Mono- and Bidentate Phosphine Ligands in the Palladium-Catalyzed Methyl Acrylate Dimerization

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Abstract: The influence of several phosphine ligands on the activity, selectivity and stability of the catalytic system $Pd(acac)_2$, ligand, $[HOEt_2][BF_4]$ was studied in the dimerization of methyl acrylate (MA). It was found that the catalyst's activity increased with increasing the basicity of the monodentate ligands used, whereas bulky phosphines lowered the linearity of the dimers and the reaction rates. With chelating PN-, PP-, and PAs-ligands the Pd-catalyst could be efficiently stabilized during the reaction. The use of 1-dibutylphosphino-2-dimethylaminoethane as ammonium tetrafluoroborate salt allowed the highest overall activity.

Keywords: dimerization; ligand; methyl acrylate; palladium; phosphine

Introduction

The dimerization of functionalized olefins is of general technical importance. For example, the palladium-catalyzed dimerization of methyl acrylate (MA) to dimethyl Δ^2-dihydromuconate (2-DHM) leads to a highly interesting intermediate which can be transformed to both fine chemicals (such as cyclopentenones) and adipic acid (Figure 1).[1] The latter reaction is of interest since it allows the synthesis of adipic acid from propene rather than from benzene.

Catalytic systems for the dimerization of methyl acrylate with Rh,[2] Ru,[3] and Ni[4] compounds have been studied and reviewed.[5] Apart from these investigations, academic research has, for more than 30 years, dealt with the Pd-catalyzed dimerization of MA. Barlow et al. described in 1970 the use of $(PhCN)_2PdCl_2$ as catalyst for this reaction.[6] They obtained the dimerization products Δ^2- und Δ^3-DHM in a ratio of 3:1, but observed rapid reductive decomposition of the Pd-catalyst. Pracejus and Oehme stabilized similar catalytic systems by addition of the reoxidizing agent benzoquinone.[7] In this manner, they converted up to 100 mol MA per mol Pd, however with low reaction rate. The reaction rate could be enhanced by the use of weakly coordinating anions (e.g., $[BF_4]^-$ instead of chloride), but this lowered catalyst stability.[8] A clear improvement concerning catalyst activity and stability was published by one of us, namely the use of dicationic Pd-complexes with tributylphosphine as the ligand.[9] Under optimized reaction conditions (temperature, ratio of ligand to catalyst) this catalytic system converted without additional solvent MA to Δ^2-DHMs in up to 96% selectivity. Again, catalyst reduction to Pd(0) was still the main problem since this afforded a complicated regeneration of the Pd after the catalytic reaction.

In the present paper we discuss the results of our systematic study on the influence of several mono- and bidentate phosphine ligands on the activity, selectivity and stability of the catalytic system $Pd(acac)_2$, ligand, $[HOEt_2][BF_4]$ in the dimerization of methyl acrylate (MA). This specific catalyst system appeared to us particularly attractive since it has been demonstrated by one of us previously[9] that the reaction leads to very high selectivity for the desired linear dimerization products.

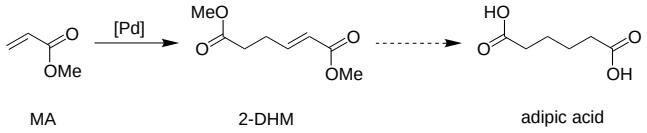

Figure 1. Dimerization of methyl acrylate (MA) to dimethyl Δ^2-dihydromuconate (2-DHM).

Results and Discussion

Ligand Synthesis

(1-Dibutylphosphinoeth-2-yl)- **1** and (1-diphenylphosphinoeth-2-yl)trimethylammonium tetrafluoroborate **2**

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are synthesized by selective methylation reaction of the corresponding aminophosphine compounds by using Meerwein's reagent $[Me_3O][BF_4]$ in a kinetically controlled reaction at $-100\,^{\circ}C$. The product was purified from traces of phosphonium salts by recrystallization. 1-Dibutylphosphino-2-dimethylaminoethane **3** and 1-dibutylphosphino-2-propylaminoethane **4** were prepared in good yields and high purity by reaction of the corresponding 1-amino-2-chloroethane with alkali metal phosphides.

Synthesis of the Cationic Allylpalladium Complexes

The complexes (η^3-allyl)[1-diphenylphosphino-2-dimethylaminoethane-κ^2-P,N]palladium(II) tetrafluoroborate **5** and (η^3-allyl)[bis(diphenylphosphino)ethane-κ^2-P,P]palladium(II) tetrafluoroborate **6** have been synthesized at ambient temperature in good yields and high purity starting from 1 equiv. bisallylpalladium chloride, 2 equiv. bidentate ligand and 2 equiv. silver tetrafluoroborate. ^{31}P and ^{1}H NMR spectra of the free and the bond ligands reveal a two coordinated bonding mode. Consistently, the molecular mass of the cations are obtained by mass spectrometry.

Catalyst Pre-formation

The *in situ* catalyst system, $Pd(acac)_2$, phosphine ligand, $[HOEt_2][BF_4]$, used for the dimerization reactions reported here was found to be extremely sensitive to the protocol of catalyst pre-formation. This has mainly two reasons:

The phosphine ligand alone is, even in absence of the Pd-catalyst, able to dimerize MA to the undesired, branched dimerization product dimethyl 2-methylenglutarate.[10] To prevent this reaction, the phosphine compound is used as a latent ligand system in form of its phosphonium salt, e.g., tributylphosphonium tetrafluoroborate.

The phosphonium salts themselves can also react with the substrate in a Michael-type addition reaction leading to a complete consumption of the ligand during the catalytic reaction. However, this reaction can be suppressed in acidic media.

Both possible side-reactions are displayed in Figure 2.

As a result of our investigations to find the best and most reproducible catalyst pre-formation protocol we first protonated the phosphine ligand with an excess of tetrafluoroboric acid, followed by addition of substrate and the solvent (if applied). Finally, the catalyst solution was added. Applying this protocol, the phosphonium salt is formed *in situ* and the Michael-addition reaction is suppressed due to the acidic media. This catalyst pre-formation has been applied in all dimerization reactions with *in situ* systems reported in this publication.

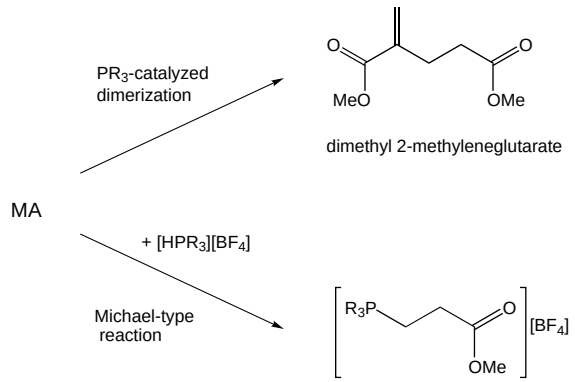


Figure 2. Possible side reactions of ligand/ligand precursor with the substrate during the pre-formation of the catalytic system

MA Dimerization with Monodentate Phosphine Ligands

MA was dimerized by activating $Pd(acac)_2$ with $[HOEt_2][BF_4]$ complex and using monodentate phosphine ligands in neat substrate without additional solvent. The activities of the different catalytic systems are displayed in Table 1 by two values: the turnover frequency (TOF) indicates the molar amount of MA converted per molar amount of Pd in the first hour of the reaction. The turnover numbers (TON) given in Table 1 represent the overall molar amount of MA converted per molar amount of Pd catalyst within the first 24 h reaction time. The selectivity of the reaction is given by the linearity of the dimers, which represents the ratio of linear dimers (Δ^2- and Δ^3-DHM) to all MA dimers. For a better correlation of the catalytic results with the ligand properties, literature values for electronic coefficients[11] and cone angles[12] of the ligands used are also given in Table 1.

Entry a in Table 1 reveals that secondary phosphines do not support the Pd-catalyzed MA dimerization, which may be due to the formation of stable, catalytically inactive palladium phosphides. For tri-*n*-alkylphosphines (entries b – e), the activity of the catalyst system increases with higher donor abilities of the ligand. The catalytic results observed in our experiments can be explained assuming both a Pd-hydride or an oxidative coupling mechanism (Figure 3). For the palladium hydride mechanism the insertion of the MA ligand into the palladium-carbon bond of the (methylcarboxylatoprop-3-yl)palladium(II) complex is proposed as the rate-determining step and should be accelerated by an electron-rich palladium center.[13] In the same manner, the oxidative coupling of two MA ligands bound to a bisphosphinopalladium(II) center should be activated by a lower redox potential of the complex caused by more basic phosphine ligands.[14]

Moreover, this result may reflect the fact that, in acidic reaction medium, the availability of the phosphine

Table 1. Pd-catalyzed MA dimerization without solvent using monodentate phosphine ligands.

	Ligand	TOF[a] [mol/(mol h)]	TON[b] [mol/mol]	Linearity[c] [%]	$^{FT}\chi$[d] [cm^{-1}]	Angle[e] [°]
a	$HPBu_2$	7	8	–	–	–
b	PMe_3	18	71	–	8.55	118
c	PEt_3	29	95	95.4	6.30	132
d	$P(n\text{-}Pr)_3$	46	174	95.0	5.40	132
e	$P(n\text{-}Bu)_3$	58	229	93.7	5.25	132
f	$P(i\text{-}Pr)_3$	38	101	88.7	3.45	160
g	PCy_3	<5	26	84.3	1.40	170
h	$P(t\text{-}Bu)_3$	0	4	–	0	182
i	PPh_3	14	49	89.7	13.25	145
j	$MePPh_2$	17	81	90.5	12.10	136
k[f]	**1**	–	269	95.2	–	–
l[f]	**2**	–	201	94.8	–	–

[a] TOF for first hour.
[b] Overall ton for first 24 h of reaction.
[c] Linearity of dimers.
[d] Electronic coefficient.
[e] Cone angle.
[f] **1** = (1-dibutylphosphinoeth-2-yl)trimethylammonium tetrafluoroborate; **2** = (1-diphenylphosphinoeth-2-yl)trimethylammonium tetrafluoroborate.
General reaction conditions: 50 mmol MA, 0.02 mmol $Pd(acac)_2$, 0.32 mmol $[Et_2OH][BF_4]$, 0.2 mmol ligand, 80 °C, 24 h.

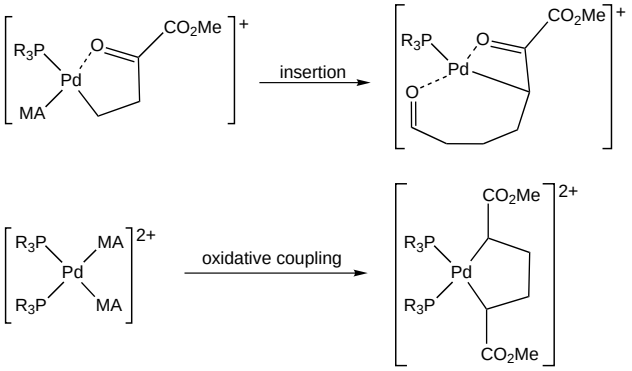


Figure 3. Proposed rate determining step for the Pd-hydride and the oxidative coupling mechanism.

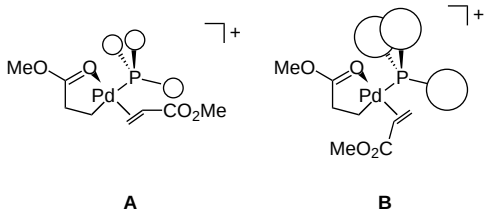


Figure 4. Effect of bulky phosphines on the MA insertion at the catalytic center.

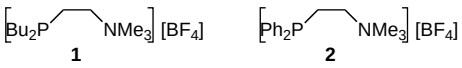
ligand for the catalyst is reduced with increasing basicity of the ligand. However, along the same line a decrease in linearity in the MA dimers is observed. The catalytic mixture is rather stable over 24 hours in all four systems, but some black palladium is observed towards the end of this period.

The use of branched, bulky phosphines leads to much lower activity and a significant drop in product linearity. Both can be understood by unfavorable steric interaction between the bulky ligand and the ester group of the substrate during the insertion step of the second MA molecule. This is illustrated in Figure 4 based on a palladium hydride mechanism. While linear products would be obtained predominantly from conformation A, the application of a bulky phosphine ligand favors conformation B leading to a higher amount of branched MA dimers. Mechanistic considerations about the ligand influence on the product linearity based on the oxidative addition mechanism lead to identical results.

The activity and the selectivity of catalytic systems with arylphosphine ligands (entries i and j) is low compared to the *n*-alkyl analogues due to steric hindrance and lower basicity of the ligands. Moreover, the reactions with arylphosphine ligands lead to almost complete decomposition of the catalyst to metallic palladium and to polymeric by-products which are presumably formed by a radical mechanism. The side reaction could be effectively suppressed by addition of inhibitors like hydroquinone. A similar radical MA polymerization initiated by decomposition of palladium complexes has been previously reported by Tian et al.[15]

Surprisingly, the use of the ammonium phosphine ligand **1** (entry k, Table 1), which has similar electronic and steric properties compared to tributylphosphine, leads to the highest activity and linearity of all catalytic systems mentioned in Table 1. The same positive influence on catalytic results is observed for the ammonium phosphine ligand **2** (entry l, Table 1) com-

pared to diphenylmethylphosphine. One explanation for this could be an intramolecular interaction between the ammonium group of the ligands and the carboxylate group of the coordinated substrate by hydrogen bond favoring the conformation A in Figure 4.



In general, the Pd-catalyzed MA dimerization with monodentate phosphine ligands suffers from decomposition problems of the catalyst to metallic palladium, which limits its practical value. The stability follows the order $PBu_3 > PMe_3 > PPh_3$ which is consistent with the ligand strength and therefore with ligand basicity. Increased amount of ligand stabilizes but deactivates the catalyst. To overcome this problem we investigated the application of chelating, bidentate ligands in a further set of experiments.

Methyl Acrylate Dimerization with Phosphine-Based Bidentate Ligands

The influence of several bidentate, chelating ligands on the activity of the Pd-catalyzed dimerization reaction of MA in the system $Pd(acac)_2$, ligand, $[HOEt_2][BF_4]$ is presented in Table 2. With the bidentate ligands, the reaction was carried out in a 1:1 mixture of MA and nitromethane to prevent precipitation of the ligands from the acidic reaction medium.

The best activity was achieved with the ligand 1-dibutylphosphino-2-dimethylaminoethane **3**. The diphenylphosphino analogue leads to lower activity, which is consistent with the results obtained by using tri-*n*-alkyl- and triarylphosphine ligands. Lowering the basicity of the amino group also deactivates the catalytic system (entry c). PP-, PAs-, PO-, and PS-ligands lead only to poor catalytic results. The formation of metallic palladium is not observed in any catalytic system displayed in Table 2, which may result from an efficient stabilization by the chelating ligands or from reoxidation of Pd(0) intermediates by the solvent nitromethane.

Table 2. Phosphine-based chelating ligands.

No.	Ligand	TOF[a] [mol/(mol h)]
a	$Bu_2PCH_2CH_2NMe_2$	161
b	$Ph_2PCH_2CH_2NMe_2$	69
c	$Bu_2PCH_2CH_2N(H)Pr$	14
d	$Bu_2PCH_2CH_2PBu_2$	0
e	$Ph_2PCH_2CH_2PPh_2$	4
f	$Ph_2P(CH_2)_4PPh_2$	2
g	$Ph_2PCH_2CH_2AsPh_2$	4
h	$Ph_2PCH_2CH_2P(O)Ph_2$	0
i	$Ph_2P(CH_2)_4P(O)Ph_2$	6
j	$Ph_2PCH_2CH_2P(S)Ph_2$	2

[a] TOF for first hour.
General reaction conditions: 50 mmol MA, 0.02 mmol $Pd(acac)_2$, 0.2 mmol ligand, 0.52 mmol $[Et_2OH][BF_4]$, 50 mass % CH_3NO_2, 80 °C, 1 h; linearity of MA dimers > 95% in all experiments.

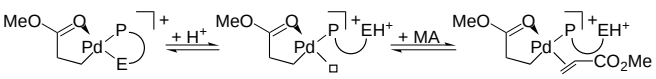


Figure 5. Two step substitution of the labile part of a chelating ligand by the substrate in the acidic medium.

The catalytic results can be understood by Figure 5, which shows a substitution reaction of one part of a bidentate ligand by the substrate on a possible catalyst intermediate in acidic media following the palladium hydride mechanism. The first step is the protonation of the most basic part of the ligand. In the second step the substrate occupies the vacant coordination site, which leads to a catalytically active species.

According to Figure 5, the observed decrease in activity by lowering the basicity of the amine group of PN-ligands can be explained by a lower amount of catalytically active ammonium-palladium compound in the equilibrium (entries a and c, Table 2). The poor activity achieved by chelating ligands mentioned in Table 2 other than PN-compounds are due to non-hemilabile properties under reaction conditions.

Support for the mechanism displayed in Figure 5 stems from the fact that the catalytic activity of the catalysts **5** and **6** in the dimerization reaction of MA shows a very different dependency on the amount of acid added to the reaction (Table 3). The activity of complex **5** with the PN-ligand strongly depends on the acidity of the media (entries a and b). In contrast, complex **6** with the PP-ligand is not activated by adding higher amounts of acid and only leads to poor catalytic results (entries c to f). The reason for this is the strong coordination of the diphosphine ligand and therefore its poor affinity to the proton.

During the course of this work, we found that the use of the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]) as a non-coordinating solvent has a significant rate-enhancing effect on the dimerization reaction. Moreover, the ionic liquid prevents the PN-compound from precipitation in acidic media. In contrast to the use of nitromethane as solvent, the ionic liquid has no potential to oxidize Pd(0) species or the ligand. These effects have been described elsewhere in detail.[16] Moreover, attempts to optimize the general protocol for the MA dimerization reaction revealed that rapid catalyst deactivation over the first 12 h can be avoided by adding $H[BF_4]$ in small portions over the reaction time.

Further experiments in this study aimed to prove the bidentate binding mode of PN-ligands in the catalyst intermediates. Therefore, comparative experiments

Table 3. Variation of the amount of acid.

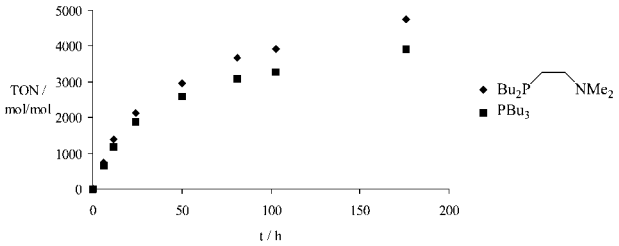
No.	Ligand	Catalyst	$[Et_2OH][BF_4]$[a] [equiv.]	TOF[b] [mol/(mol h)]	TON[c] [mol/mol]
a	$Ph_2PCH_2CH_2NMe_2$	**5**	1	35	100
b			2	155	461
c	$Ph_2PCH_2CH_2PPh_2$	**6**	1	13	19
d			2	13	18
e			4	13	20
f			8	13	22

[a] Equivalents of acid related to catalyst.
[b] TOF for first hour.
[c] Overall TON for first 24 h of reaction.
General reaction conditions: 50 mmol MA, 0,05 mmol catalyst, 80 °C, 24 h; linearity of MA dimers >95% in all experiments.

with the bidentate ligand 1-diphenylphosphino-2-dimethylaminoethane and the monodentate ligand (1-diphenylphosphinoeth-2-yl)trimethylammonium tetrafluoroborate **2** have been carried out (Table 4). All experiments displayed in Table 4 have been performed using the ionic liquid $[BMIM][BF_4]$ as solvent.

All systems show nearly the same activity in the first 24 hours, which origins from the similar electronic and steric properties of the two ligands. After 81 hours the highest TON is achieved with the bidentate PN-ligand due to stabilization of the catalyst (entry a). In the latter case the formation of metallic palladium is not observed. In contrast, a significant decomposition of the catalyst was found when the monodentate ligand was used even if tributylamine was added as a second equivalent of amine (entries b and c). These results support a stabilization of the catalyst by the bidentate ligand due to its chelating effect.

A comparison of the catalytic systems with the bidentate ligand 1-dibutylphosphino-2-dimethylaminoethane **3** and the monodentate ligand tributylphosphine over a longer reaction time is presented in Figure 6. As for the experiments displayed in Table 4, the optimized reaction conditions (including $[BMIM][BF_4]$ as solvent and addition of small portions of $H[BF_4]$ over the reaction time) were applied.



General reaction conditions: 100 mmol MA, 0.02 mmol $Pd(acac)_2$, 0.2 mmol ligand, 50 mass % $[BMIM][BF_4]$, $[Et_2OH][BF_4]$: 0.32 mmol (PBu_3) and 0.52 mmol (**2**); 80 °C; additions: 0.14 mmol $[Et_2OH][BF_4]$ after 6, 12, 24, 81 and 103 h; 50 mmol MA after 103 h.

Figure 6. Catalytic activity of the systems with tributylphosphine and 1-dibutylphosphino-2-dimethylaminoethane **3** over time.

Table 4. Comparison of catalytic systems with aminophosphine and phosphorus-ammonium ligands.

No.	Ligand system	TON [mol/mol]	
		24 h	81 h
a	$Ph_2PCH_2CH_2NMe_2$	201	324
b	$[Ph_2PCH_2CH_2NMe_3][BF_4]$	203	252
c	$[Ph_2PCH_2CH_2NMe_3][BF_4]/NBu_3$	207	210

General reaction conditions: 100 mmol MA, 0.02 mmol $Pd(acac)_2$, 0.2 mmol ligand, 50 mass % $[BMIM][BF_4]$, $[Et_2OH][BF_4]$: 0.52 mmol (PN-ligand), 0.32 mmol (**2**) and 0.52 mmol (**2**/NBu_3); 80 °C; additions: 0.14 mmol $[Et_2OH][BF_4]$ after 6, 12 and 24 h; linearity of MA dimers >95% in all experiments.

In the first 50 hours the activity of the catalytic system with the bidentate PN-ligand is constantly about 10% higher. After that time, the decomposition of the catalyst starts in the case of tributylphosphine, which leads to a significant drop in activity. In contrast, the catalyst is very well stabilized by the PN-ligand. In this case, no formation of metallic palladium over the whole reaction time is observed. With the PN-ligand a TON of 4768 over 176 hours is achieved, which is about 22% more than the overall activity obtained with the monodentate ligand (TON = 3910).

In both cases the rate of dimerization decreases over the reaction time. The addition of further 50 mmol of the substrate after 103 hours activates the catalyst again. This procedure lead to a reaction mixture that mimics the situation after 24 hours (about 40 to 50% conversion). Nevertheless, the catalytic activity for the last 73 hours is significantly lower compared to the average rate between 24 and 103 hours reaction time. That might be due to inhibition of the catalyst by the product, which occurs if the product is a comparably good ligand as the substrate. The dimers can coordinate to palladium(II)

compounds with their alkene and carboxylate groups in a bidentate manner, whereas the methyl acrylate ligand is less attractive. This assumption is supported by the observation that an addition of 1000 equiv. of dimethyl adipate (a model substance for the product) at the beginning of the dimerization significantly lowers the rate of reaction. After 8 hours reaction time a TON = 23 is obtained at 70 °C compared to a TON = 69 for the reaction in neat substrate. The same effect of strongly reduced catalytic activity was observed by adding 1000 equivalents of the isolated product from previous catalytic runs at the start of the experiment. However, in this case an exact quantification of the remaining, very low catalytic activity proved to be difficult.

Using the PN-ligand the amount of linear dimers among the dimer fraction is 98.0% compared to 97.6% for tributylphosphine. In both systems the linearities are constant over the reaction time, but the dimer distribution changes to less *trans*-2-DHM and more other linear dimers revealing a kinetically favored formation of *trans*-2-DHM and a slide isomerization activity of the catalytic systems. The increase in linearity by using the PN-ligand compared to tributylphosphine could be due to intramolecular interaction between the ammonium group, *in situ* built in acidic media by protonation of the amine, and the carboxylate group of the coordinated substrate rather than to the chelating properties of the ligand. The support for this proposal stems from the observed increase in linearity by using the ammonium phosphine ligands **1** and **2**, which is shown in Table 1.

Conclusion

In our systematic study on the effect of different mono- and bidentate phosphine ligands on the reactivity, stability and selectivity of the catalyst system $Pd(acac)_2$, $[Et_2OH][BF_4]$ in the dimerization of MA, we revealed that the reaction rate is enhanced with increasing basicity of the applied phosphine ligand, whereas bulky phosphines lowered the linearity of the dimers and the reaction rates. In contrast to monodentate phosphines, the catalyst is efficiently stabilized by chelating PN-, PP-, PAs-, and PO-ligands, but only the use of hemilabile ligands allows high reaction rates. In this respect, the PN-ligand 1-dibutylphosphino-2-dimethylaminoethane was found to be a particularly promising ligand by combining good complex stabilization with high catalyst activity.

Experimental Section

General Remarks

All syntheses and catalysis runs were carried out using standard Schlenk techniques under argon as inert gas. Methyl acrylate and all solvents were dried and distilled under argon. Methyl acrylate, di-*n*-butyl ether, dimethyl glutarate, tetrafluoroboric acid (~ 54% in ether), trialkyl- and triarylphosphines and Meerwein reagent were purchased from Fluka. 1,2-Bis(diphenylposphino)ethane, 1,4-bis(diphenylphosphino)butane and 1-diphenylphosphino-2-(diphenylarsino)ethane were purchased from Strem. $Pd(acac)_2$,[17] 1,2-bis(dibutylphosphino)ethane,[18] 1,2-bis(diphenylphosphino)ethane monoxide,[19] 1,2-bis(diphenylposphino)ethane monosulfide,[20] 1,2-bis(diphenylposphino)butane monoxide,[16] and 1-diphenylphosphino-2-(dimethylamino)ethane[21] were prepared according to the literature.

Gas chromatograms were obtained on Siemens Synchromat systems equipped with a 50 m Pona column using nitrogen as carrier gas. Yields of MA dimers were obtained with the use of the internal standard method (dibutyl ether or dimethyl glutarate). NMR spectra in solution were recorded on a Bruker DPX 300 instrument. ^{31}P NMR chemical shifts relative to 85% phosphoric acid are reported with positive values downfield from the reference. Mass spectra were performed on a Finnigan MAT 95 with an NBA matrix.

General Procedure for the Synthesis of the Ammonium-Phosphine Ligands

One equivalent of Meerwein reagent (MWR) is suspended in dichloromethane (DCM) and 1 equiv. of aminophosphine is added dropwise at − 100 °C. The temperature is kept constant over 5 h, while the white crystalline MWR is slowly consumed. Then the mixture is slowly warmed up to RT, the solvent is evaporated and the residue is recrystallized to obtain the white ammonium salt.

(1-Dibutylphosphinoeth-2-yl)trimethylammonium tetrafluoroborate **1**: MWR (0.56 g, 2.58 mmol) is suspended in 30 mL DCM and reacted with 1-dibutylphosphino-2-dimethylaminoethane (0.38 g, 2.50 mmol). The crude material is recrystallized in 15 mL THF at − 78 °C to obtain the ammonium salt; yield: 0.68 g (85.3%). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.36 (m, 2H, $[Me_3N\text{-}CH_2\text{-}]^+$), 2.22 (s, 6H, $[N(CH_3)_3]^+$), 1.54 (m, 2H, $Bu_2P\text{-}CH_2\text{-}$), 1.45 (br. m, 12H), 0.88 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.0 (s, 3C, $[N(CH_3)_3]^+$), 28.3 (d, J = 12.7 Hz, 2C), 26.6 (d, J = 12.3 Hz, 2C), 24.7 (d, J = 11.4 Hz, 2C), 14.2 (s, 2C); ^{31}P NMR (121 MHz, $CDCl_3$): δ = − 30.6 (s, 1P, $\text{-}PBu_2$); ^{19}F NMR (282 MHz, $CDCl_3$): δ = − 151.6 (s, 4F, $[BF_4]^-$).

(1-Diphenylphosphinoeth-2-yl)trimethylammonium tetrafluoroborate **2**: MWR (0.78 g, 5.11 mmol) is suspended in 40 mL DCM and reacted with 1-diphenylphosphino-2-dimethylaminoethane (1.32 g, 5.13 mmol). The crude material is recrystallized in a mixture of 5 mL THF and 15 mL DCM at − 20 °C to obtain the ammonium salt; yield: 1.45 g (78.9%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54 – 7.44 (10H), 3.35 (m, 2H, $[Me_3N\text{-}CH_2\text{-}]^+$), 3.10 (s, 9H, $[\text{-}N(CH_3)_3]^+$), 2.60 (m, 2H, $Bu_2P\text{-}CH_2\text{-}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.2 (s), 134.2 (s), 131.0 (s), 130.5 (s); ^{31}P NMR (121 MHz, $CDCl_3$): δ = − 30.6 (s, 1P, $\text{-}PPh_2$); $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ = − 151.6 (s, 4F, $[BF_4]^-$).

General Procedure for the Synthesis of Aminophosphine Ligands

Dibutylphosphine is dissolved in THF and deprotonated with a solution of butyllithium in hexane at 0 °C for 1 h. After that the corresponding 1-chloro-2-aminoethane is added dropwise at 0 °C, and the pale yellow solution rapidly turns colorless. After addition is completed the reaction mixture is allowed to warm up to RT and stirred for 1h. Then the solvent is evaporated and the residue is diluted with pentane. The mixture is filtered over Celite and the filtrate is distilled under vacuum.

1-Dibutylphosphino-2-dimethylaminoethane **3**: Dibutylphosphine (2.31 g, 15.80 mmol) is dissolved in 30 mL THF and reacted with a solution of butyllithium in hexane (10.0 mL, 16.0 mmol) and 1-chloro-2-dimethylaminoethane (2.00 g, 18.59 mmol). The product is obtained at 80 °C under 2.5 mbar as a colorless liquid. yield: 2.71 g (79.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.36 (m, 2H, Me_2N-CH_2-), 2.22 (s, 6H, -N[CH_3]$_2$), 1.54 (m, 2H, Bu_2P-CH_2-), 1.45 (br. m, 12H), 0.88 (t, 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 57.0 (d, J = 19.6 Hz, 1C, Me_2N-CH_2-), 45.6 (s, 2C, -N[CH_3]$_2$), 28.4 (d, J = 12.1 Hz, 2C), 27.2 (d, J = 11.6 Hz, 2C), 25.9 (d, J = 12.8 Hz, 2C, Bu_2P-CH_2-), 24.9 (d, J = 10.9 Hz, 2C), 14.2 (s, 2C); ^{31}P NMR (121 MHz, $CDCl_3$): δ = − 32.1 (s, 1P, -PBu_2).

1-Dibutylphosphino-2-propylaminoethane **4**: Dibutylphosphine (0.56 g, 3.80 mmol) is dissolved in 10 mL THF and reacted with a solution of butyllithium in hexane (2.4 mL, 3.9 mmol) and 1-chloro-2-propylaminoethane (0.66 g, 4.00 mmol). The product is obtained at 120 °C under 3.8 mbar as a colorless liquid. yield: 0.31 g (33.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.55 (t, J = 6.6 Hz, 2H, PrN-CH_2-), 1.60 – 1.30 (20H), 0.86 (br. m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 62.4 (s, 1C, PrN-CH_2-), 51.9 (s, 1C), 34.9 (d, J = 10.0 Hz, 1C, Bu_2P-CH_2-), 28.4 (d, J = 12.1 Hz, 2C), 27.4 (s, 1C), 27.3 (d, J = 12.9 Hz, 2C), 24.9 (d, J = 11.0 Hz, 2C), 22.5 (s, 1C), 14.2 (s, 2C); ^{31}P NMR (121 MHz, $CDCl_3$): δ = − 29.5 (s, 1P, -PBu_2).

General Procedure for the Synthesis of the Cationic Allylpalladium Complexes

One half of an equivalent of (η^3-allyl)palladium chloride dimer is dissolved in DCM and 1 equiv. of the corresponding bidentate ligand is added at RT. The mixture is stirred for 1 h, before 1 equiv. of silver tetrafluoroborate is added. After 5 min the mixture is filtered over Celite, the solvent is evaporated and the residue is washed three times with pentane. Recrystallization leads to white crystals of the pure product.

(η^3-Allyl)[1-diphenylphosphino-2-dimethylaminoethane-κ^2-P,N]palladium(II) tetrafluoroborate **5**: (η^3-Allyl)palladium chloride dimer (291.6 mg, 0.80 mmol) is reacted with 1-diphenyl-phosphino-2-(dimethylamino)ethane (409.2 mg, 1.60 mmol) in 20 mL DCM. After recrystallization from a mixture of 15 mL THF and 5 mL DCM at − 78 °C the product is obtained as a white solid; yield: 544.0 mg (69.5%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 – 7.49 (m, 10H), 5.82 (m, 1H), 4,80 (m, 1H), 4.00 – 3.90 (m, 2H), 3.07 (s, 3H), 2.95 (s, 3H), 2.88 – 2.65 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.2, 129.8, 123.9; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 39.9 (s, 1P, -PPh_2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = − 151.6 (s, 4F, [BF_4]$^-$); MS: m^+/z = 404, m^-/z = 87.

(η^3-Allyl)[bis(diphenylphosphino)ethane-κ^2-P,P]palladium(II) tetrafluoroborate **6**: (η^3-Allyl)palladium chloride dimer (218.2 mg, 0.60 mmol) is reacted with 1,2-bis(diphenylphosphino)ethane (475.2 mg, 1.20 mmol) in 20 mL DCM. After recrystallization from a mixture of 15 mL ethanol and 5 mL DCM at − 20 °C the product is obtained as a white solid; yield: 583.0 mg (92.1%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.59 – 7.48 (m, 20H), 5.78 (m, 1H), 4.91 (m, 2H), 3.36 (m, 2H), 2.67 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 133.5, 133.2, 133.0, 124.2, 62.3, 27.9; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 52.5 (s, 2P, -PPh_2); ^{19}F NMR (282 MHz, $CDCl_3$): δ = − 151.6 (s, 4F, [BF_4]$^-$); MS: m^+/z = 545, m^-/z = 87.

Catalytic Reaction Procedure for *in situ* Systems

In a Schlenk tube (ST1) are successively added under argon the relevant amounts of ligand, tetrafluoroboric acid etherate and eventually solvent (nitromethane or [BMIM][BF_4]). The mixture is diluted with MA (distilled off from stabilizer) and transferred into a Schlenk tube (ST2) containing the appropriate amount of $Pd(acac)_2$ in MA. Depending on the catalytic test, the total amount of ester corresponds to 4.6 mL (4.3 g, 50 mmol) or 9.2 mL (8.6 g, 100 mmol). The mixture is stirred at RT for 15 min (starting from the beginning of the addition). ST2 is heated in an oil bath maintained at 80 °C under controlled stirring for the required time. The reaction is stopped by cooling at − 78 °C (acetone-dry ice). The reaction mixture is neutralized with an aqueous solution of Na_2CO_3. n-Bu_2O (*ca.* 1 mL) or methyl benzoate (*ca.* 1 mL) is added as an internal GC standard and the mixture is diluted with Et_2O before GC analysis.

Catalytic Reaction Procedure for Cationic Allylpalladium Complexes

The catalyst (0.05 mmol) is dissolved in 4.6 mL (4.3 g, 50 mmol) MA (distilled off from stabilizer). The appropriate amount of tetrafluoroboric acid etherate is added and the mixture is stirred at RT for 15 min before it is heated in an oil bath maintained at 80 °C under controlled stirring for the required time. The reaction is stopped by cooling at − 78 °C (acetone-dry ice). The reaction mixture is neutralized with an aqueous solution of Na_2CO_3. n-Bu_2O (*ca.* 1 mL) or methyl benzoate (*ca.* 1 mL) is added as an internal GC standard and the mixture is diluted with Et_2O before GC analysis.

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References

[1] a) U. Onken, A. Behr, *Lehrbuch der Technischen Chemie*, Band 3, Chemische Prozeßkunde, Thieme, Stuttgart, **1996**; b) *Ullmann's Encyclopedia of Industrial Chemistry*, 6th Edition on CD-ROM, Wiley-VCH, Weinheim, **1998**.

[2] a) M. Brookhart, S. Sabo-Etienne, *J. Am. Chem. Soc.* **1991**, *113*, 2777; b) E. Hauptmann, S. Sabo-Etienne, P. S. White, M. Brookhart, J. M. Garner, P. J. Fagan, J. C. Calabrese, *J. Am. Chem. Soc.* **1994**, *116*, 8038.
[3] a) T. Alderson, E. L. Jenner, R. V. Lindey, *J. Am. Chem. Soc.***1965**, *87*, 5638; b) R. J. McKinney, M. C. Colton, *Organometallics* **1986**, *5*, 1080; c) R. Sustmann, H. J. Jornung, T. Schupp, B. Patzke, *J. Mol. Catal.* **1993**, *85*, 149; d) B. Patzke, R. Sustman, *J. Organomet. Chem.* **1994**, *480*, 65.
[4] a) G. Wilke, K. Sperling, L. Stehling, *BRD Patent* 3,336,391, **1985**; b) K. Sperlich, *Dissertation*, Ruhr-Universität Bochum, **1983**.
[5] G. L. Tembe, A. R. Bandyopadhyay, P. A. Ganeshpure, S. Satish, *Catal. Rev.-SCL. Eng.* **1996**, *38*, 299-327.
[6] M. G. Barlow, M. J. Bryant, R. N. Haszeldine, A. G. Mackie, *J. Organomet. Chem.* **1970**, *21*, 215-218.
[7] H. Pracejus, H. J. Krause, G. Oehme, *Z. Chem.* **1980**, *20*, 24.
[8] G. Oehme, H. Paracejus, *J. Organomet. Chem.* **1987**, *320*, C 56-C58.
[9] a) I. Tkatchenko, P. Grenouillet, D. Neibecker, *French Patent* 2,524,341, **1983**; b) I. Tkatchenko, P. Grenouillet, D. Neibecker, *French Patent* 2,596,390, **1987**; c) I. Tkatchenko, P. Grenouillet, D. Neibecker, *U. S. Patent* 4,889,949, **1989**.
[10] a) D. Kissling, K. O. Knackmass, H. Schicht, F. Winn, R. Schoellner, *J. Prakt. Chem.* **1973**, *315*, 577-586; b) R. Schoellner, D. Kisslich, H. Schicht, H. Hossbach, *J. Prakt. Chem.* **1973**, *315*, 829-842; c) D. Kisslich, W. Flock, O. U. Longer, R. Schoellner, *Z. Phys. Chem.* **1975**, *256*, 80-86.
[11] P. B. Dias, M. E. M. de Piedade, J. A. M. Simoes, *Coord. Chem. Rev.* **1994**, *135/136*, 737-807.
[12] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 314-348.
[13] G. M. DiRenzo, P. S. White, M. Brookhart, *J. Am. Chem. Soc.* **1996**, *118*, 6225-6234.
[14] I. Guibert, D. Neibecker, I. Tkatchenko, *J. Chem. Soc. Chem. Commun.* **1989**, 1850-1852.
[15] G. Tian, H. W. Boone, B. M. Novak, *Makromolecules* **2001**, *34*, 7656-7663.
[16] J. Zimmermann, P. Wasserscheid, I. Tkatchenko, S. Stutzmann, *Chem. Commun.* **2002**, 760-761.
[17] D. A. White, *J. Chem. Soc.(A)* **1971**, 143-145.
[18] J. Lewis, M. S. Khan, A. K. Kakkar, P. R. Raithby, K. Fuhrmann, R. H. Friend, *J. Org. Chem.* **1992**, *433*, 135-139.
[19] S. J. Higgins, R. Taylor, B. L. Shaw, *J. Organomet. Chem.* **1987**, *325*, 285-292.
[20] I. M. Aladzheva, O. V. Bykhoskaya, D. I. Lobanov, P. V. Petrovdkii, T. A. Mastryukova, M. I. Kabachnik, *Z. Obshch. Khim.* **1995**, *65*, 1586-1591.
[21] R. T. Smith, M. C. Baird, *Inorg. Chim. Acta.* **1982**, *62*, 135-139.