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Rationally Designed Pincer-Type Heck Catalysts Bearing Aminophosphine Substituents: Pd^{IV} Intermediates and Palladium Nanoparticles

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Abstract: The aminophosphine-based pincer complexes $[C_6H_3\text{-}2,6\text{-}\{XP(piperidinyl)_2\}_2Pd(Cl)]$ (X = NH **1**; X = O **2**) are readily prepared from cheap starting materials by sequential addition of 1,1′,1″-phosphinetriyltripiperidine and 1,3-diaminobenzene or resorcinol to solutions of $[Pd(cod)(Cl)_2]$ (cod = cyclooctadiene) in toluene under N_2 in "one pot". Compounds **1** and **2** proved to be excellent Heck catalysts and allow the quantitative coupling of several electronically deactivated and sterically hindered aryl bromides with various olefins as coupling partners at 140 °C within very short reaction times and low catalyst loadings. Increased reaction temperatures also enable the efficient coupling of olefins with electronically deactivated and sterically hindered aryl chlorides in the presence of only 0.01 mol % of catalyst. The mechanistic studies performed rule out that homogeneous Pd^0 complexes are the catalytically active forms of **1** and **2**. On the other hand, the involvement of palladium nanoparticles in the catalytic cycle received strong experimental support. Even though pincer-type Pd^{IV} intermediates derived from **1** (and **2**) are not involved in the catalytic cycle of the Heck reaction, their general existence as reactive intermediates (for example, in other reactions) cannot be excluded. On the contrary, they were shown to be thermally accessible. Compounds **1** and **2** show a smooth halide exchange with bromobenzene to yield their bromo derivatives in DMF at 100 °C. Experimental observations revealed that the halide exchange most probably proceeded via pincer-type Pd^{IV} intermediates. DFT calculations support this hypothesis and indicated that aminophosphine-based pincer-type Pd^{IV} intermediates are generally to be considered as reactive intermediates in reactions with aryl halides performed at elevated temperatures.

Keywords: aminophosphines · C–C coupling · nanoparticles · palladium · pincer reagents

Introduction

The palladium-catalyzed arylation of alkenes has proven to be one of the most important methods for carbon–carbon bond formation in organic chemistry.[1] Various types of palladium complexes have been employed to promote the Heck reaction, but even though some efficiently couple sterically hindered substrates or occasionally even aryl chlorides, their syntheses are often time-consuming, difficult, and/or require the use of expensive starting materials. In addition, many catalytically active systems suffer from their poor thermal stability, as well as poor stability towards air and moisture.[2–5]

Although recent developments have achieved a considerable increase in the activity of Heck catalysts, a typical protocol for this reaction still requires prolonged reaction times and relatively high catalyst loadings, and there is still a clear need for more efficient systems. Pincer complexes of palladium are among the most efficient Heck catalysts and continuously attract attention because of their unique balance between stability and reactivity. Seemingly slight electronic and steric modifications of the pincer core and/or the phosphine substituents have been demonstrated to dramatically influence their catalytic activities.[2a,d,6,7] Although nowadays pincer complexes are in most cases considered as depot forms of palladium nanoparticles, the involvement of Pd^{IV} intermediates in the catalytic cycle still cannot be excluded completely.[8–10]

We report herein the catalytic activity of aminophosphine-based pincer complexes of palladium with the general formula $[(C_6H_3\text{-}2,6\text{-}\{XP(piperidinyl)_2\}_2Pd(Cl)]$ (X = NH **1**; X = O **2**) in the arylation of olefins. Aminophosphine-based systems were chosen because of their high σ-donor strength and the possibility to facilitate the accessibility of Pd^{IV} inter-

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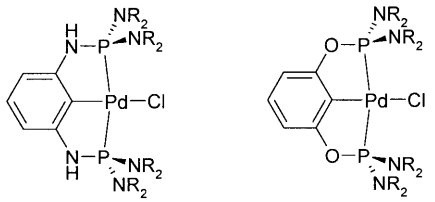
mediates by additional electron donation through the nitrogen lone pairs. On the other hand, if pincer complexes are stable and clean sources of palladium nanoparticles, the aminophosphines should promote their formation and lead to enhanced catalytic activities when compared with their phosphine and phosphite analogues. Our results indicate that homogeneous Pd^0 species derived from **1** (and **2**) are not the active forms of the catalysts, whereas the involvement of palladium nanoparticles in the catalytic cycle received strong experimental support. Although pincer-type Pd^{IV} intermediates are not involved in Heck reactions catalyzed by **1** (and **2**) and also never have been detectable with other pincer-type complexes, their general accessibility cannot be excluded in reactions with aryl halides performed at elevated temperatures. In contrast, our experimental findings clearly indicate that pincer-type Pd^{IV} intermediates (derived from **1** and **2**) are accessible and thus, should be considered as intermediates in reactions involving aryl halides at elevated temperatures.

Results and Discussion

The aminophosphine-based pincer complexes **1** and **2** were readily prepared by the sequential addition of 1,1′,1″-phosphinetriyltripiperidine and 1,3-diaminobenzene or resorcinol to solutions of $[Pd(cod)(Cl)_2]$ (cod = cyclooctadiene) in toluene under N_2 in "one pot".[11] Removal of the volatiles under reduced pressure and subsequent extractions with diethyl ether gave pure **1** and **2** in high yields.[7]



1 R = piperidyl **2**

Both complexes show exceptional high activity in the catalytic arylation of olefins with aryl bromides, leading to very high conversion rates and quantitative yields in short reaction times using low catalyst loadings, even for the use of electronically deactivated and sterically hindered substrates (Table 1). In Heck reactions performed with aryl bromides, catalyst **2** is generally less active than **1**.[12] For example, bromobenzene and styrene underwent complete C–C coupling in the presence of only 0.002 mol% of **1** and K_2CO_3 within 2.5 h in DMF at 140 °C, whereas a reaction time of 10 h was necessary with catalyst **2** (Table 1, entries 1 and 2). Complete conversion of 1,3-dibromobenzene and styrene into 1-[2-phenylvinyl]-3-[2-phenylvinyl]benzene was achieved after 3.5 h (Table 1, entry 4). The same level of activity was observed with the electronically deactivated 4-bromoanisole and 4-methoxystyrene, as well as the sterically hindered 2-bromotoluene (Table 1, entries 5–8). A decrease in activity was observed by using 2-bromo-*m*-xylene as substrate, for which 95% conversion was obtained after 8 h (Table 1, entry 9). Heck reactions performed with *N,N*-dimethyl acrylamide exhibit very similar conversion rates and yields to those with styrene (Table 1, entries 10–16). Complete product formation and excellent selectivities but slightly retarded conversion rates were observed with *n*-butyl acrylate as coupling partner (Table 1, entries 17–21). For instance, using deactivated 4-bromoanisole or sterically hindered 2-bromotoluene as substrate led to quantitative ($\geq$97%) product formation within 4.5 h in the presence of only 0.005 mol% of **1**. A conversion of 65% was observed after 12 h when 2-bromo-*m*-xylene was coupled with *n*-butyl acrylate (Table 1, entry 22). Quantitative product formation but further retardation of the conversion rates accompanied by low selectivity was observed after 5–8 h with 0.005 mol% of **1** with the electronically deactivated *n*-butyl vinyl ether (Table 1, entries 23–28). Even the sterically hindered 2-bromo-*m*-xylene was converted to 72% of product after only 8 h (Table 1, entry 28). When the amount of catalyst was increased to 0.02 mol%, 4-vinylpyridine undergoes quantitative coupling with bromobenzene, electronically deactivated 4-bromoanisole, and sterically hindered 2-bromotoluene within 8–12 h (Table 1, entries 29–31). An 85% yield was obtained within 44 h when 2-bromo-*m*-xylene was used as coupling partner (Table 1, entry 32). Heck reactions performed with 4-vinylpyridine are slower due to the ligating property of the substrate, as shown by reactions between $[(C_6H_3\text{-}\{NHP(piperidinyl)_2\}_2Pd][BF_4]$ (**3**) and pyridine, which resulted in its stable adduct **4**.[13] Further retardation was noticed with 2-vinylpyridine (Table 1, entry 33), most probably due to chelation.

The exceptional high catalytic activity of **1** was demonstrated further in an exemplary "large-scale" reaction, in which bromobenzene (210 mL; 2.0 mol) and styrene (250 mL; 2.4 mol) were coupled in the presence of only 0.00002 mol% of catalyst. Quantitative conversion was achieved after 36 h (Table 1, entry 3). When the reaction temperature was raised to 160 °C, 1,1′,1″-ethene-1,1,2-triyltribenzene was quantitatively formed within 20 h on addition of 1.1 equivalents of bromobenzene to solutions of (*E*)-stilbene in DMF (Table 1, entry 34). Notably, the same product was formed quantitatively within 24 h under identical reaction conditions by either using 1,1-diphenylethene as substrate, or by adding 2.2 equivalents of bromobenzene to solutions of styrene in DMF.

Remarkably, in contrast to Heck reactions performed with aryl bromides, catalysts **1** and **2** show the same level of activity with aryl chlorides as substrates.[14] For instance, when in the presence of 0.01 mol% of catalyst and about 15% of tetrabutylammonium bromide in 1-methyl-2-pyrrolidone (NMP) at 160 °C, the electronically activated 4-chloroacetophenone and *N,N*-dimethyl acrylamide or styrene were coupled almost quantitatively to (2*E*)-3-(4-acetylphenyl)-*N,N*-dimethylprop-2-enamide and 1-{4-[(*E*)-2-phenylethenyl]phenyl}ethanone, respectively, within 2.5 h (Table 2, en-

Table 1. Heck coupling of aryl bromides with various olefins catalyzed by $[C_6H_3$-2,6-{XP(piperidinyl)$_2$}$_2$Pd(Cl)] (X = NH **1**; X = O **2**).[a]

Entry	Aryl halide	Olefin	Cat. (ppm)	Conv. [%][b] (*cis*/*trans*/*gem*)	*t* [h]	TOF[c]	TON[d]
1	bromobenzene	styrene	**1** (20)	>99 (0/10/1)	2.5	19880	49700
2	bromobenzene	styrene	**2** (20)	96 (0/10/1)	10	4800	48000
3[e]	bromobenzene	styrene	**1** (0.2)	>99 (0/10/1)	36	138333	4980000
4	1,3-dibromobenzene	styrene	**1** (20)	>99 (1/7/0)[f]	3.5	14157	49550
5	4-bromoanisole	styrene	**1** (20)	99 (0/10/1)	2.5	19800	49500
6	4-bromoanisole	styrene	**2** (20)	97 (0/10/1)	11	4409	48500
7	bromobenzene	4-methoxystyrene	**1** (20)	97 (0/10/1)	2.5	19400	48500
8	2-bromotoluene	styrene	**1** (20)	98 (0/20/1)	2.5	19600	49000
9[g]	2-bromo-*m*-xylene	styrene	**1** (50)	95 (2/80/1)	8	2375	19000
10	bromobenzene	*N,N*-dimethyl acrylamide	**1** (20)	100 (1/20/0)	2	25000	50000
11	bromobenzene	*N,N*-dimethyl acrylamide	**2** (20)	100 (1/25/0)	10	5000	50000
12	1,3-dibromobenzene	*N,N*-dimethyl acrylamide	**1** (20)	>99 (1/10/0)[f]	2.5	19872	49680
13	4-bromoanisole	*N,N*-dimethyl acrylamide	**1** (20)	99 (1/20/0)	2.5	19800	49500
14	4-bromoanisole	*N,N*-dimethyl acrylamide	**2** (20)	95 (2/80/1)	12	3958	47500
15	2-bromotoluene	*N,N*-dimethyl acrylamide	**1** (20)	100 (1/40/0)	4	12500	50000
16[g]	2-bromo-*m*-xylene	*N,N*-dimethyl acrylamide	**1** (50)	79 (0/1/0)	8	1975	15800
17	bromobenzene	*n*-butyl acrylate	**1** (50)	100 (1/100/1)	4.5	4444	20000
18	bromobenzene	*n*-butyl acrylate	**2** (50)	93 (1/100/0)	12	775	9300
19	1,3-dibromobenzene	*n*-butyl acrylate	**1** (50)	>99 (1/20/0)[f]	4.5	4436	19960
20	4-bromoanisole	*n*-butyl acrylate	**1** (50)	99 (1/100/0)	4.5	4400	19800
21	2-bromotoluene	*n*-butyl acrylate	**1** (50)	97 (1/200/0)	4.5	4311	19400
22[g]	2-bromo-*m*-xylene	*n*-butyl acrylate	**1** (50)	65 (1/100/0)	12	1083	13000
23	bromobenzene	*n*-butyl vinyl ether	**1** (50)	100 (2/4/3)	5	4000	20000
24	bromobenzene	*n*-butyl vinyl ether	**2** (50)	99 (2/4/3)	16	1238	19800
25	1,3-dibromobenzene	*n*-butyl vinyl ether	**1** (50)	>99[h]	8	2493	19940
26	4-bromoanisole	*n*-butyl vinyl ether	**1** (50)	96 (1/2/3)	5	3840	19200
27	2-bromotoluene	*n*-butyl vinyl ether	**1** (50)	98 (2/4/3)	6	3267	19600
28[g]	2-bromo-*m*-xylene	*n*-butyl vinyl ether	**1** (50)	72 (5/3/5)	8	1800	14400
29[g]	bromobenzene	4-vinylpyridine	**1** (200)	100 (2/50/0)	8.5	589	5000
30[g]	4-bromoanisole	4-vinylpyridine	**1** (200)	>99 (1/20/0)	8.5	585	4972
31[g]	2-bromotoluene	4-vinylpyridine	**1** (200)	100 (1/20/0)	12	417	5000
32[g]	2-bromo-*m*-xylene	4-vinylpyridine	**1** (200)	85 (1/40/0)	44	97	4250
33[g]	bromobenzene	2-vinylpyridine	**1** (200)	53 (1/10/0)	60	44	2650
34[i]	bromobenzene	(*E*)-stilbene	**1** (50)	98	20	980	19600

[a] Reaction conditions: 4.0 mmol aryl halide, 4.4 mmol olefin, 4.4 mmol K_2CO_3, 5 mL DMF, catalyst (synthesized in one pot and used without purification) added in solution (toluene), reaction performed at 140 °C under N_2 atmosphere. [b] Determined by GC/MS, based on aryl halide. [c] Defined as mol product per mol of catalyst per hour. [d] Defined as mol product per mol of catalyst. [e] 2.0 mol aryl halide, 2.4 mol olefin, 2.4 mol K_2CO_3, 1 L DMF. [f] Product distribution refers to (*cis*–*trans*/*trans*–*trans*/*gem*–*trans*). [g] Reactions performed in NMP. [h] All possible isomers with similar yields were obtained. [i] Reaction performed at 160 °C.

tries 1–4). When the reaction temperature was raised to 200 °C, even nonactivated, deactivated, and *ortho*-substituted aryl chlorides were successfully coupled with olefins. For example, reactions performed with chlorobenzene and *N,N*-dimethyl acrylamide afforded the coupling product in 77% yield in the presence of catalyst **1** and in 91% yield with catalyst **2** after 16 h (Table 2, entries 5 and 6). Remarkably, even the sterically hindered 2-chloro-*m*-xylene was converted to about 60% of the product after 28 h in the presence of **1** with *N,N*-dimethyl acrylamide as coupling partner (Table 2, entry 7). A prolonged reaction time was required with the electronically deactivated 4-chloroanisole as substrate (Table 2, entry 8). A conversion of 80% was achieved within 12 h when chlorobenzene was coupled with 4-methylstyrene (Table 2, entry 9). Even higher conversions were observed after 18 h when chlorobenzene or 4-chlorotoluene were allowed to react with 4-methylstyrene or 4-methoxystyrene as coupling partners (Table 2, entries 10–13).

Overall, **1** and **2** belong to the most active and most convenient Heck catalysts reported up to date, since their catalyst solutions are readily prepared from very cheap starting materials in "one pot", whose solutions in toluene can be used directly for catalytic reactions without purification. The catalyst solutions remain stable for several months at room temperature, affording the coupling products at essentially the same conversion rates and yields as freshly prepared catalyst solutions from pure **1** and **2**, respectively. In addition, **1** (and to a minor extent **2**) are more efficient in the majority of the coupling reactions performed with aryl bromides than the reference systems $[(PC^{NHC}P)Pd(Cl)]Cl$ ($PC^{NHC}P$ = 1,3-bis[2-(diphenylphosphanyl)ethyl]-1*H*-imidazol-3-ium-2-ide),[15] $[Pd(OAc)_2]$,[16] $[C_6H_3$-2,6-$(CH_2PiPr_2)_2Pd(TFA)]$,[2a] (TFA = trifluoroacetate) cationic $[(C_5H_3N$-2,6-$(NHC^{Me})Pd(Br)]^+$ (NHC^{Me} = 3,3′-(pyridine-2,6-diyldimethanediyl)bis(1-methyl-1*H*-imidazol-3-ium-2-ide)[17] and also Herrmann's systems such as $[(NHC^{Me})_2Pd]$, $[(C_6H_4$-2-{$CH_2P(tBu)_2$}$Pd(OAc)]$ and $[(C_7H_6)(PPh_3)Pd(Cl)_2]$.[18] Comparisons with the highly active $[Pd_2(dba)_3]/P(tBu)_3$ (dba = dibenzylideneactone)[3b,4] are difficult, since the Heck reactions were generally performed at room temperature. Similarly, Heck

Table 2. Heck coupling of aryl chlorides with various olefins catalyzed by $[C_6H_3\text{-}2,6\text{-}\{XP(piperidinyl)_2\}_2Pd(Cl)]$ (X = NH **1**; X = O **2**).[a]

Entry	Aryl halide	Olefin	Cat.	Conv. [%][b] (*cis*/*trans*/*gem*)	*t* [h]	TOF[c]	TON[d]
1[e]	4-chloroacetophenone	styrene	**1**	100 (5/100/1)	2.5	4000	10000
2[e]	4-chloroacetophenone	styrene	**2**	95 (0/1/0)	2.5	3800	9500
3[e]	4-chloroacetophenone	*N,N*-dimethyl acrylamide	**1**	99 (0/1/0)	2.5	3960	9900
4[e]	4-chloroacetophenone	*N,N*-dimethyl acrylamide	**2**	96 (0/20/1)	2.5	3840	9600
5	chlorobenzene	*N,N*-dimethyl acrylamide	**1**	77 (3/100/1)	16	583	7000
6	chlorobenzene	*N,N*-dimethyl acrylamide	**2**	91 (0/60/1)	16	683	8200
7	2-chloro-*m*-xylene	*N,N*-dimethyl acrylamide	**1**	57 (0/1/0)	28	204	5700
8	4-chloroanisole	*N,N*-dimethyl acrylamide	**1**	66 (0/1/0)	72	92	6600
9	chlorobenzene	4-methylstyrene	**1**	82 (1/80/10)	12	683	8200
10	4-chlorotoluene	4-methylstyrene	**1**	80 (1/7/0)	18	444	8000
11	chlorobenzene	4-methoxystyrene	**1**	90 (1/100/10)	18	500	9000
12	chlorobenzene	4-methoxystyrene	**2**	100 (1/100/10)	18	556	10000
13	4-chlorotoluene	4-methoxystyrene	**2**	98 (0/8/1)	18	544	9800

[a] Reaction conditions: 4.0 mmol aryl halide, 6.0 mmol olefin, 4.4 mmol K_2CO_3, 0.6 mmol tetrabutylammonium bromide, 5 mL NMP, 0.01 mol% of catalyst (synthesized in one pot and used without purification) added in solution (toluene), reaction performed at 200°C under N_2 atmosphere. [b] Determined by GC/MS, based on aryl halide. [c] Defined as mol product per mol of catalyst per hour. [d] Defined as mol product per mol of catalyst. [e] Reaction performed at 160°C.

reactions performed with aryl chlorides are difficult to compare because most of the reference systems, such as $[C_6H_3\text{-}2,6\text{-}(OPiPr_2)_2Pd(Cl)]$,[2d] $[Pd_2(dba)_3]/P(tBu)_3$[3b] and $[Pd(Cl)_2]/PR_3$[19] perform the Heck reaction at different reaction temperatures.

The change of base or solvent strongly influences the conversion rates and yields: best results were observed with K_2CO_3 or K_3PO_4 as base, whereas sodium acetate, sodium hydroxide, or potassium *tert*-butoxide were not appropriate, since they lead to fast deposition of inactive palladium black. Also the use of amines, such as NEt_3, is not practical due to their ligating properties and inhibits catalysis efficiently. Similarly, while comparable activities were found in DMF and NMP, replacement of these solvents by *p*-xylene or DMSO led to a dramatic drop in activity.[20] Lowering the reaction temperature has the same effect: reactions performed with bromobenzene and styrene in DMF in the presence of 0.002 mol% of catalyst **1** only led to about 7% conversion after 3 h at 100°C. Almost no catalytic activity was observed below 80°C. Catalyst concentrations of >0.1 mol% are also not appropriate and led to fast deposition of inactive palladium black.

Accordingly, experiments were carried out to gain mechanistic insights. The addition of mercury to reaction mixtures of aryl bromides, olefins, and **1** (or **2**) efficiently inhibit catalysis.[8f–h,21,22] Sigmoidal-shaped kinetics with induction periods between 30 and 45 min were observed in all the coupling reactions performed with aryl bromides (Figure 1). The same observations were made with $[C_6H_3\text{-}2,6\text{-}\{NHP(piperidinyl)_2\}_2Pd][BF_4]$ (**3**). The addition of 2–3 drops of water to the reaction mixtures (to promote the formation of palladium nanoparticles) leads to significantly decreased induction periods.[23] Whereas the induction period remains unchanged when tetrabutylammonium bromide (ca. 15 mol% relative to the aryl halide) was added to catalytic reactions performed with aryl bromides, retarded conversion rates were noticed.[24,25] This is in sharp contrast to the observations made at 200°C in NMP with aryl chlorides as

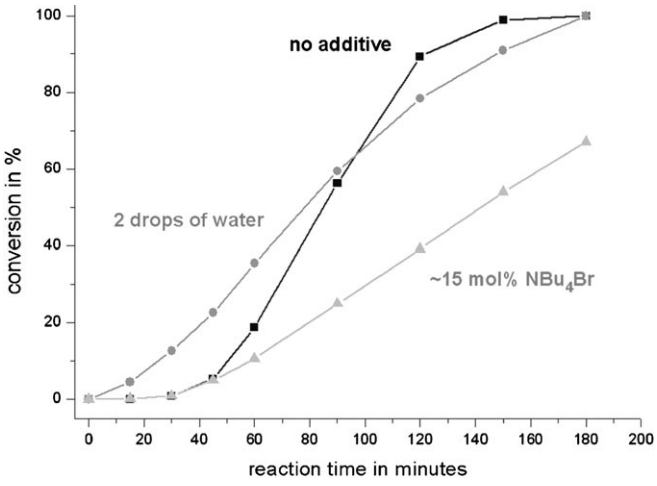


Figure 1. Kinetics of the coupling reaction of 4-bromoanisole with styrene in the presence and in the absence of additives, catalyzed by 0.002 mol% of **1** at 140°C in DMF (Table 1, entry 5).

coupling partners: whereas only low conversions were observed in the absence of tetrabutylammonium bromide (fast deposition of inactive palladium black was observed), significantly improved conversion rates and yields were found when about 15 mol% of tetrabutylammonium bromide was present in the reaction mixtures. The presence of 0.3 equivalents of thiophene or 0.05 equivalents of PPh_3 relative to the catalyst neither had an influence on the conversion rate nor on the yield.[26,27] This is in sharp contrast to CS_2, which effectively stopped catalysis when 0.5 equivalents (relative to catalyst) were present. The effect of CS_2 on the performance in the Heck reaction catalyzed by **1** (and **2**) is due to catalyst degradation involving P–N bond cleavage and (partial) formation of the bis(piperidine-1-carbodithioato)palladium complex $[Pd(S_2CNpiperidyl)_2]$ (**5**), which shows no catalytic activity in the Heck reaction. Indeed, reactions of **1** (and **2**) with an excess (ca. 20 equiv) of CS_2 at room temperature yielded complex **5** in almost quantitative yield. The identity

of **5** was confirmed by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy as well as by X-ray diffraction crystallographic analysis.[13,28] Under catalytic reaction conditions, piperidine-1-carbodithioate probably dissociates from **5**, and blocks the active centers of the palladium nanoparticles, if formed. Overall, **1**, **2**, (and **3**) most probably are pre-catalysts and palladium nanoparticles are their active form. This would be in line with the fact that neither **1** nor **2** (nor their bromo derivatives) were detectable in the reaction mixtures after catalysis (different catalyst concentrations were tested) and the observation that the turnover frequency (TOF) increases with increasing substrate/catalyst ratios.[29]

To test if transformations of **1** (or **2**) into homogeneous Pd^{0} complexes are involved in the catalytic cycle, the following new method to trace such species *under catalytic reaction conditions* was developed. Benzyl chloride is known to induce clean and fast electron transfers from Pd^{0} complexes, thereby forming dibenzyl. For instance, $[C_6H_3\text{-}2,6\text{-}(CH_2P\textit{i}Pr_2)_2Pd(Cl)]$ (**6**) undergoes collapse of the pincer framework to form a binuclear Pd^{0}/Pd^{II} complex $[Pd\{C_6H_3\text{-}2,6\text{-}(CH_2P\textit{i}Pr_2)_2\}Pd]$ (**7**) incorporating a 14-electron linear Pd^{0} center and a "butterfly"-type Pd^{II} 16-electron center under strongly reducing reaction conditions. Subsequent addition of an excess (5.0 equiv) of benzyl chloride to solutions of **7** in DMF (or NMP) instantly induced an electron transfer, regenerating the pincer complex **6** accompanied by the formation of a corresponding amount of dibenzyl.[31] Similarly, reactions between benzyl chloride and $[Pd(PPh_3)_4]$ (**8**), $[Pd(C_6H_5CH_2P\textit{i}Pr_2)_2]$[32] (**9**) or $[Pd\{P(piperidinyl)_3\}_2]$[13] (**10**), which was prepared in high yields (93%) by direct reduction of $[Pd\{P(piperidinyl)_3\}_2(Cl)_2]$ (**11**) with sodium metal overnight, cleanly gave their Pd^{II} chloro derivatives and a corresponding amount of dibenzyl, as detected by GC/MS. An X-ray structure analysis of **10** is shown in Figure 2. Compound **11** and a corresponding amount of dibenzyl were detected when benzyl chloride was added to pre-heated (140°C) reaction mixtures of **10**, bromobenzene, styrene, and K_2CO_3. Importantly, in the reference reactions (solutions of **1** (or **2**) in DMF containing either an excess of benzyl chloride or reaction mixtures of benzyl chloride, bromobenzene, styrene, and K_2CO_3) no dibenzyl was detectable after 4 h at 140°C, offering the possibility to trace homogeneous Pd^{0} complexes by dibenzyl detection *under catalytic reaction conditions*.[34] Since in the Heck reactions catalyzed by **1** (or **2**) no dibenzyl was detectable,[35] the involvement of complexes with Pd^{0} centers as the active form of the catalysts were excluded. The same results were obtained with **6** (and **14**), which thereby rules out that homogeneous Pd^{0} complexes are the catalytically active form of phosphine- and phosphite-based pincer complexes. This is in line with previous investigations performed on **6** and **14**.[2a,b,h]

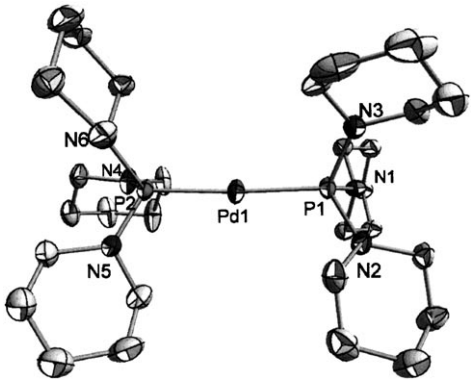


Figure 2. ORTEP diagram of a molecule of **10**, showing the atom labeling scheme (50% probability).[33] Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd1–P1 2.2590(11), Pd1–P2 2.2567(12), P1–N1 1.716(4), P1–N2 1.673(4), P1–N3 1.684(4), P2–N4 1.659(5), P2–N5 1.691(4), P2–N6 1.722(4); P1-Pd1-P2 174.88(4).

Although Pd^{IV} intermediates derived from **1** (and **2**) are not involved in the catalytic cycle in the Heck reaction, it is important to mention that their thermal accessibility received strong experimental and computational (see below) support. Reaction mixtures of **1** (and **2**) and bromobenzene show a halide exchange in DMF (or NMP) at 100°C, leading to their bromo derivatives $[C_6H_3\text{-}2,6\text{-}\{XP(piperidinyl)_2\}_2Pd(Br)]$ (X=NH **12**; X=O **13**) and phenyl chloride, as detected by GC/MS.[36,37] In analogy to the catalytic arylation of olefins, lowering the reaction temperatures reduces the conversion rates. Similarly, the halide exchange is strongly solvent dependent and exhibits the highest conversion rates in DMF and NMP, whereas the lowest rates are observed in *p*-xylene and DMSO.[39] This observation could be interpreted by the formation of ion pairs, such as $[C_6H_3\text{-}2,6\text{-}\{XP(piperidinyl)_2\}_2Pd]Cl$ or $[C_6H_3\text{-}2,6\text{-}\{XP(piperidinyl)_2\}_2Pd(Br)(Ph)]Cl$ (X=NH or O). This anticipation got experimental support from the addition of equimolar amounts (relative to bromobenzene) of pyridine to solutions of **1** (or **2**) and bromobenzene in DMF, which significantly retarded the halide exchange due to adduct formation. The oxidative addition of bromobenzene to **1** (and to **2**) became evident from the observation that no halide exchange at all was observed when **6** or $[C_6H_3\text{-}2,6\text{-}(OP\textit{i}Pr_2)_2Pd(Cl)]$ (**14**) were treated with bromobenzene under identical reaction conditions.[2h] Steric parameters of these complexes are almost identical and hence, should have no effect. Apparently, the electron density on the metal centers is not relevant either: whereas the electron density of **6** is comparable to that of **1**, the one of **14** is the lowest.[40] Thus, reaction paths involving a nucleophilic attack of chloride on the C_{ipso} atom of coordinated bromobenzene can be excluded. The nitrogen lone pairs of the aminophosphines, which apparently facilitate the formation of Pd^{IV} intermediates, provide the only explanation for the striking difference in the reactivity of **1** and **2** when compared with that of the pincer complexes **6** and **14**, respectively.[37] To gain more mechanistic insights into the halide-exchange reaction of **1** (and **2**) with bromobenzene, DFT calculations were performed using the experimental system with the sterically demanding $P(piperidinyl)_2$ groups. The potential energy surface is simulated in DMF as solvent and is shown in Figure 3 along with a schematic illustration of the local minima and transition states.[42] Dissociation of the chloride ligand from **1** to form ion pair **A** (+

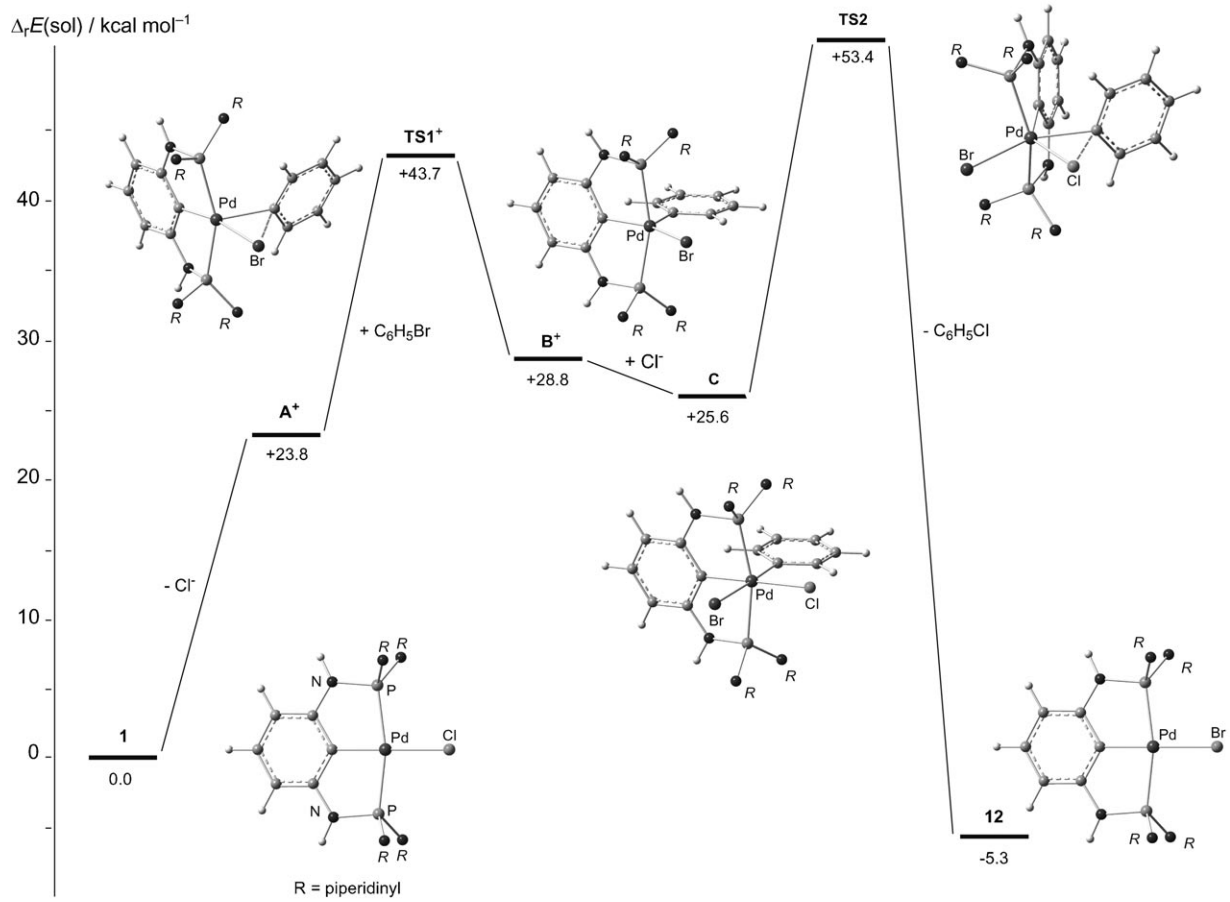


Figure 3. Calculated reaction pathway of the reaction of **1** with bromobenzene in DMF.

23.8 kcal mol^{-1}) is anticipated to initiate the reaction sequence.[43] Oxidative addition of bromobenzene to $\mathbf{A}^+$ results in the cationic Pd^{IV} intermediate $\mathbf{B}^+$ (+28.8 kcal mol^{-1}), which is only 5.0 kcal mol^{-1} higher in energy than $\mathbf{A}^+$. The energetic barrier, that is, the energy difference between $\mathbf{A}^+$ and the transition state $\mathbf{TS1}^+$, is only +19.9 kcal mol^{-1}. Re-coordination of the chloride generates **C**, which has a computed energy of +25.6 kcal mol^{-1}. The reductive elimination of chlorobenzene from **C** to yield complex **12** is exothermic (the energy difference between **1** and **12** is −5.3 kcal mol^{-1}) and accompanied by a calculated barrier (**TS2**) of +27.8 kcal mol^{-1}.

In conclusion, the halide exchange demonstrated that pincer-type Pd^{IV} intermediates (derived from **1** and **2**) are principally accessible at elevated reaction temperatures (in particular when polar solvents, such as DMF or NMP, or pincer complexes containing labile anionic ligands are used) in reactions with aryl halides.[44] Although palladium nanoparticles are the active form in the Heck reaction catalyzed by *aminophosphine*- (and *phosphite*-) based pincer complexes,[2h] this is not necessarily the case for *phosphine*-based pincer complexes, where Pd^{IV} species might indeed be the key intermediates in the catalytic cycle.[2a,45]

Conclusion

The aminophosphine-based pincer complex **1** is nowadays one of the most efficient and convenient Heck catalysts, promoting quantitative C–C coupling of deactivated and sterically hindered aryl bromides with various olefins in very short reaction times and with low catalyst loadings. Increased reaction temperatures offer the possibilities to either quantitatively prepare trisubstituted olefins or to perform coupling reactions even with deactivated and sterically hindered aryl chlorides with various olefins as coupling partner. Mechanistic investigations indicate that homogeneous Pd^0 complexes are not the active form of pincer-type palladium catalysts (a new method to test this possibility was developed), which is in line with previous investigations. On the other hand, the involvement of palladium nanoparticles in the Heck reactions catalyzed by **1** (and **2**) received strong experimental evidence (sigmoidal-shaped kinetics, of which the induction periods were significantly shortened, for example, by the addition of few drops of water). Although our results indicate that palladium nanoparticles are the active form of *aminophosphine*-based pincer complexes, the accessibility of aminophosphine-based Pd^{IV} intermediates, however, was experimentally and computationally shown. This implies that its Pd^{IV} intermediates are generally to be consid-

ered as reactive intermediates in reactions (such as the Suzuki–Miyaura cross-coupling) catalyzed by pincer complexes of palladium with aryl halides performed at elevated temperatures. Detailed computational studies addressing this issue in the Heck reaction catalyzed by pincer complexes are currently in progress.

Experimental Section

General procedures: All synthetic operations were carried out in oven-dried glassware using a combination of glovebox (M. Braun 150B-G-II) and Schlenk techniques under a dinitrogen atmosphere. Solvents were reagent grade or better, freshly distilled under a N_2 atmosphere by standard procedures, and degassed by freeze–thaw cycles before use. Deuterated solvents were purchased from Armar, stored in a Schlenk tube (Teflon tap) over CaH_2, distilled, and degassed prior to use. All the chemicals were purchased from Aldrich Chemical Co., Acros Organics, or Fluka, and used without further purification.

Analysis: ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR data were recorded at 500.13, 125.76, and 202.46 MHz, respectively, on a Bruker DRX-500 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm), coupling constants (J) are in Hz. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as an internal standard for ^{1}H ($\delta = 5.32$ ppm dichloromethane) and *all*-D solvent signals for ^{13}C ($\delta = 53.5$ ppm dichloromethane). ^{31}P{^{1}H} NMR data are reported downfield relative to external 85% H_3PO_4 in D_2O at $\delta = 0.0$ ppm. All measurements were carried out at 298 K. Abbreviations used in the description of NMR data are as follows: s, singlet; d, doublet; t, triplet; dist q, distinct quartet; m, multiplet; v, virtual. IR spectra were obtained by ATR methods with a Bio-Rad FTS-45 FTIR spectrometer. Elemental analyses were performed on a Leco CHNS-932 analysator at the University of Zurich, Switzerland.

Preparation of $[C_6H_3\{NHP(piperidinyl)_2\}_2Pd(NC_5H_5)][BF_4]$ (4): $AgBF_4$ (14.5 mg, 0.07 mmol) was added to a solution of **1** (48.0 mg, 0.07 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 15 min under rigorous exclusion of light and then filtered through celite. Subsequent addition of two drops of pyridine yielded complex **4**. After removal of the solvent and residual pyridine under reduced pressure, the solid was washed with diethyl ether (2×5 mL). The residue was dried in vacuo to **4** as a white solid (53.7 mg, 0.07 mmol; 93%).

^{31}P{^{1}H} NMR (CD_2Cl_2, TMS): $\delta = 117.5$ (s, $P\{CH(CH_3)_2\}_2$); ^{1}H NMR (CD_2Cl_2, TMS): $\delta = 8.56$ (dt, $^4J_{H,H} = 1.8$ Hz, $^3J_{H,H} = 1.5$ Hz, 2H; Ar'_{ortho}), 8.04 (tt, $^3J_{H,H} = 6.3$ Hz, $^4J_{H,H} = 1.8$ Hz, 1H, Ar'_{para}), 7.64 (dt, $^3J_{H,H} = 6.3$ Hz, $^3J_{H,H} = 1.5$ Hz, 2H; Ar'_{meta}), 6.87 (tt, $^3J_{H,H} = 7.8$ Hz, $^4J_{P,H} = 2.1$ Hz, 1H; Ar_{para}), 6.21 (d, $^3J_{H,H} = 7.8$ Hz, 2H; Ar_{meta}), 4.93 (s, 2H; N*H*), 3.01 (broad s, 16H; NCH_2), 1.56 (m, 8H; $NCH_2CH_2CH_2$), 1.47 ppm (m, 16H; NCH_2CH_2); ^{13}C{^{1}H} NMR (CD_2Cl_2, TMS); 152.3 (s, Ar'_{ortho}), 151.1 (vt, $J_{P,C} = 63.5$ Hz, *Ar*NHP), 146.1 (s, Ar'_{para}), 129.9 (s, Ar_{para}), 127.0 (s, Ar'_{meta}), 120.0 (unresolved t, Ar_{ipso}), 103.5 (vt, $J_{P,C} = 39.0$ Hz, Ar_{meta}), 47.4 (vt, $J_{P,C} = 13.2$ Hz, PNCH_2), 26.9 (vt, $J_{P,C} = 11.9$ Hz, $PNCH_2CH_2$), 25.2 ppm (s, $PNCH_2CH_2CH_2$); elemental analysis calcd (%) for $C_{31}H_{50}BF_4N_7P_2Pd$: C 47.99, H 6.49, N 12.64; found: C 48.31, H 6.65, N 12.42.

Preparation of $[Pd(S_2CNpiperidyl)_2]$ (5): An excess (ca. 20 equiv) of CS_2 was added to a solution of **1** (28.0 mg, 0.04 mmol) in dichloromethane (2 mL). Degradation of complex **1** was noticed within a few minutes, as shown by ^{31}P{^{1}H} NMR spectroscopy. Large crystals of **5** (17.9 mg, 0.04 mmol; 97%) were grown within two weeks from the reaction mixture. The crystals were isolated, washed with small portions of cold pentane, dried, and analyzed by various NMR techniques and X-ray diffraction.[21]

Preparation of $[Pd\{P(piperidinyl)_3\}_2]$ (10): A solution of $[Pd(Cl)_2\{P(piperidinyl)_3\}_2]$ (230 mg, 0.310 mmol) in THF (20 mL) and a large excess of sodium metal (ca. 100 equiv) was stirred at room temperature overnight. After filtration of the reaction mixture through celite, the solvent was removed under reduced pressure. Compound **10** was extracted with pentane (3×10 mL), filtered, and dried again. The product was obtained in 93% yield (194 mg, 0.288 mmol).

^{31}P{^{1}H} NMR (CD_2Cl_2, TMS): $\delta = 105.8$ ppm (s, $P(CH(CH_3)_2)_2$); ^{1}H NMR (CD_2Cl_2, TMS): $\delta = 3.17$ (br.s, 24H; NCH_2), 1.57 (br.s, 12H; $NCH_2CH_2CH_2$), 1.51 ppm (br.s, 24H; NCH_2CH_2); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 48.5$ (vt, $J_{P,C} = 13.6$ Hz; NCH_2), 27.2 (vt, $J_{P,C} = 8.3$ Hz; NCH_2CH_2), 25.7 (s, $NCH_2CH_2CH_2$); elemental analysis calcd (%) for $C_{30}H_{60}N_6P_2Pd$: C 53.53, H 8.98, N 12.48; found: C 53.26, H 8.98, N 12.38.

Preparation of $[C_6H_3$-2,6-$(OPiPr_2)_2Pd(CO)][BF_4]$: $AgBF_4$ (13.0 mg, 0.07 mmol) was added to a solution of $[C_6H_3$-2,6-$(OPiPr_2)_2Pd(Cl)]$ (32.2 mg, 0.07 mmol) in dichloromethane (10 mL). The reaction mixture was stirred for 15 min under rigorous exclusion of light. The reaction mixture was filtered through celite. The solvent was removed under reduced pressure. Treating a solution of $[C_6H_3$-2,6-$(OPiPr_2)_2Pd][BF_4]$ in CD_2Cl_2 with an excess (ca. 50 equiv) of CO gas yielded its carbonyl adduct. CO release was observed under reduced pressure, hence an elemental analysis was not obtained.

^{31}P{^{1}H} NMR (CD_2Cl_2, TMS): $\delta = 186.4$ ppm (s, $P(CH(CH_3)_2)_2$); ^{1}H NMR (CD_2Cl_2, TMS): $\delta = 7.26$ (t, $^3J_{H,H} = 8.3$ Hz, 1H; Ar*H*), 6.78 (d, $^3J_{H,H} = 8.3$ Hz, 2H; Ar*H*), 2.61 (m, 4H; $CH(CH_3)_2$), 1.31 (dist q, $J_= 7.8$ Hz, 12H; $CH(CH_3)_2$), 1.22 ppm (dist q, $J_= 7.8$ Hz, 12H; $CH(CH_3)_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2, TMS): $\delta = 180.8$ (t, $^2J_{P,C} = 11.1$ Hz, *C*O), 167.4 (vt, $J_{P,C} = 6.2$ Hz, *Ar*), 134.8 (s, *Ar*), 133.2 (s, *Ar*), 107.6 (t, $^2J_{P,C} = 7.1$ Hz, *Ar*), 30.6 (vt, $J_{P,C} = 11.6$ Hz, $CH(CH_3)_2$), 17.8 (s, $CH(CH_3)_2$), 17.1 ppm (s, $CH(CH_3)_2$); IR (ATR): $\tilde{\nu} = 2141$ cm^{-1} (s, CO).

Reactions with benzyl chloride: Benzyl chloride (3.0 equiv) was added to solutions of **8**, **9**, and **10** (30 mg), respectively, in dichloromethane, and stirred for about 15 min. Samples taken from the reaction mixtures were diluted with dichloromethane and analyzed by GC/MS. After evaporation of the solvent the reaction mixtures were washed with small portions of cold pentane (3×2 mL), which gave the pure dichloropalladium complexes with the general formula $[Pd(PR_3)_2(Cl)_2]$ ($PR_3 = PPh_3$, $C_6H_5CH_2PiPr_2$ or P(piperidinyl)$_3$) as shown by various NMR techniques.

Procedure for the "one-pot" synthesis of catalyst solutions of 1 and 2: In a Young Schlenk $[Pd(cod)Cl_2]$ (100 mg, 0.35 mmol) was suspended in toluene (50 mL). After the addition of solutions containing two equivalents of 1,1′,1″-phosphinetriyltripiperidine (198.5 mg, 0.70 mmol) in toluene (20 mL), the reaction mixture was stirred for 10 min. Subsequently, an equimolar amount of resorcinol or 1,3-diaminobenzene, was added to these solutions. The reaction mixtures were heated up to 100 °C and stirred until decoloration occurred. After the mixtures had been cooled to room temperature and the insoluble reaction products had been precipitated, the concentrations of the catalyst solutions were determined. Appropriate amounts from these solutions were used for catalysis.

General procedure for Heck reactions: In a Young Schlenk (10 mL) were placed appropriate amounts of the olefin, aryl halide, K_2CO_3, tetrabutylammonium bromide (in reactions performed with aryl chlorides), and the solvent. Then the correct amount of catalyst was added by syringe as a solution in toluene. The mixture was vigorously stirred and heated up to the reaction temperature. Samples, taken from the reaction mixture, were diluted with dichloromethane and analyzed by GC/MS. At the end of catalysis the reaction mixtures were allowed to cool to room temperature, quenched with aqueous HCl (2 M, 40 mL), extracted with dichloromethane (3×40 mL), and the combined extracts were dried ($MgSO_4$) and evaporated to dryness. The crude material was purified by flash chromatography on silica gel.

Acknowledgement

This work was supported by the University of Zurich and the Swiss National Science Foundation (SNSF).

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[11] The resulting catalyst solutions were used for catalytic reactions without purification and remain stable in solution for several months at room temperature, affording the coupling products at essentially the same conversion rates and yields as freshly prepared catalyst solutions from pure **1** and **2**, respectively. The concentrations of the catalyst solutions were determined prior to use.

[12] Since the steric bulk of **1** and **2** is almost identical, the higher catalytic activity of **1** can be attributed to electronic factors (the metal center of **1** being more electron-rich than **2**)[7] if Pd^{IV} intermediates are involved in the catalytic cycle. The higher stability of **2** compared with **1** could provide an explanation for its lower catalytic activity if palladium nanoparticles are the active form.

[13] See Experimental Section.

[14] The higher reaction temperature could provide an explanation for the leveled out catalytic activity of catalysts **1** and **2**, if palladium nanoparticles are the catalytically active form of the catalysts.

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[20] The low conversion rates observed in these solvents can be explained by both, ion pair and palladium nanoparticle formation. Whilst their formation is not promoted in *p*-xylene, the ligating properties of DMSO could either suppress the coordination of substrate molecules at the metal centers or stabilize the catalysts, which, in turn, would retard the formation of palladium nanoparticles.

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[22] It is important to note that the mercury drop test is not applicable here, since halide-exchange reactions of **1** (and **2**) with bromobenzene at 100 °C in DMF to form chlorobenzene and their bromo derivatives **11** (and **12**) also were inhibited in the presence of mercury (for more details regarding the halide exchange, see below).

[23] The reason for the effect of water on the induction period could be explained by decomposition of the pincer core to form the active catalyst (i.e. palladium nanoparticles). However, it should be mentioned that Shaw et al. envisioned a possible pathway in which the olefin first coordinates to the Pd center and a nucleophile then attacks the olefin, forming a palladium alkyl complex, which could facilitate the oxidative addition of the aryl halide.[9b] Water could serve as a nucleophile, thereby explaining the shortened induction period in the presence of water. To test this possibility tetrabutylammonium bromide (ca. 15 mol %) was added to the reaction mixtures. If the mechanism would proceed according to Shaw's mechanism, the added bromide should greatly reduce the induction period. The induction period remained unchanged in the presence of added bromide, which is inconsistent with Shaw's mechanism.

[24] Tetrabutylammonium bromide is known to stabilize palladium nanoparticles. See for instance: a) T. Jeffery in *Advances in Metal-Organic Chemistry, Vol. 5* (Ed.: L. S. Liebeskind), JAI Press, Greenwich, **1996**, p. 153; b) M. T. Reetz, E. Westermann, *Angew. Chem.* **2000**,

112, 170; *Angew. Chem. Int. Ed.* **2000**, *39*, 165; c) A. Zapf, M. Beller, *Chem. Eur. J.* **2001**, *7*, 2908.

[25] The presence of tetrabutylammonium bromide is anticipated to retard the conversion rates if Pd^{IV} intermediates are involved in the catalytic cycle; the bromide anions suppress the coordination of the substrate molecules at the metal center. On the other hand, the low concentration of palladium nanoparticles (if formed) may not need to be stabilized. In contrast, tetrabutylammonium bromide may slow down their formation and/or reduces their activity.

[26] a) J. A. Widegren, R. G. Finke, *J. Mol. Catal. A* **2003**, *198*, 317; b) Y. Lin, R. G. Finke, *Inorg. Chem.* **1994**, *33*, 4891; c) K. S. Weddle, J. D. Aiken III, R. G. Finke, *J. Am. Chem. Soc.* **1998**, *120*, 5653.

[27] Quantitative poisoning experiments are usually performed at temperatures below 50 °C, whereas our experiments were conducted at 140 °C. High temperatures may lead to dissociation of thiophene or PPh_3 from heterogeneous systems, thereby regenerating the catalyst. However, examples of Heck reactions performed at 180 °C with resorcinol-derived pincer complexes of palladium were effectively stopped after addition of the corresponding amounts of CS_2, thiophene, or PPh_3.[2g]

[28] a) F. Shaheen, A. Badshah, M. Gielen, M. Dusek, K. Fejfarova, D. de Vos, B. Mirza, *J. Organomet. Chem.* **2007**, *692*, 3019; b) F. Shaheen, A. Badshah, S. Anjum, A. Saqib, *Acta Crystallogr. Sect. E* **2006**, *62*, m329; c) L. Marcheselli, C. Preti, M. Tagliazucchi, V. Cherchi, L. Sindellari, A. Furlani, A. Papaioannou, V. Scarcia, *Eur. J. Med. Chem.* **1993**, *28*, 347; d) C. G. Sceney, R. Magee, *J. Inorg. Nucl. Chem.* **1974**, *10*, 323.

[29] Increasing TOF with increasing substrate/catalyst ratios is believed to be caused by the palladium which is present in the form of nanoparticles.[16a,30] At higher substrate/catalyst ratios more palladium will be in the catalytic cycle. In addition, the size of the nanoparticles will be smaller at higher substrate/catalyst ratios, making the ratio between palladium on the outer rim and palladium on the inside of the particles more favorable.

[30] M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559.

[31] C. M. Frech, L. J. W. Shimon, D. Milstein, *Angew. Chem.* **2005**, *117*, 1737; *Angew. Chem. Int. Ed.* **2005**, *44*, 1709.

[32] C. M. Frech, G. Leitus, D. Milstein, *Organometallics* **2008**, *27*, 894.

[33] CCDC-671437 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[34] Dibenzyl formation was not observed when $[Pd(OAc)_2]$—a system known to form palladium nanoparticles—was used as catalyst.

[35] Various catalyst concentrations were tested: 0.05, 0.02, 0.002, and 0.0005 mol% of **1** and **2**, respectively.

[36] A 60% conversion of **1** into **11** and a 32% conversion of **2** into **12** was observed after 5 h.

[37] The aminophosphines provide an explanation for the striking difference in the reactivity of **1** and **2** in the halide exchange when compared with that of **6** and **14**, if Pd^{IV} intermediates are traversed. Apart from the high σ-donor strength of the P atom of aminophosphines, which is similar to those of its phosphine analogues, the nitrogen lone pairs may donate additional electron density towards the phosphorus atom and hence, towards the metal center.[38] Although the following mechanisms would not provide an explanation for the striking difference in the reactivity of **1** (and **2**) towards bromobenzene when compared with that of **6** and **14**, they cannot be excluded completely: Decomposition of a minor amount of **1** (or **2**) to form the anionic complexes $[ArPdBr_2]^-$ or its dimer via Pd^0 intermediates may occur to promote the halide exchange with the pincer complexes. Alternatively, a bromide ligand could dissociate from $[ArPdBr_2]^-$ or its dimer (possibly as a dimethylammonium salt from DMF) and exchange with the pincer complexes directly.

[38] a) M. L. Clarke, D. J. Cole-Hamilton, M. Z. Slawin, J. D. Woollins, *Chem. Commun.* **2000**, 2065; b) K. G. Moloy, J. L. Peterson, *J. Am. Chem. Soc.* **1995**, *117*, 7696.

[39] For example, only 10% conversion was observed in *p*-xylene at 100 °C over night.

[40] The CO stretching frequency of the cationic carbonyl derivatives $[C_6H_3\text{-}2,6\text{-}(CH_2PCy_2)_2Pd(CO)][OTf]$ ($\nu_{CO} = 2105\ cm^{-1}$),[41] $[C_6H_3\text{-}2,6\text{-}(OPiPr_2)_2Pd(CO)][BF_4]$ ($\nu_{CO} = 2141\ cm^{-1}$) and $[C_6H_3\{XP(piperidinyl)_2\}_2Pd(CO)][BF_4]$ (X = NH, $\nu_{CO} = 2106\ cm^{-1}$; X = O, $\nu_{CO} = 2133\ cm^{-1}$) are indicative of the electron density at the metal centers.[7,13]

[41] Y. Jong Gook, S. Jung Min, L. Kap Duk, K. Sangha, P. Soonheum, *Bull. Korean Chem. Soc.* **1996**, *17*, 311.

[42] Full geometry optimizations were performed with the Gaussian03 program package using the *m*PW1PW91 functional. Computational details and a complete scheme with all calculated intermediates and transition states, simulated in different solvents is given in the Supporting Information.

[43] Oxidative addition of bromobenzene on **1** is not possible, since the calculated energy barrier is 71.8 kcal mol^{-1}.[42]

[44] According to our findings it seems indeed to be the case that Pd^{IV} intermediates are the key intermediates in the Suzuki–Miyaura cross-coupling reaction mediated by **1** (and **2**), as it was recently suggested.[7]

[45] This anticipation got experimental support from Heck reactions performed with bromobenzene and *n*-butyl acrylate in NMP at 140 °C with 0.01 mol% of catalyst and K_2CO_3 as base. Whereas dramatically retarded conversion rates were observed with the *phosphine*-based pincer complex **6** in the presence of 1-methyl-1,4-cyclohexadiene,[2b] only a marginal effect was noticed under identical reaction conditions with catalyst **1** (as well as with **14**). These results rule out that the catalytically active species derived from **1** (or **14**) and from **6** are of the same type, and in turn imply that different reaction mechanisms are operative in Heck reactions catalyzed by aminophosphine- (or phosphite-) and phosphine-based pincer complexes. The addition of 1-methyl-1,4-cyclohexadiene also had a negligible influence on the conversion rate of $[Pd(OAc)_2]$-catalyzed Heck reactions, adding further support to the fact that palladium nanoparticles probably are not the active form of phosphine-based pincer complexes. This, however, would indicate that pincer-type Pd^{IV} intermediates are involved in the catalytic cycle of *phosphine*-based pincer complexes, since the formation of homogeneous Pd^0 complexes was already excluded. Nevertheless, it is important to note that when styrene was used as coupling partner, a dramatic retardation in the conversion rate was observed in all cases when 1-methyl-1,4-cyclohexadiene was present, implying that this test is not definitive.

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