This could explain why the larger dppb ligand is preferred in this case.

The importance of the flexibility of the P/P ligands in the carbamate synthesis was also expressed by the reduced catalytic activity in the presence of the rigid ligands P/P-1 and P/P-2. This is in sharp contrast with the bidentate nitrogen ligands (e.g. bpy and phen) where the rigidity of the ligand is very important to maintain bidentate coordination throughout the reaction. This is probably due to the intrinsically weaker coordination of nitrogen ligands compared to phosphorus ligands.

All active, flexible ligands gave about the same amount of carbamate, except dppf. In view of the large bite angle of dppf [32,36], this ligand would be expected to be the most suitable ligand for a Pd(0) species. In the presence of a rigid bidentate nitrogen ligand the Pd(0) intermediates in the catalytic cycle are held responsible for the formation of the azoxybenzene side product [6,23]. If the conversion of nitrobenzene under the influence of the bidentate P/P ligands were to proceed through the same mechanism, this would thus lead to an enhanced production of azoxybenzene in the case of the Pd/dppf catalyst system. Because the reduced selectivity toward the carbamate under the influence of dppf is the result of an increased aniline production (Table 1), the influence of the dppf ligand on the selectivity probably is an electronic effect instead of a steric one. The presence of the iron centre in the ligand might cause an aberrant electron-density on the palladium metal. For instance, the [Pd(dppf)(PPh$_3$)][BF$_4$]$_2$ complex is known to contain a dative Fe → Pd bond in which the iron atom in the ferrocene nucleus donates its non-bonding electrons to the palladium centre [37]. Such a feature might strongly facilitate the reoxidation of a Pd(0) intermediate in the catalytic cycle, similar to the rapid oxidation that was observed in a reaction between tetrakis(triphenylphosphine)palladium(0) and

Table 2
P–Pd–P angles and Pd–P distances in various Pd(P/P)(X)$_2$ complexes (X = Cl, NCS, SCN)

Complex	P–Pd–P (deg)	Pd–P (Å)	Ref.
Pd(dppm)Cl$_2$	72.7	— [a]	[31]
Pd(dppe)Cl$_2$	85.8	2.230	[31]
Pd(dppp)Cl$_2$	90.6	2.246	[31]
Pd(dppf)Cl$_2$	99.1	2.292	[32]
Pd(dppe)(SCN)(NCS)	85.1	2.251	[33]
Pd(dppp)(SCN)(NCS)	89.0	2.270	[34]
Pd(dppb)(SCN)(NCS)	92.8	2.283	[34]
Pd(P/P-2)(SCN)$_2$	86.2	2.253	[34]

[a] An average Pd–P distance has no meaning for the Pd(dppm)Cl$_2$ complex because there is a significant difference in the two Pd–P bond lengths: Pd–P$_1$ = 2.234 Å and Pd–P$_2$ = 2.250 Å [31].
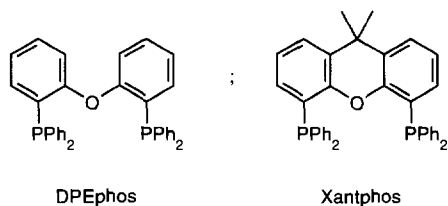
Scheme 4. Diphosphine ligands with a relatively large bite angle [39].

1,2,3-trithia[3]ferrocenophane. The resulting, stable $Pd(Fe(\eta^5\text{-}C_5H_4S)_2(PPh_3)$ complex again contains the dative Fe → Pd bond [38].

To study the steric effects on the selectivity, two diphosphine ligands with very large bite angles (> 100°) were tried in the reductive carbonylation of nitrobenzene under the conditions of catalyst system II (bis(2-diphenylphosphino-phenyl)ether (DPEphos) and 9,9-dimethyl-4,6-bis(diphenylphosphino)xanthene (Xantphos)) [39] (see Scheme 4). X-ray structures of Pd(DPEphos)(TCNE) (TCNE = 1,1,2,2-tetracyanoethylene) and Pd(Xantphos)(TCNE) have been elucidated and P–Pd–P angles of 101.5° and 104.6° respectively were found [40]. Using Xantphos a t.o.f. of $33\,mol(mol\,h)^{-1}$ was measured and a selectivity towards the carbamate of only 28%. The remaining 72% of the product distribution consisted fully of azoxybenzene. With DPEphos, even 100% selectivity towards azoxybenzene was obtained at a t.o.f. of $15\,mol(mol\,h)^{-1}$. The high azoxybenzene production can be explained by the formation of the very stable Pd(0) intermediates obtained with these large diphosphine ligands [23,41]. In contrast to the results obtained with dppf, this is purely a steric effect. The high stability of the Pd(0) intermediates probably also explains the relatively low activities found with these ligands as the reoxidation to Pd(II) becomes more difficult. Under the influence of P/P ligands with such large bite angles this reoxidation might even become the rate-determining step in the catalytic cycle.

2.7. Oxidation of the P / P ligands

Though the bidentate phosphine ligands yield fairly active catalyst systems, their activities remain far behind those of the systems containing bpy or phen [12,20]. This might be caused by the oxidation of the phosphine ligands by the nitro substrate, because in all experiments concerning the P/P ligands only signals of the fully oxidised ligands could be found in the ^{31}P NMR spectra of the reaction mixtures at the end of the catalytic runs. Therefore, a more detailed study was conducted concerning the influence of the oxidation of the P/P ligand on the catalytic activity, using dppp because this ligand gave the best results.

By taking samples from the autoclave, both the catalytic activity and the degree of oxidation of the

ligand were monitored in time. Fig. 1 shows the overall conversion of nitrobenzene and the percentage of oxidised dppp as function of the time. The oxidation of the ligand appeared to occur very rapidly; already after 45 min 90% of the dppp turned out to be fully oxidised, and after 1 h the signal of the unreacted ligand could no longer be observed in the ^{31}P NMR spectra of the samples. Initially the reaction rate increases but the reaction slows down when all dppp has been oxidised. This suggests that excess dppp mainly assists formation of the active catalyst and prevents catalyst decomposition in the initial stage of the reaction. The overall t.o.f. of $76\,mol(mol\,h)^{-1}$ is in good agreement with the value for the dppp ligand in an experiment over 3 h without any samples being taken. A separate experiment has shown that after the first 3 h the reaction slows down even more, yielding a total conversion of the nitro substrate after 25 h that is only slightly more than the conversion obtained after 3 h.

Experiments in the absence of the Pd metal have shown complete oxidation of the ligand but no conversion of nitrobenzene into any of the known products. The large excess of nitrobenzene to dppp (58.4-fold excess) together with the conversion up to 35% also rules out the possibility of a stoichiometric reaction, thus implying that the reductive carbonylation is indeed palladium-catalysed.

Experiments were conducted with a presynthesised $Pd(dppp)(OAc)_2$ complex, keeping the overall dppp:Pd ratio at 10. These experiments gave approximately the same results as the ones starting with $Pd(OAc)_2$ and dppp. An average t.o.f. of $72\,mol(mol\,h)^{-1}$ was found with a selectivity towards carbamate of 73%. Again, only oxidised dppp could be observed in the ^{31}P NMR spectra at the end of the catalytic runs. Because the catalytic activity was not significantly enhanced by the use of the presynthesised complex, it seems reasonable to assume that the original coordination of the dppp ligand, which is present in large excess, to the palladium metal centre is not hampered by the oxidation of the ligand by the substrate.
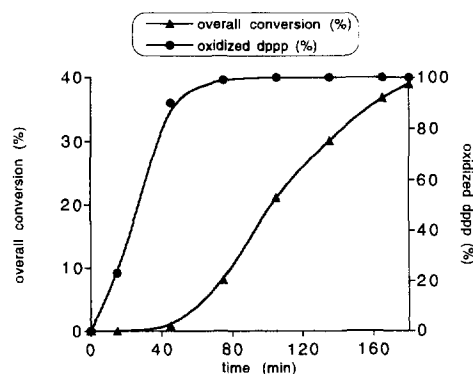

Fig. 1. Conversion of nitrobenzene and oxidation of the total amount of dppp as a function of time.

The results of experiments with Pd(dppp)(OAc)$_2$ + 9 equiv. of dppp, Pd(dppp)(OAc)$_2$ + 9 equiv. of preoxidised dppp and Pd(dppp)(OAc)$_2$ without free (preoxidised) ligand are compared in Table 1. It becomes clear that the addition of free dppp has a strongly positive influence on the catalytic activity, despite the rapid oxidation of the ligand (Fig. 1). This influence cannot be mimicked by the addition of preoxidised dppp as free ligand. By replacing the 9 equiv. of free dppp by 9 equiv. of preoxidised dppp the t.o.f was reduced by a factor of ca. 2.5. In the presence of the preoxidised dppp the same activity was obtained as in the absence of any additional ligand. The selectivity towards the carbamate was clearly not influenced by the preoxidised dppp ligand either, while a significant effect could be measured upon addition of the normal dppp. Apparently, the oxidised form of the dppp ligand no longer exerts any influence on the catalytic behaviour of the palladium metal centre. This was confirmed by an experiment with Pd(OAc)$_2$, TMBA, and preoxidised dppp in which no conversion at all was obtained.

As a Pd–dppp complex probably acts as catalytically active species, there is presumably more of this active compound formed upon addition of free dppp to the

reduced by the oxidation of the phosphorus donor atom by the nitro substrate, a feature that was shown to influence strongly the catalytic activity of bidentate phosphine ligands as well.

Flexible diphosphine ligands turned out to give rise to more efficient catalyst systems for the reductive carbonylation of nitrobenzene than their more rigid counterparts. The highest activity was found for with 1,3-bis(diphenylphosphino)propane (dppp).

4. Experimental section

4.1. Materials and analyses

PdCl$_2$ and Pd(acetate)$_2$ were purchased from Degussa and used as-received. 1,4-Bis(diphenylphosphino)butane (dppb) was obtained from Strem Chemicals. All other chemicals were purchased from Aldrich or Acros.

The solvents were purified prior to use. Acetone was distilled from anhydrous K$_2$CO$_3$, methanol from CaH$_2$ (5 g l^{-1}), diethyl ether, THF, benzene, and toluene from sodium–benzophenone. Aniline, 2,4-dimethylaniline,

70–230 mesh ASTM, purchased from Merck) as the stationary phase.

Infrared (IR) spectra were recorded on a Nicolet 510m FT-IR spectrophotometer. NMR spectra were obtained on a Bruker AMX 300 instrument. Chemical shifts are given in parts per million relative to TMS (^{1}H NMR) and H_3PO_4 (^{31}P-{^{1}H} NMR). Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

The reductive carbonylation of nitrobenzene was performed in a stainless steel (SS 316) 180 ml autoclave, equipped with a glass liner, a gas inlet, a sample probe, a thermocouple, a cooling coil working on air, and a magnetic stirrer. CO 3.0 was obtained from Praxair and used as-purchased. The results were analysed by HPLC on a Gilson HPLC apparatus, using a Dynamax C18 column (eluent gradient: 45% water in methanol to 100% methanol in 20 min).

4.2. Synthesis

4.2.1. N-(2'-Diphenylphosphinobenzylidene)-arylamine (P/N-1–3)

The P/N ligands with Ar = phenyl (P/N-1), 4-chlorophenyl (P/N-2), and 2,4-dimethoxyphenyl (P/N-3) were prepared in the same way. A solution of 0.61–0.65 g of 2-diphenylphosphinobenzaldehyde (2.1–2.4 mmol) and an equimolar amount of the amine in 20 ml of toluene containing molecular sieves was refluxed for 16 h. After cooling to room temperature the molecular sieves were filtered off and the solvent was evaporated. The resulting oil was azeotropically distilled with 2 × 1 ml of diethyl ether, yielding the desired solid product.

4.2.1.1. Ar = phenyl (P/N-1). Yield: 0.79 g of pink powder (2.16 mmol, 97%). IR (toluene): 1618 (m) (= = N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.08 (d, 1H, H–C=N), 8.14 (dd, 1H, H$_{3'}$), 7.47 (m, 14H, H$_{6'}$ + H$_2$ + H$_4$ + H$_6$ + P(C$_6$H$_5$)$_2$), 7.17 (dd, 1H, H$_{4'}$), 6.94 (d, 2H, H$_3$ + H$_5$) ppm. ^{31}P NMR (CDCl$_3$): δ − 12.8 (s) ppm. M.p. 106–108 °C.

4.2.1.2. Ar = 4-chlorophenyl (P/N-2). Yield: 0.79 g of yellow powder (1.95 mmol, 97%). IR (toluene): 1618 (m) (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.08 (d, 1H, H–C=N), 8.14 (dd, 1H, H$_{3'}$), 7,47 (t, 1H, H$_{5'}$) 7.36 (m, $\overline{13}$H, H$_{6'}$ + H$_2$ + H$_4$ + P(C$_6$H$_5$)$_2$), 6.95 (dd, 1H, H$_{4'}$), 6.83 (d, 2H, H$_3$ + H$_5$) ppm. ^{31}P NMR (CDCl$_3$): δ − 12.5 (s) ppm. M.p. 100–102 °C.

4.2.1.3. Ar = 2,4-dimethoxyphenyl (P/N-3). Yield: 0.81 g of yellow powder (1.91 mmol, 91%). IR (toluene): 1609 (m) (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.23 (d, 1H, H–C=N), 8.31 (dd, 1H, H$_{3'}$), 7.44 (t, 1H, H$_{5'}$), 7,32 (m, 11H, H$_{6'}$ + P(C$_6$H$_5$)$_2$), 6.91 (dd, 1H, H$_{4'}$),

6.66 (d, 1H, H$_6$), 6.48 (d, 1H, H$_3$), 6.39 (d, 1H, H$_5$), 3.80 (s, 3H, OCH$_3$), 3.78 (s, 3H, OCH$_3$) ppm. ^{31}P NMR (CDCl$_3$): δ − 13.7 (s) ppm. M.p. 106–107 °C.

4.2.2. N-(2'-Diphenylphosphinobenzylidene)-2,4-dimethylaniline (P/N-4)

N-(2'-Diphenylphosphinobenzylidene)-2,4-dimethylaniline (P/N-4) was prepared analogously to N-(2'-diphenylphosphinobenzylidene)aniline (P/N-1). A solution of 0.82 g of 2-diphenylphosphinobenzaldehyde (2.83 mmol) and 0.34 g of 2,4-dimethylaniline (2.83 mmol) in 15 ml of THF containing molecular sieves was refluxed for 24 h. The reaction mixture was worked up similarly to the reaction mixture of P/N-1. Yield: 0.67 g of yellow powder (1.7 mmol, 61%). IR (toluene): 1624 (m) (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 9.00 (d, 1H, H–C=N), 8.26 (dd, 1H, H$_{3'}$), 7.47 (t, 1H, H$_{5'}$), 7,37 (m, 11H, H$_{6'}$ + P(C$_6$H$_5$)$_2$), 6.99 (s, 1H, H$_3$), 6.94 (dd, 1H, H$_{4'}$), 6.91 (d, 1H, H$_6$), 6.39 (d, 1H, H$_5$), 2.31 (s, 3H, CH$_3$), 2.22 (s, 3H, CH$_3$) ppm. ^{31}P NMR (CDCl$_3$): δ − 13.0 (s) ppm. M.p. 105–107 °C.

4.2.3. N-(2'-Diphenylphosphinobenzylidene)-tert-butylamine (P/N-5)

A solution of 0.99 g of 2-diphenylphosphinobenzaldehyde (3.41 mmol) in 10 ml of tert-butylamine (95 mmol) was refluxed for 2 h. The excess of tert-butylamine was distilled off, yielding a sticky product. Azeotropic distillation with 3 × 2 ml of toluene gave the desired solid compound. Yield: 1.09 g of white powder (3.0 mmol, 93%). IR (toluene): 1631 (m) (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.78 (d, 1H, H–C=N), 7.92 (dd, 1H, H$_{3'}$), 7.34 (t, 1H, H$_{5'}$), 7,32 (m, 11H, H$_{6'}$ + P(C$_6$H$_5$)$_2$), 6.94 (dd, 1H, H$_{4'}$), 1.05 (s, 9H, tert-butyl) ppm. ^{31}P NMR (CDCl$_3$): δ − 11.7 (s) ppm. M.p. 118–120 °C.

4.2.4. 8-(Diphenylphosphino)quinoline (P/N-7)

A solution of 1.19 g of 8-bromoquinoline (5.3 mmol) in 40 ml of THF was added dropwise to a solution of 2.12 ml of 2.5 M n-BuLi in hexanes (5.3 mmol) in 25 ml of THF at − 78 °C. After 20 min of stirring, 0.95 ml of chlorodiphenylphosphine (5.3 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature. This was stirred for 2 h after which it was concentrated to ca. 3 ml. Diethyl ether (60 ml) was added to the slurry and the brown precipitate was filtered off. The precipitate was washed with 2 × 10 ml of water, azeotropically distilled with 3 × 3 ml of toluene, and dried under vacuum. The crude product was purified by means of column chromatography on silica gel using dichloromethane as eluent. Yield: 1.04 g of white powder (3.3 mmol, 63%). ^{1}H NMR (DMSO-d_6): δ 8.85 (dd, 1H, H$_2$), 8.45 (d, 1H, H$_4$), 8.05 (d, 1H, H$_5$), 7.58 (m, 2H, H$_3$ + H$_6$), 7.29 (m, 10H, P(C$_6$H$_5$)$_2$), 7.00 (dd, 1H, H$_7$) ppm. ^{31}P NMR (DMSO-d_6): δ − 11.4 (s) ppm. M.p. 192–194 °C.

4.2.5. Pd(bidentate ligand)₂(BF₄)₂ complexes

These types of complex were prepared for bis(p-anisylimino)acenaphthene (**pAn-BIAN**), N-(2'-diphenylphosphinobenzylidene)-tert-butylamine (**P/N-5**), 2-(2'-(diphenylphosphino)ethyl)pyridine (**P/N-6**), and 8-(diphenylphosphino)quinoline (**P/N-7**) using one general procedure. A solution of 89 mg of $Pd(CH_3CN)_4(BF_4)_2$ (0.2 mmol) in 20 ml of acetone was added dropwise to a solution of 0.4 mmol of bidentate ligand in 30 ml of acetone. The solution was stirred at room temperature for 3 h after which it was concentrated to ca. 3 ml. Diethyl ether (40 ml) was added in order to obtain complete precipitation of the complex. The solvents were decanted and the precipitate was washed with 3 × 5 ml of diethyl ether and dried under vacuum.

4.2.5.1. Ligand = pAn-BIAN.
Yield: 162 mg of red powder (0.15 mmol, 74%). ^{1}H NMR (DMSO-d_6): δ 8.35 (d, 2H, H₅), 7.66 (t, 2H, H₄), 6.95 (m, 8H, $C_6\underline{H}_4(OCH_3)$), 6.19 (dd, 2H, H₃), 3.88 (s, 6H, O$C\underline{H}_3$) ppm.

4.2.5.2. Ligand = P/N-5.
Yield: 126 mg of white powder (0.13 mmol, 65%). ^{1}H NMR (DMSO-d_6): δ 8.98 (d, 1H, H–C=N), 8.18 (d, 1H, H₃'), 8.08 (t, 1H, H₅'), 7.79 (d, $\overline{1H}$, H₆'), 7.56 (m, 10H, P($C_6\underline{H}_5$)₂), 7.36 (t, 1H, H₄'), 1.17 (s, 9H, tert-butyl) ppm. ^{31}P NMR (DMSO-d_6): δ 40.9 (s) ppm.

4.2.5.3. Ligand = P/N-6.
Yield: 124 mg of white powder (0.14 mmol, 72%). ^{1}H NMR (DMSO-d_6): δ 8.49 (d, 1H, H₆), 8.06 (t, 1H, H₄), 7.82 (d, 1H, H₃), 7.43 (m, 11H, P($C_6\underline{H}_5$)₂), 4.14 (m, 2H, H₂'), 2.99 (m, 2H, H₁') ppm. ^{31}P N$\overline{M}$R (DMSO-d_6): δ 38.4 (s) ppm.

4.2.5.4. Ligand = P/N-7.
Yield: 170 mg of white powder (0.19 mmol, 94%). ^{1}H NMR (DMSO-d_6): δ 9.12 (m, 1H, H₃), 9.04 (d, 1H, H₄), 8.53 (d, 1H, H₅), 8.30 (dd, 1H, H₂), 8.16 (d, 1H, H₇), 7.97 (t, 1H, H₆), 7.54 (m, 10H, P($C_6\underline{H}_5$)₂) ppm. ^{31}P NMR (DMSO-d_6): δ 50.2 (s) ppm.

4.2.6. Pd(dppp)(OAc)₂

A solution of 247 mg of dppp (0.60 mmol) in 40 ml of benzene was added dropwise to a solution of 89.8 mg of Pd(OAc)₂ (0.40 mmol) in 40 ml of benzene. The reaction mixture was stirred at room temperature for 1 h after which 50 ml of petroleum ether 60–80 was added. The resulting precipitate was filtered off, washed with 3 × 2 ml of petroleum ether 60–80, azeotropically distilled with 3 × 2 ml of toluene, and dried under vacuum. Yield: 214 mg of white powder (0.34 mmol, 84%). IR (KBr): 1583 (vs) (OAc), 1436 (vs) (OAc), 1384 (vs) (OAc), 1325 (s) (OAc). ^{1}H NMR (DMSO-d_6): δ 7.74 (dd, 8H, H$_m$ of P(C_6H_5)₂), 7.46 (t, 4H, H$_p$ of

P(C_6H_5)₂), 7.39 (d, 8H, H$_0$ of P(C_6H_5)₂), 2.72 (t, 4H, H₁ + H₃), 1.83 (q, 2H, H₂) ppm. ^{31}P NMR (DMSO-d_6): δ 12.3 (s) ppm.

4.3. Catalysis

4.3.1. Pd(bidentate ligand)₂(BF₄)₂–bidentate ligand

In a standard experiment using a presynthesised Pd(bidentate ligand)₂(BF₄)₂ complex the autoclave was charged with 1.5 ml of nitrobenzene and 20 ml of methanol. Pd(bidentate ligand)₂(BF₄)₂ (0.04 mmol) and 0.12 mmol of the free ligand (overall ligand:Pd = 5) were dissolved in this mixture. The autoclave was pressurised with 60 bar of CO and heated to 135 °C within 15 min. The initial working pressure at 135 °C was approximately 80 bar. After 2 h the autoclave was rapidly cooled and the pressure was released.

4.3.2. Pd(CH₃CN)₄(BF₄)₂–bidentate ligand

Experiments with the in situ generated Pd(bidentate ligand)₂(BF₄)₂ complexes were carried out as described for the presynthesised complexes, with 17.8 mg of Pd(CH₃CN)₄(BF₄)₂ (0.04 mmol) and 0.20 mmol of the bidentate ligand (overall ligand:Pd = 5).

4.3.3. Pd(OAc)₂–bidentate ligand–2,4,6-trimethylbenzoic acid

Experiments with the in situ prepared catalyst systems from Pd(OAc)₂, a ligand, and TMBA were performed as described for the presynthesised complexes with the following modifications. Nitrobenzene (3.0 ml, 29.2 mmol) was used as substrate in the reaction under influence of 11.2 mg of Pd(OAc)₂ (0.05 mmol), 0.5 mmol of the bidentate ligand (overall ligand:Pd = 10), and 205 mg of TMBA (1.25 mmol, acid:Pd = 25). The reaction time was prolonged to 3 h.

Acknowledgements

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