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Palladium-Catalyzed Isomerization and Hydroformylation of Olefins

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Abstract: The palladium-catalyzed hydroformylation of 1-octene has been studied in the presence of different phosphines and acid cocatalysts. The best results are achieved in the presence of in situ-generated palladium complexes with bidentate phosphines. It is demonstrated that the acid concentration is a crucial factor for obtaining high linear selectivity. A novel optimized catalyst based on an arylheteroarylphosphine has been applied for hydroformylation of different aliphatic and aromatic olefins. Good activity and excellent selectivity towards the linear aldehydes is achieved.

Keywords: homogeneous catalysis · hydroformylation · isomerization · palladium · P ligands

Hydroformylation consists of the addition of a formyl group and a hydrogen atom to an unsaturated carbon–carbon bond.[1] This reaction was discovered accidentally by Otto Roelen at Ruhrchemie in Germany nearly 70 years ago.[2] Since then, hydroformylations have been widely applied in organic synthesis, for example, natural product synthesis,[3] and stereoselective synthesis.[4] In addition, various processes for fine and bulk chemicals have been developed.[5] With respect to industry, the hydroformylation of olefins has witnessed continuous growth since its discovery: Recently, the production capacity of aliphatic aldehydes reached $>8\times10^6$ tons.[6] Hence, in terms of scale, hydroformylation is the largest applied homogeneously catalyzed reaction and the most important industrial process for the production of aldehydes. The resulting products are easily converted into many secondary products, such as alcohols, which are further converted to detergents and plasticizer esters.

Typically, industrial hydroformylation processes are performed at medium to high pressure (20–100 bar) of synthesis gas (carbon monoxide/hydrogen) at temperatures between 100–140 °C in the presence of rhodium or cobalt carbonyl complexes. While the first generation of hydroformylation catalysts was based on simple $[Co_2(CO)_8]$, later on phosphine-modified catalysts were introduced. Since the 1970s rhodium became the metal of choice for the hydroformylation of lower aliphatic olefins. Indeed, the first ligand-modified rhodium-based processes came on stream in 1974 (Celanese) and 1976 (UCC), in which triphenylphosphine was applied as ligand and propene as substrate. In 1984, the Ruhrchemie-Rhone Poulenc process was introduced,[7] which makes use of a biphasic solvent system with water as the catalyst phase.[8] Here, in general, the catalyst can be easily isolated by phase separation.

Despite the significant industrial interest in hydroformylation reactions, comparatively little work has been done with catalysts based on metals other than rhodium or cobalt. In fact, there is a general belief that the hydroformylation activity of transition-metal carbonyl complexes follow the order shown in Scheme 1.[9]

Rh >> Co >> Ir,Ru > Os > Pt > Pd > Fe > Ni

Scheme 1. Hydroformylation activity of metal carbonyls.

Notably, this order of reactivity has been established under a special set of reaction conditions for unmodified metal carbonyl complexes. Hence, by introduction of ligands and cocatalysts the activity of a given metal complex should be significantly altered. Indeed, Drent and co-workers demonstrated that palladium(II) diphosphine complexes in the presence of weakly or non-coordinating counterions are rel-

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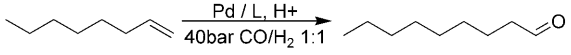
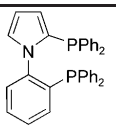
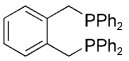
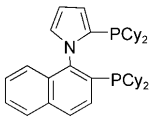
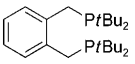
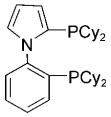
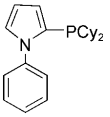
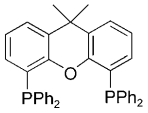
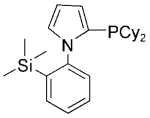
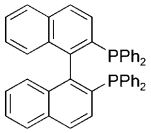
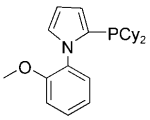
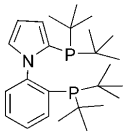
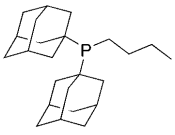
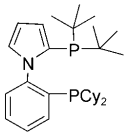
atively active in the hydroformylation of olefins. Notably, by variation of the ligand, anion, and solvent, the course of the reaction can be controlled to give alcohols, aldehydes, ketones, or oligoketones. For example, by using non-coordinating anions and arylphosphine ligands primarily (oligo)ketones are produced, while increasing the ligand basicity or anion coordination strength shifted the product selectivity towards aldehydes and alcohols.[10]

Herein, we report the development of new palladium-based catalyst systems that enable the hydroformylation of different terminal and internal olefins in good selectivity and activity. Based on our previous work in hydroformylations and hydroaminomethylations with phosphine-modified rhodium catalysts,[11] we became interested in similar reactions with palladium catalysts. For some years we have also been involved in the development of novel ligands for palladium catalysts for various applications. For example, we developed palladacycles,[12] adamantyldialkylphosphines,[13] carbene ligands,[14] and 2-phosphino-*N*-arylindoles and -pyrroles,[15] as well as 2-phosphino-*N*-arylimidazoles.[16] Notably, the latter phosphines are conveniently synthesized by selective mono- or double-metalation. Thus, a variety of such ligands is easily available and can be efficiently prepared in a modular synthesis. Here, we describe for the first time the use of *N*-arylheteroarylphosphines in palladium-catalyzed hydroformylations.

Initial catalytic experiments were performed with 1-octene as a model olefin in the presence of 0.2 mol% [Pd(acac)$_2$] and 0.5 mol% of 2-(dicyclohexylphosphino)-1-(2-(dicyclohexylphosphino)naphthalen-1-yl)-1*H*-pyrrole at 100°C (Table 1, entry 3). This ligand was prepared in a straightforward manner from *N*-naphthylpyrrole in one step.[17] As demonstrated by the previous work of Drent and co-workers, the addition of acid as cocatalysts is required

Table 1. Pd-catalyzed hydroformylation of 1-octene. Variation of ligand.[a]



Entry	Ligand[a]	L/Pd	Conv. [%]	Aldehyde [%][b]	*n*	*iso*	*iso*-Octenes [%]	Entry	Ligand[a]	L/Pd	Conv. [%]	Aldehyde [%][b]	*n*	*iso*	*iso*-Octenes [%]
1[c]		2.5	95	13	64	36	42	9[c]		4	74	18	86	14	41
2[c,d]		2.5	99	56	75	25	26	10		4	63	9	79	21	38
3[c]		4	93	42	74	26	36	11		4	59	0	–	–	38
4[c]		4	94	42	76	24	40	12		10	96	26	70	30	51
5		2.5	23	1	–	–	6	13		5	30	2	76	24	16
6[c]		4	98	41	80	20	38	14		5	17	2	79	21	10
7		2.5	13	0	–	–	2	15		10	39	2	81	19	19
8		4	47	8	77	13	26	16	PPh_3	5	13	1	–	–	3

[a] Reaction conditions: 100°C, 16 h, 5.1 mmol 1-octene, 0.2 mol% [Pd(acac)$_2$], 0.8 mol% *p*-toluenesulfonic acid, 2 mL diglyme. [b] The yield is determined by GC. [c] Aldol products are observed as side products. [d] Trifluoroacetic acid is used.

for hydroformylation activity.[10] Hence, the testing was carried out in the presence of 0.8 mol% *p*-toluenesulfonic acid as cocatalyst. Unfortunately, under these conditions significant amounts of internal olefins (68%) are produced as main products. Apparently, the in situ-generated palladium hydride complex isomerizes 1-octene much faster than catalyzing the the desired hydroformylation reaction. Indeed, even by stirring 1-octene at room temperature in the presence of the catalyst system without any hydrogen pressure fast isomerization reactions took place!

As shown in Figure 1 already after five minutes less than 10% of the terminal olefin remained in the reaction mixture. After 1 hour, 1-octene is almost equilibrated to a mixture of internal octenes. Clearly, this observation implies that there is no difference for active palladium catalysts using pure terminal olefins or olefin mixtures.[18]

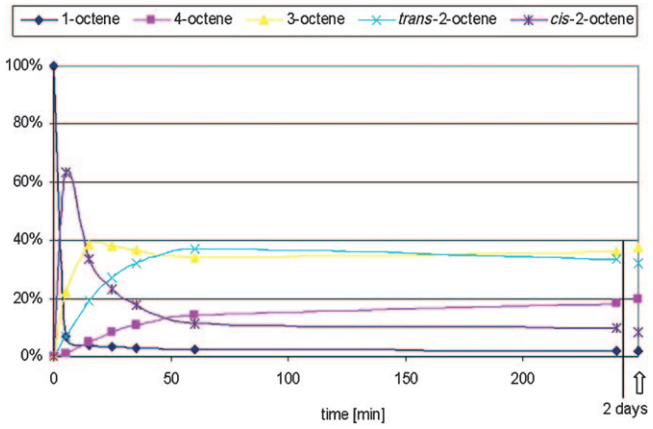


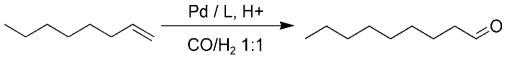
Figure 1. Isomerization of 1-octene with [Pd(acac)$_2$]/L/*p*-TsOH; Pd/L/*p*-TsOH = 1:4:4.

It is well known that the influence of ligands on hydroformylation reactions is crucial. Thus, we examined the effect of several mono- and bidentate phosphorus-containing ligands on the model reaction (Table 1). Among the various phosphines tested for this reaction, 1,3-bis(diphenylphosphino)propane (DPPP) gave the best product yield. This observation is in accordance with the work of Drent and co-workers, who showed the superiority of DPPP in combination with trifluoroacetic acid.[10] However, the combination of [Pd(acac)$_2$] and several other bidentate ligands are also able to catalyze the hydroformylation of octene (Table 1, entries 1–11). Applying biaryl-type ligands such as BINAP (2,2′-bis(diphenylphosphino)-l,1′-binaphthyl) or heteroarylarylphosphines a higher selectivity towards the linear products is obtained. Advantageously, hydroformylation proceeds in the presence of *p*-toluenesulfonic acid instead of trifluoroacetic acid or trifluoromethanesulfonic acid. Except for triphenylphosphine and 2,2'-bis(di-*tert*-butylphosphino)-*N*-phenylpyrrole (Table 1, entries 7 and 16), all other ligands led to moderate to high conversion and significant amounts of isomerized octenes were obtained.

Apparently, there is no clear trend between steric hindrance and basicity of the ligand and isomerization activity. Interestingly, 2-dicyclohexyl-phosphinopyrrole also showed some hydroformylation activity (Table 1, entry 12). However, in accordance with the previous work, other monodentate phosphines such as P*n*Bu$_3$ or Buchwald-type ligands gave no aldehyde products.

Next, the catalyst performance of the [Pd(acac)$_2$]/2-(dicyclohexyl-phosphino)-1-(2-(dicyclohexylphosphino)naphthalen-1-yl)-1*H*-pyrrole catalyst was studied in more detail (Table 2). The pressure of synthesis gas had a significant influence on the product yield. While at 20 bar only 10% of aldehydes are observed (Table 2, entry 5), the product yield rose to 74% at 100 bar (Table 2, entry 9).

Table 2. Palladium-catalyzed hydroformylation of 1-octene: Variation of reaction conditions.[a]

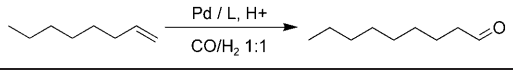


Entry	*T* [°C]	*P* [bar]	Conv. [%]	Product [%][b]	*n*	*iso*	*iso*-Octenes [%]
1	80	40	98	24	70	30	68
2[c]	90	40	98	36	74	26	56
3[c]	100	40	99	33	73	27	62
4[c]	120	40	99	14	71	29	71
5	100	20	100	10	76	24	61
6[c]	100	40	98	46	81	19	38
7[c]	100	60	100	61	77	23	31
8[c]	100	80	99	72	81	19	23
9[c]	100	100	100	74	76	24	16
10[d]	100	40	97	37	76	24	59
11[c,e]	100	40	99	59	80	20	23
12[c,f]	100	40	99	47	73	27	28
13[g]	100	40	53	20	68	32	27

[a] Reactions were carried out at 100 °C for 16 h with 5.1 mmol 1-octene as substrate, 0.2 mol% [Pd(acac)$_2$], 0.8 mol% L, , L = 2-(dicyclohexyl-phosphino)-1-(2-(dicyclohexylphosphino)naphthalen-1-yl)-1*H*-pyrrole 0.8 mol% *p*-toluenesulfonic acid, and 2 mL diglyme. [b] The yield was determined by GC. [c] Aldol products are observed as side products. [d] Solvent: methanol; main product: methyl ester. [e] Solvent: THF. [f] Solvent: toluene. [g] Solvent: water; main product: carboxylic acid.

Variation of the temperature demonstrated that above 100 °C aldol side reactions led to product decomposition (Table 2, entry 4). Using protic solvents such as methanol or water gave the corresponding ester and carboxylic acid products (Table 2, entries 12 and 13). Except for the experiment with water, in all cases high conversion is observed and isomerized octenes are produced. Noteworthy, the variation of temperature, pressure, or solvent has relatively little influence on the regioselectivity of the carbonylation step. On the other hand, the addition of acid is crucial for the activity and regioselectivity of the palladium catalyst (Table 3). Without any acidic cocatalyst present, no conversion took place (Table 3, entry 8). Also the addition of Lewis acids, for example, $ZnCl_2$ or $FeCl_3$, and other typical Brönstedt acids such as HCl did not promote hydroformylation reactions (Table 3, entries 9–12). However, in the pres-

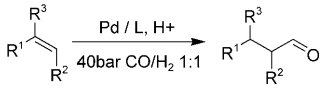
Table 3. Influence of acid in the palladium-catalyzed hydroformylation.[a]

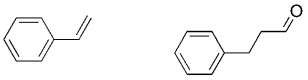
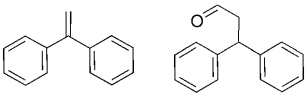
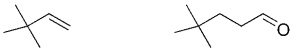
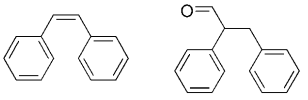
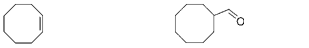
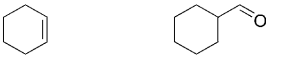
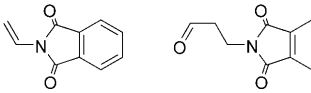
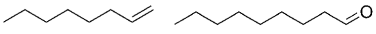


Entry	Acid	Conv. [%]	Aldehyde [%][b]	*n*	*iso*	*iso*-Octenes [%]	*P* [bar]
1[c]	10% TsOH	99	10	54	46	45	40
2[c]	1.2% TsOH	99	42	72	28	36	40
3[c]	0.8% TsOH	98	46	81	19	38	40
4[c]	0.4% TsOH	98	54	81	19	39	40
5	0.2% TsOH	99	51	86	14	40	40
6	0.1% TsOH	98	53	89	11	46	40
7	0.075% TsOH	48	33	95	5	15	40
8	–	0	–	–	–	–	40
9	0.8% HBF_4	74	<5	–	–	64	60
10	0.8% HCl	2	<5	–	–	2	60
11	0.8% $ZnCl_2$	62	<5	–	–	60	60
12	0.8% $FeCl_3 \cdot 6H_2O$	15	<5	–	–	17	60
13	0.8% TFA	82	53	85	15	26	60
14	0.1% TsOH	99	74	90	10	22	80
15[c]	0.8% TsOH	100	68	81	19	22	80
16[c]	0.8% MsOH[d]	100	57	74	26	21	80
17[c]	0.8% DsOH[e]	100	46	65	35	22	80
18[c]	0.8% CamOH[f]	100	62	73	27	18	80
19	0.8% TfOH[g]	97	–	–	–	51	80

[a] Reactions were carried out at 100 °C for 16 h with 5.1 mmol 1-octene as substrate, 0.2 mol% [Pd(acac)$_2$], 0.8 mol% L, , L = 2-(dicyclohexylphosphino)-1-(2-(dicyclohexylphosphino)naphthalen-1-yl)-1*H*-pyrrole, 0.8 mol% *p*-toluenesulfonic acid and 2 mL diglyme. [b] The yield was determined by GC. [c] Aldol products are observed as side products. [d] MsOH = Methanesulfonic acid. [e] DsOH = Dodecylsulfonic acid. [f] CamOH = Camphersulfonic acid. [g] TfOH = Trifluoromethanesulfonic acid.

Table 4. Palladium-catalyzed hydroformylation: Different substrates[a]



Entry	Substrate	Product	Conv. [%]	Yield [%][b]	*n*/*iso*
1			96	88[c]	85:15
2			89	89	>99:1
3			–	53	>99:1
4			100	>99	–
5			57	57	–
6			15	15	–
7			100	>95[d]	98:2
8			98	72[e]	81:19

[a] Reactions were carried out at 100 °C with 60 bar of synthesis gas for 16 h with 5.1 mmol as substrate, 0.2 mol% [Pd(acac)$_2$], 0.8 mol% L, L = 2-(dicyclohexyl-phosphino)-1-(2-(dicyclohexylphosphino)naphthalen-1-yl)-1*H*-pyrrole 0.8 mol% *p*-toluenesulfonic acid and 2 mL diglyme. [b] The yield was determined by GC. [c] Side product: phenylpropanol (8%), *n*/*iso* = 78:22. [d] Yield and selectivity determined by NMR spectroscopy. [e] 80 bar synthesis gas.

ence of different sulfonic acids the desired reaction took place. Noteworthy, the concentration of *p*-toluenesulfonic acid has a major influence on the regioselectivity of the hydroformylation! For example, in the presence of 0.075 mol% TsOH the *n*/*iso* ratio is 95:5, while applying 10 mol% of acid nonanal and 2-methyloctanal are obtained in a ratio of 54:46 (Table 3, entries 1 and 7). We explain this influence by increased isomerization reactions at higher acid concentration. The resulting internal olefins led to lower selectivity compared to 1-octene. Indeed, using a technical mixture of octenes gave 23% aldehydes with an *n*/*iso* ratio of 68:32. It is notable that no hydroformylation is observed in the presence of the phosphonium salt of the respective ligand. Hence, we conclude that under the reaction conditions applied, not all of the ligand is protonated.

Finally, we investigated the generality of our novel catalyst system. As demonstrated in Table 4, different aromatic and aliphatic olefins are hydroformylated with good to excellent selectivity towards the linear isomer. Most notably, *N*-vinylphthalimide gave the corresponding aldehyde in 95% yield with high regioselectivity (98:2). To the best of our knowledge this is the highest linear selectivity so far reported for this substrate. In addition, other substrates, which typically form the branched aldehyde, for example, styrene, gave selectively the linear aldehyde. With respect to reactivity, cyclic olefins are challenging substrates that are known to be quite stable. Nevertheless, cyclooctenecarbaldehyde is obtained in 57% yield, and even cyclohexene gave the respective aldehyde without further optimization of the reaction conditions.

So far, most work on hydroformylation catalysts has focused on rhodium- or cobalt-based catalysts. Here, we introduce a novel palladium catalyst system based on bidentate 2,2'-heteroarylarylphosphines and *p*-TsOH. By applying optimal conditions, good to excellent regioselectivity is obtained for the hydroformylation of aliphatic and aromatic olefins. It is shown that a low acid concentration is crucial for obtaining high degrees of the linear isomer. Hence, by carefully controlling the reaction conditions Pd complexes constitute a promising class for selective hydroformylations and should be considered more often as catalysts for this important transformation.

Experimental Section

General procedure: A glass vial was charged under argon with palladium acetylacetonate (10.2 μmol), ligand (40.8 μmol), and diglyme (1 mL). After the catalyst had been generated in situ by stirring, a solution of diglyme and 1-octene (1 mL, 5.1 mmol) containing *p*-toluenesulfonic acid (4.1 μmol) was added. The glass vial was moved into an autoclave. After flushing with nitrogen the autoclave was pressurized with synthesis gas

and heated to 100 °C. The reaction was carried out for 16 h; then, the pressure was released and isooctane (internal standard) was added to the solution. The yield was measured by GC. Product characterization was done by comparison with authentic samples and HR-MS.

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[17] In a 250 mL schlenk flask with reflux condenser under argon 1-(naphthalen-1-yl)-1*H*-pyrrole (5 g, 25.9 mmol) was dissolved in Et_2O (100 mL), and TMEDA (6.04 g, 7.8 mL, 52 mmol) was added at room temperature. After addition of 1.6 N *n*BuLi (32.5 mL, 52 mmol) the solution was stirred for 5 h at room temperature. Then, dicyclohexylchlorophosphine (12.06 g, 11.4 mL, 52 mmol) was added. After stirring for 1 h at room temperature, degassed water (50 mL) was introduced. The organic phase was washed degassed water (3×20 mL) and the solvents were removed in vacuum. The residue was recrystallized from MeOH (200 mL). The resulting white solid was filtered to give 2-(dicyclohexylphosphino)-1-(2-(dicyclohexylphosphino)naphthalen-1-yl)-1*H*-pyrrole (13.5 g, 90 % yield). ^{31}P NMR (121.5 MHz, $CDCl_3$): $\delta = -14.4$, -26.6 ppm (dd, $J_{PP} = 14.8$ Hz); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.27$ (d, $J = 7$ Hz, 1H), 8.24 (d, $J = 8$ Hz, 1H), 8.04 (dd $J = 8.5$ Hz, $J = 1.4$ Hz, 1H), 7.84 (td,

$J=7$ Hz, $J=1$ Hz, 1H), 7.7 (td, $J=8$ Hz, $J=1$ Hz, 1H), 7.2 (d, $J=8$ Hz, 1H), 6.9 (dd, $J=4$ Hz, $J=1$ Hz, 1H), 6.7 (t, $J=4$ Hz, 1H,), 2.6 (m, 1H,), 2.4 (quint, $J=2.5$ Hz, 1H,), 2.35–1.0 ppm (m, 40H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.7$ (s), 144.4 (s), 133.7 (s), 132.9 (dd, $J_{PC}=3.3$ Hz, $J_{PC}=1.5$ Hz), 131.6 (s), 128.8 (d, $J_{PC}=2.8$ Hz), 128.4 (s), 127.6 (s), 127.4 (s), 126.9 (s), 126.5 (s), 124.9 (s), 115.8 (brs), 108.3 (s), 37.4 (d, $J_{PC}=16.3$ Hz), 35.7 (d, $J_{PC}=9.2$ Hz), 34.7 (d, $J_{PC}=9.8$ Hz), 34.0 (d, $J_{PC}=13.6$ Hz), 32.2 (d, $J_{PC}=15$ Hz), 31.3 (d, $J_{PC}=15$ Hz), 31.1 (s), 30.9 (s), 30.8 (d, $J_{PC}=4.5$ Hz), 30.3 (d, $J_{PC}=13.5$ Hz), 30.2 (d, $J_{PC}=6.4$ Hz), 29.6 ($J_{PC}=6.5$ Hz), 29.0 (d, $J_{PC}=8.3$ Hz), 27.9–27.1 (m), 26.7 (d, $J_{PC}=7.4$ Hz), 26.4 ppm (d, $J_{PC}=5$ Hz); MS (70 eV, EI): m/z (%): 584 (0.9) ($[M-1]^+$), 502 (100), 420 (3), 388 (6.9), 305 (4.8), 254 (4.9), 222 (46.4), 197(2.3), 115 (6.9), 67 (11), 55 (13); HR-MS: calcd: 584.35695 for $C_{38}H_{52}N_1P_2$ $[M-1]^+$; found: 584.357226.

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