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Synthesis, structure and catalytic application of palladium(II) complexes bearing *N*-heterocyclic carbenes and phosphines☆

Wolfgang A. Herrmann [a,*], Volker P.W. Böhm [b], Christian W.K. Gstöttmayr [a], Manja Grosche [a], Claus-Peter Reisinger [c], Thomas Weskamp [d]

[a] *Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany*
[b] *Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599–3290, USA*
[c] *Bayer AG, Central Research, R 79, 47812 Krefeld, Germany*
[d] *Symyx Technologies, 3100 Central Expressway, Santa Clara, CA 95051, USA*

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Abstract

A variety of mixed palladium(II) complexes bearing *N*-heterocyclic carbenes (NHCs) and triaryl- and trialkylphosphines [NHC(R_2)]Pd(PR'_3)I_2 (R = Me, *t*-Bu, (*R*)-1-phenylethyl; R′ = Ph, *o*-tolyl, cyclohexyl, *t*-Bu) have been prepared. Crystal structure details of *trans*-diiodo(1,3-di-*tert*-butylimidazolin-2-ylidene)(triphenylphosphino)palladium(II) are presented. The complexes were tested as catalysts in the Mizoroki–Heck, Suzuki–Miyaura and Stille reactions as well as in the dimerization of phenylacetylene. In catalytic studies of the Suzuki–Miyaura cross-coupling reaction, the performance of these novel complexes was compared to the results obtained by the corresponding bis(NHC) and bis(phosphine) complexes. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: CC-coupling; Heck reactions; *N*-Heterocyclic carbenes; Phosphines; Palladium

1. Introduction

The performance of homogeneous catalysts is highly dependent on the ancillary ligand coordinated to the metal center [1]. Important roles of ligands include stabilizing effects and governing activity and selectivity by electronic and steric influences. *N*-Heterocyclic carbenes (NHCs) in conjunction with widely used phosphines have broadened the spectrum for the screening of ligands for desired properties [2]. NHC ligands in metal complexes are known to have electronic similarities with trialkylphosphines but appear to be stronger coordinating ligands which undergo little to no dissociation from the metal in solution [3]. In contrast to most metal–carbene complexes which have found extensive application in organic synthesis and which incorporate the carbene moiety into the organic product [4], NHCs act as non-participating ligands in catalytic processes and are not consumed [2]. With ruthenium(II) complexes bearing both types of alkylidine moiety on the same metal center, this fundamental difference was verified [5]. Experimental X-ray evidence shows M–C(NHC) bond lengths to be virtually the same as M–C(hydrocarbyl) single bonds [2b,3,6] and ab initio studies show π-back bonding to be not significant with these ligands [7]. The fact that NHC form stable compounds with beryllium, which has no p-electrons to back donate, also supports this view [8].

Various complexes of palladium(II) with NHC ligands have been prepared [3c,9–12]. Most of these complexes can be used as catalysts for various carbon carbon bond formations and related reactions [3c,11–14]. Therefore, theoretical studies have also dealt with these reactions [15] and reviews about this type of ligands in catalysis have appeared [2]. Nevertheless, bis(phosphine) complexes of palladium(II) are even better known and are more widely used as catalysts for various reactions including the above mentioned ones

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* Corresponding author. Tel.: +49-89-28913080; fax: +49-89-28913473.

E-mail address: sekretariat.ac@ch.tum.de (W.A. Herrmann).

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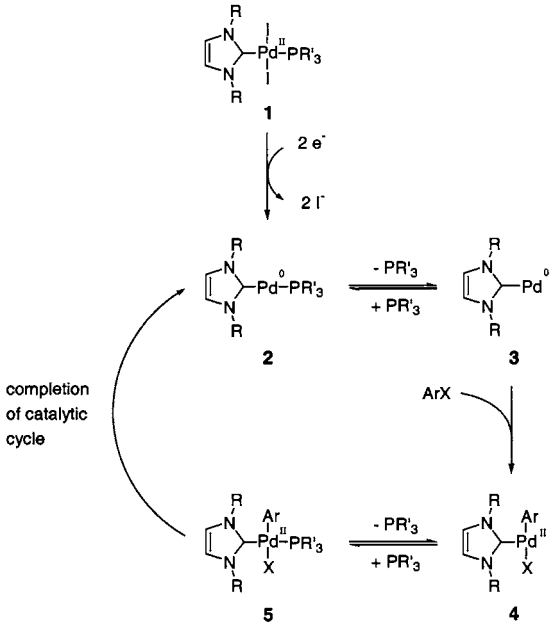


Scheme 1. Proposed mechanism for the oxidative addition of aryl halides to mixed NHC/phosphine complexes of palladium.

[16]. Despite of the success of both types of ligands, mixed NHC/phosphine complexes of palladium(II) have not been studied in detail until now, neither have they been tested as catalysts for C–C coupling [10].

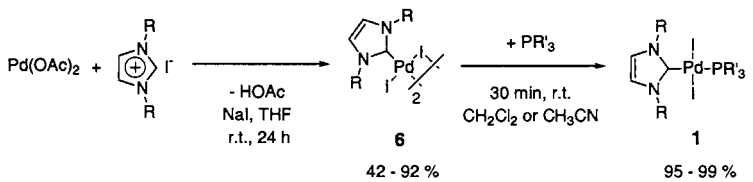
Results with mixed NHC/phosphine ruthenium(II) alkylidene complexes as catalysts in the olefin metathesis reaction show that fine tuning of catalysts can be achieved by combining these two types of similar ligands [3b,17]. Due to those observations we wondered whether a similar effect of a tightly bound directing ligand like an NHC and a more labile bound stabilizing ligand like a phosphine could also be observed in palladium mediated reactions. Mechanistic features of palladium catalyzed Heck-type reactions favor elemental steps during which one of the ligands has to dissociate whereas the other ligand is supposed to stay with the palladium in order to stabilize the active catalyst (Scheme 1). Using tightly bound NHC as the resting ligand and a phosphine as the ligand to dissociate during catalysis should thus have beneficial effects. Both stability and activity of the catalyst can be addressed this way. Furthermore, recent publications show Lewis-basic, sterically demanding tri(*tert*-butyl)phosphine P(t-Bu)$_3$ and related ligands, which are analogous to NHC, to be excellent ligands for cross-coupling reactions of chloroarenes [18–21].

Preliminary results have shown that high catalytic activity is thus achievable in the Suzuki-Miyaura and the Stille cross-coupling reactions [12]. As NHC constitute strong donor ligands they should favor the oxidative addition of aryl halides to the catalytically active palladium(0) species **2** and **3** which are formed under reaction conditions [11h]. Fine tuning of the catalysts' ability for the other elemental steps in the catalytic cycle, like e.g. transmetallation, reductive elimination, olefin insertion or β-hydride elimination can then be achieved by the variation of the phosphine ligand. After formation of species **2** by reduction of complex **1**, the dissociation of a phosphine ligand produces the highly active 12-electron palladium(0) species **3** which allows the rapid oxidative addition of an aryl halide [22]. Species **4** is thus formed and is stabilized by the re-addition of the phosphine ligand to result in complex **5**. Subsequent steps of the catalytic cycle, which are explained by established mechanistic ideas [16], allow the re-formation of species **2** by reaction of complex **5** with the desired coupling reagent, e.g. an olefin in the Mizoroki–Heck reaction or an aryl boronic acid in the Suzuki–Miyaura reaction.

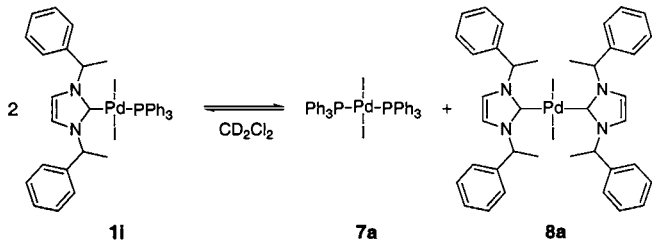
2. Results

2.1. Synthesis and properties of the catalysts (*1*)

The mixed complexes **1a**–**1l** were prepared from a dichloromethane solution of the well soluble mono-(NHC) complexes **6a**–**6c** [(NHC)PdI$_2$]$_2$ by addition of one equivalent of phosphine at ambient temperature. Rapid change of the color to yellow or light red indicates a fast reaction. Subsequent crystallization affords the yellow crystalline products. The starting compounds [(NHC)PdI$_2$]$_2$ (**6a**–**6c**) have been prepared from Pd(OAc)$_2$ and the appropriate imidazolium salt in the presence of K(Ot-Bu) and NaI (Scheme 2) [9m]. The preparation in analogy to chelating bis(NHC) complexes of palladium(II) failed [9e,9f,14b]: the reaction of one equivalent of Pd(OAc)$_2$ and one equivalent of imidazolium salt in DMSO results in mixtures of different complexes.

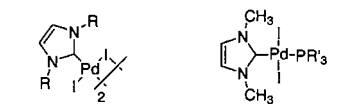


Scheme 2. Preparation of complexes **1a**–**1l** and **6a**–**6c**.



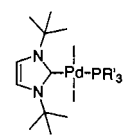
Scheme 3. Ligand exchange. Equilibrium of the complexes **1i**, **7a** and **8a**.

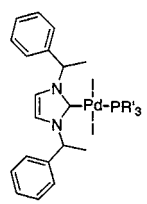
NMR experiments of complexes **1** show only one set of signals in a symmetrical surrounding indicating a rapid equilibrium of the *cis*- and the *trans*-isomers. This was also confirmed by VT-NMR as at -80°C only one set of signals was observed for **1i**. The ^{13}C–NMR signals of the coordinated carbene carbon atoms are shifted to lower field as compared to their signals in the dimeric parent complexes **6**. This can be explained by the lower electron density on the carbene carbon atom due to an electron poorer palladium(II) center because of the phosphine ligand's capability to π-accept electron density. In this regard, the ^{31}P-NMR signal of the coordinated phosphine is shifted to higher field as compared to bis(phosphine) complexes of palladium-(II). The replacement of one of the phosphine ligands by an NHC ligand being a strong σ-donating ligand alters the electron density on the palladium center. As an effect, the electron density on the remaining coordinated phosphorous atoms is also altered due to enhanced π-donation of the metal center. With complex **1i**, phosphorous coupling over the palladium metal center is observed only to the olefinic carbon and hydrogen atoms on the NHC ring system but not to the carbene carbon atom directly attached to the palladium center.



6a: R = CH_3
6b: R = $C(CH_3)_3$
6c: R = $CH(CH_3)C_6H_5$

1a: R' = C_6H_5
1b: R' = 2-$(CH_3)C_6H_4$
1c: R' = *cyclo*-C_6H_{11}
1d: R' = $C(CH_3)_3$





1e: R' = C_6H_5
1f: R' = 2-$(CH_3)C_6H_4$
1g: R' = *cyclo*-C_6H_{11}
1h: R' = $C(CH_3)_3$

1i: R' = C_6H_5
1j: R' = 2-$(CH_3)C_6H_4$
1k: R' = *cyclo*-C_6H_{11}
1l: R' = $C(CH_3)_3$

Complex **1i** did not decompose to palladium black in solutions of THF, toluene or CD_2Cl_2 over a period of several days. But in the case of CD_2Cl_2 as the solvent, it could be proved by NMR-analysis that the ligands were exchanged in an equilibrium reaction (Scheme 3) which was not observed, e.g. in toluene. The solution contained the mixed complex **1i** as well as the symmetrical complexes diiodobis(triphenylphosphino)palladium-(II) (**7a**) and diiodobis{1,3-di[(*R*)-1-phenylethyl]-imidazolin-2-yliden}palladium(II) (**8a**)[1]. The ratio of **1i**:**7a** = **1i**:**8a** is at 71:29 as determined by integration of the phosphorus signals. Due to the ligand exchange reaction of complex **1i** it is of advantage not to store the catalysts **1** in solution. Nevertheless, the rate of the exchange reaction is smaller than the rate of catalysis which still allows the use of the catalysts **1** if they are brought into solution only at the start of the reaction.

Comparison of the NMR spectra of the isolated complexes **1** with an equimolar mixtures of the corresponding complexes **6** and the phosphines revealed no difference at all. The only species generated are the desired complexes **1**. Therefore and because of the observed ligand exchange (vide supra) we considered the generation of the complexes **1** just before their use in catalysis to be not only more convenient but also superior to the pre-isolation and storage (vide infra).

2.2. Crystal structure of *1e*

Yellow crystals of the complexes **1e** were found suitable for X-ray diffraction. They were grown from a saturated solution in dichloromethane by slow evaporation of the solvent at ambient temperature. The structure is depicted in Fig. 1. A *trans*-coordination was found in the crystal structure while a *cis*-coordination of a phosphine and a functionalized NHC on a palladium(II) center has been reported before [10a].

In the *trans*-complex **1e** the coordination of the ligands is not exactly linear. The angle C1–Pd–P deviates with 175.5(1)° from the expected 180° as does the angle I1–Pd–I2 with 173.33(2)°. The iodine atoms are bent towards the NHC ligand. The planar ring of the NHC ligand is perpendicular to the plane which is formed by the square planar coordination of the palladium(II) metal center. Thus, the steric interaction of the *tert*-butyl residues with the other ligands is minimized. In comparison to the free carbene the angle N1–C1–N2 is widened to 105.7(3)° as expected after coordination [2]. The bond length C1–Pd of the NHC ligand to the metal is 2.031(4) Å and compares to the bond lengths in other palladium(II)–NHC complexes [2]. The

[1] (*R*)-1-phenylethyl will further be referred to as 1-phenylethyl or 1-PhEt.

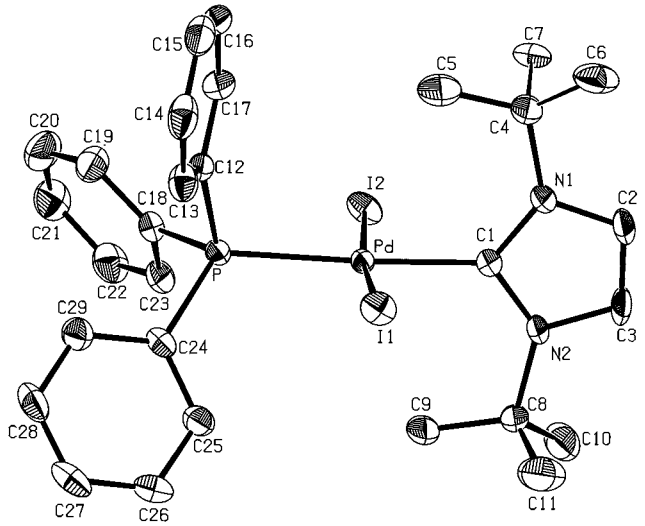


Fig. 1. Molecular structure of *trans*-diiodo(1,3-di-*tert*-butylimidazolin-2-ylidene)(triphenylphosphino)palladium(II) (**1e**). Thermal ellipsoids are drawn at the 50% probablility level. For clarity the hydrogen atoms are omitted and only one part of the distorted atoms is shown. Selected bond lengths (Å) and angles (°): Pd–P = 2.334(1), Pd–C1 = 2.031(4), Pd–I1 = 2.6325(8), Pd–I2 = 2.6175(8), P–Pd–C1 = 175.5(1), I1–Pd–I2 = 173.33(2), N1–C1–N2, 105.7(3), Pd–P–C12 = 105.5(1), Pd–P–C18 = 119.8(1), Pd–P–C24 = 118.9(1).

P-Pd bond measures with 2.334(1) Å in the expected range [23].

3. Catalysis

The formation of CC-bonds between arenes and sp^2 or sp-carbon atoms is an important reaction in modern synthetic arene chemistry [16b]. In particular, palladium catalyzed reactions have proven themselves most versatile in these reactions in terms of selectivity and tolerance towards functional groups [16].

3.1. Cross-coupling

The cross-coupling of differently substituted arenes to form unsymmetrical biaryls can be achieved by the reaction of aryl halides and arenes bearing organometallic directing groups [16]. Boronic acid derivatives are used as the organometallic reagent in the Suzuki–Miyaura reaction [24,25], and stannanes in the Stille reaction [26,27]. Biaryl moieties are important structural units in drugs [28] as well as in non-linear optical materials [29]. The Suzuki–Miyaura reaction possesses the practical advantages over the Stille reaction that the boron-containing by-products are non-toxic and that they are easily separable from the desired product.

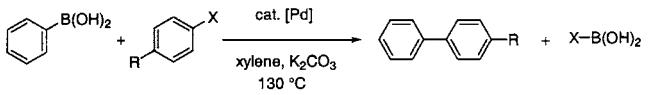
In the Suzuki–Miyaura cross-coupling reaction the steric bulk of the residues both on the NHC and the phosphine are decisive factors governing activity [12]. As the residues on the NHC do not have significant effects on the electronic properties of the ligands the observed differences of **6a**–**6c** can only account to differences in steric bulk. Furthermore, the basic trialkyl phosphines P(*t*-Bu)$_3$ and PCy$_3$ (Cy = cyclohexyl) prove to be superior to triarylphosphines. As mentioned above, no difference in activity was observed if the pre-isolated complexes **1** or a mixture of **6** and the corresponding phosphine were used. Results obtained in xylene with potassium carbonate as the base are shown in Table 2. The optimized catalyst in this system is **1k** which was identified by the reaction of 4-bromoanisole and phenylboronic acid in xylene. The use of Cs_2CO_3 increases the yield, especially in the case of non-activated chloroarenes (entries 11–13, Table 2). Comparison with diiodobis(1,3-dimethylimidazolin-2-ylidene)palladium(II) stresses the need for the phosphine ligand to be present: the bis(NHC) complex does not show any catalytic activity with 4-chloroanisole in the Suzuki–Miyaura reaction under the conditions described above (entry 14, Table 2).

Table 1
Crystal data and details for structure determination for compound **1e**

Empirical formula	$C_{29}H_{35}I_2N_2PPd$
Formula weight	803.26
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	9.142(2)
b (Å)	11.804(2)
c (Å)	14.854(4)
α (°)	111.960(10)
β (°)	92.900(10)
γ (°)	99.130(10)
V (Å^3)	1457.2(6)
Z	2
ρ_{calc} (g cm^{-3})	1.831
μ (mm^{-1})	2.8
Crystal size (mm)	$0.32 \times 0.21 \times 0.05$
Temperature (K)	153(2)
λ (Å)	0.71073
$\theta_{min/max}$	3.0/27.6
Total data	9100
Unique data	6626
Observed data [$I > 2\sigma(I)$]	5630
[a] $R_1(F_o)$	0.0301
[b] $wR_2(F_o^2)$	0.0645
Goodness-of-fit [c]	1.03
$\Delta/\rho_{min/max}$ (e Å^{-3})	−0.76/0.57

[a] $R_1 = \Sigma\|\|F_o| - |F_c\|\|/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] GoF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$.

Table 2
The Suzuki–Miyaura reaction: coupling of different aryl halides and phenylboronic acid using complexes **1** as the catalysts (1-PhEt = 1-phenylethyl, *o*-Tol = *o*-tolyl, Cy = cyclohexyl) [a]

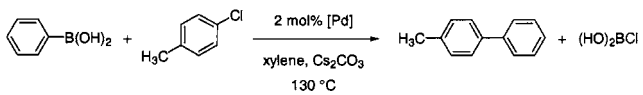


No.	X	R	mol% Pd	*t* (h)	R_{NHC}	PR_3	Catalyst	Yield (%) [b]
1	Br	$C(O)CH_3$	1.0	14	1-PhEt	–	**6c**	>99
2	Br	$C(O)CH_3$	0.1	13	1-PhEt	PPh_3	**1i**	100
3	Br	H	1.0	13	1-PhEt	PPh_3	**1i**	100
4	Br	OCH_3	1.0	14	1-PhEt	PPh_3	**1i**	100
5	Br	OCH_3	1.0	14	1-PhEt	$P(o\text{-Tol})_3$	**1j**	95
6	Br	OCH_3	1.0	12	1-PhEt	$P(t\text{-Bu})_3$	**1l**	99
7	Br	OCH_3	1.0	12	1-PhEt	PCy_3	**1k**	100
8	Br	OCH_3	1.0	12	*t*-Bu	PCy_3	**1g**	55
9	Br	OCH_3	1.0	12	Me	PCy_3	**1c**	31
10	Cl	$C(O)CH_3$	1.0	13	1-PhEt	PCy_3	**1k**	90
11	Cl	H	1.0 [c]	13	1-PhEt	PPh_3	**1i**	7
12	Cl	H	1.0 [c]	32	1-PhEt	PCy_3	**1k**	87
13	Cl	OCH_3	1.0 [c]	32	1-PhEt	PCy_3	**1k**	69
14	Cl	OCH_3	3.0 [c,d]	32	Me	–	–	0

[a] One equivalent of aryl halide, 1.2 equivalents of phenylboronic acid, 1.5 equivalents of K_2CO_3, xylene, $T = 130°C$. The catalysts **1** were generated in xylene just before the reaction.
[b] GC-yield using diethyleneglycol-di-*n*-butylether as the internal standard.
[c] Using Cs_2CO_3 as the base.
[d] Diiodobis(1,3-dimethylimidazolin-2-ylidene)palladium(II) as the catalyst.

The corresponding bis(phosphine) complexes $(R_3P)_2PdI_2$ (**7**) are known to readily decompose to palladium black at elevated reaction temperatures. However, the stability of the NHC–phosphine complexes **1** is comparable to the one of the bis(NHC) complexes **8**. Palladium black precipitation only occurs after prolonged reaction times in these cases. In order to evaluate the differences in activity, the coupling of 4-chlorotoluene with phenylboronic acid was followed over time (Fig. 2). The mixed ligated complex **1k** shows an initial activity being lower than the one of diiodobis(tricyclohexylphosphino)palladium(II) (**7b**) but much higher than the one of diiodobis[1,3-di(1-phenylethyl)-imidazolin-2-ylidene]palladium(II) (**8a**). Although the phosphine catalyst **7b** is more active at the beginning of the reaction, catalyst **1k** reaches better final results after 3 h reaction time (100 versus 95% conversion). This is a result of the increased thermal stability of the catalyst **1k** in comparison to **7b**. Catalyst **8a** needs longer reaction times to achieve useful turnovers. Additionally, after an induction period, **1k** and **7b** do not differ much in terms of the maximum turnover frequency; the induction period of catalyst **1k** is just longer than the one of **7b** which is another sign for the high thermal stability of the complexes bearing NHC ligands. In regard of the equilibrium shown in Scheme 3, nothing can be said about the participation of the bis(phosphine) complex **7b** when catalyst **1k** is used.

The reduction of **1k** to the catalytically active palladium(0) species **2** can be forced by the addition of sodium formate as a reducing agent. Catalysis with



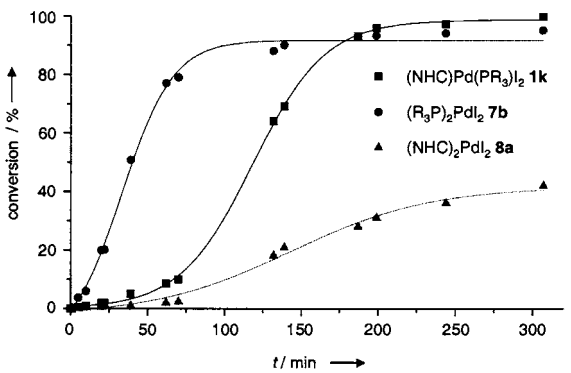


Fig. 2. Influence of the ligands on the activity of palladium(II) catalysts in the Suzuki–Miyaura reaction: comparsion of the time-conversion properties in the rection of 4-chlorotoluene and phenylboronic acid using diiodo[1,3-di(1-phenylethyl)imidazolin-2-ylidene](tricyclohexylphosphino)palladium(II) (**1k**), diiodobis[1,3-di(1-phenylethyl)imidazolin-2-ylidene]palladium(II) (**8a**) and diiodobis(tricyclohexylphosphino)palladium(II) (**7b**) as the catalysts [NHC = 1,3-bis(1-phenylethyl)imidazolin-2-ylidene, PR_3 = tricyclohexylphosphine (PCy_3)].

complexes **1** is then commenced without an induction period. But this procedure is accompanied by visible palladium black formation and reduced activity of the catalysts in terms of turnover numbers (TON).

The successful application of the catalysts **1** in the Suzuki–Miyaura cross-coupling reaction prompted us to test them in the related Stille reaction [26,27]. Until now, NHC complexes were not known to catalyze the cross-coupling of aryl bromides and aryl stannanes. The identification of complex **1i** as the most active catalyst was achieved by the coupling of 4-bromoacetophenone and phenyltributylstannane in toluene without any promoting additives. In contrast to the Suzuki–Miyaura reaction, the less basic and less sterically demanding triphenylphosphine PPh_3 proved to be superior to any other phosphine in conjunction with the sterically demanding residue R = 1-phenylethyl on the NHC. With catalyst **1i** aryl bromides can be coupled with good turnovers but the system fails in the case of aryl chlorides (Table 3). Further variation of the phosphine ligand, e.g. tri(2-furyl)phosphine or triphenylarsine, showed no beneficial effect [12].

3.2. Olefination

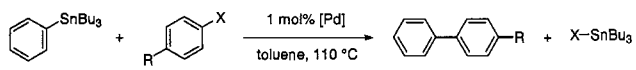
The coupling of arenes and olefins is called the Mizoroki–Heck reaction [30,31]; most commonly aryl halides are used as the arene source [16]. Aryl olefins are frequent building blocks in natural products as well as in fine chemicals making the Mizoroki–Heck reaction one of the most important modern synthetic methods [31a].

The most active catalyst **1j** was identified in the reaction of 4-bromoanisole and styrene in DMAc (dimethylacetamide) without any additives. The use of tri(*ortho*-tolyl)phosphine ($P(o\text{-Tol})_3$) yields slightly better turnovers than PPh_3. In comparison to the cross-coupling reactions (vide supra), sterical bulk both on the phosphine as well as on the NHC is important but the less basic triarylphosphines are more efficient in this reaction. Thus, aryl bromides can be coupled with good turnovers but the system fails in the case of aryl chlorides (Table 4). The superiority of the mixed catalysts **1** is shown again by the comparison to the bis(NHC) complex diiodobis(1,3-dimethylimidazolin-2-ylidene)-palladium(II) for the coupling of 4-bromoanisole and styrene under the conditions described (entry 10, Table 4).

3.3. Alkyne coupling

When we tried to perform the Sonogashira reaction of 4-bromoanisole with phenylacetylene and catalyst **1i** in triethylamine as the solvent and the base, we encountered low activity and selectivity for the desired reaction. The undesired side reaction was identified as the dimerization of the phenylacetylene to symmetrical enynes **10**. When copper(I) iodide was added as the co-catalyst neither the activity of the system nor its selectivity was increased in the Sonogashira reaction. Only the type of side reaction changed to the oxidative dimerization of the phenylacetylenes to the corresponding diyne **9**. Both reactions are known to be catalyzed by palladium complexes but have not yet been observed for NHC complexes [32,33]. In contrast, the Sonogashira reaction works very well with bis(NHC) complexes of palladium(II) and none of the two side reactions was

Table 3
The Stille reaction: coupling of different aryl halides and phenyltributylstannane using complexes **1** as the catalysts (1-PhEt = 1-phenylethyl, *o*-Tol = *o*-tolyl, Cy = cyclohexyl) [a]

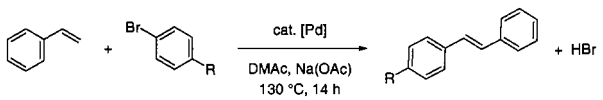


No.	R	X	*t* (h)	R_{NHC}	PR_3	Catalyst	Yield (%) [b]
1	$C(O)CH_3$	Br	17	1-PhEt	–	**6c**	11
2	$C(O)CH_3$	Br	17	1-PhEt	PPh_3	**1i**	100
3	$C(O)CH_3$	Br	17	1-PhEt	$P(o\text{-Tol})_3$	**1j**	65
4	$C(O)CH_3$	Br	17	1-PhEt	$P(t\text{-Bu})_3$	**1l**	47
5	$C(O)CH_3$	Br	17	1-PhEt	PCy_3	**1k**	9
6	$C(O)CH_3$	Br	17	*t*-Bu	PPh_3	**1e**	72
7	$C(O)CH_3$	Br	17	Me	PPh_3	**1a**	23
8	H	Br	17	1-PhEt	PPh_3	**1i**	91
9	OCH_3	Br	25	1-PhEt	PPh_3	**1i**	82
10	$C(O)CH_3$	Cl	17	1-PhEt	PPh_3	**1i**	4

[a] One equivalent of aryl halide, 1.2 equivalents of phenyltributylstannane, toluene, $T = 110°C$. The catalysts **1** were generated in toluene just before the reaction.

[b] GC-yield using diethyleneglycol-di-*n*-butylether as the internal standard.

Table 4
The Mizoroki–Heck reaction: coupling of different aryl halides and styrene using complexes **1** as the catalysts (1-PhEt = 1-phenylethyl, *o*-Tol = *o*-tolyl, Cy = cyclohexyl) [a]



No.	R	mol% Pd	R_{NHC}	PR_3	Catalayst	Yield (%) [b]
1	$C(O)CH_3$	1.0	1-PhEt	PPh_3	**1i**	98
2	H	1.0	1-PhEt	–	**6c**	87
3	H	1.0	1-PhEt	PPh_3	**1i**	92
4	OCH_3	1.0	1-PhEt	Pcy_3	**1k**	62
5	OCH_3	1.0	1-PhEt	$P(t\text{-Bu})_3$	**1l**	83
6	OCH_3	1.0	1-PhEt	PPh_3	**1i**	90
7	OCH_3	1.0	1-PhEt	$P(o\text{-Tol})_3$	**1j**	98
8	OCH_3	1.0	*t*-Bu	PPh_3	**1e**	60
9	OCH_3	1.0	Me	PPh_3	**1a**	25
10	OCH_3	3.0 [c]	Me	–	–	5

[a] One equivalent of aryl bromide, 1.5 equivalents of styrene, 1.5 equivalents of Na(OAc), DMAc (dimethylacetamide), $T = 130°C$, $t = 14$ h. The catalysts **1** were generated in DMAc just before the reaction.
[b] GC-yield using diethyleneglycol-di-*n*-butylether as the internal standard.
[c] Diiodobis(1,3-dimethylimidazolin-2-ylidene)palladium(II) as the catalyst.

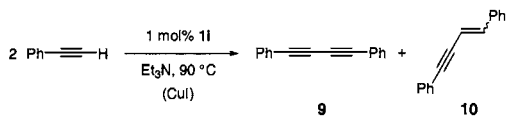
observed there [11f]. Both **9** and **10** are versatile building blocks in organic synthesis. The dimer of acetylene related to **9** is used in the technical synthesis of neoprene rubber [34], and **10** is a starting material in the enyne-diene [4 + 2] cycloaddition reaction to form 1-arylalkynes [35].

When phenylacetylene is employed only, the alkyne is consumed almost quantitatively. The selectivity of the reaction towards 1,4-diphenylbutadiin (**9**) or 1,4-diphenylbut-1-en-3-in **10** can be controlled via the addition of co-catalytic amounts of CuI. With 5 mol% CuI compound **9** is formed exclusively; without CuI the formation of compound **10** is strongly favored with a product ratio of approximately 9:1 (Table 5). From the isomers of **10** the (*E*)-isomer is formed preferentially. For the oxidative coupling of phenylacetylene to form **9** it is crucial to use non-degassed triethylamine as the solvent in order to bring sufficient amounts of oxygen into the system.

3.4. Discussion

Mechanistic interpretations of the efficiency of the complexes **1** as catalysts for the Heck-type reactions have to consider both basicity and sterical bulk of the ligands. The basic NHC ligands facilitate the oxidative addition of the aryl halide to the palladium(0) center. The dissociation of the phosphine further activates the catalyst for the oxidative addition as well as possibly for other elemental steps of the catalytic cycle, e.g. transmetallation, reductive elimination, olefin insertion and β-hydride elimination. The dissociation is supported by the sterical bulk of the NHC and explains the higher efficiency of the sterically demanding NHC with R_{NHC} = 1-phenylethyl over the NHC with R_{NHC} = methyl. The fact that the NHC merely dissociate from the metal accounts for the increased stability of the catalyst as compared to the corresponding bis(phosphine) complexes. This enables the use of elevated reaction temperatures, which is generally necessary for palladium(II) catalyst systems in Heck-type reactions with unactivated substrates.

Table 5
The alkyne dimerization: coupling of phenylacetylene using complex **1i** as the catalyst; influence of the co-catalyst CuI [a]



No.	CuI (mol%)	*t* (h)	Yield **9** (%) [b]	Yield **10** (%) [b]
1	5	4	100	–
2	3	4	98	–
3	1	4	65	17 (99:1:0)
4	–	4	2	20 (95:5:0)
5	–	8	6	68 (80:14:6)
6	–	12	9	91 (76:16:8)

[a] The catalyst **1i** was generated in Et_3N just before the reaction.
[b] GC-yield (*cis*:*trans*:*geminal*); using diethyleneglycol-di-*n*-butylether as the internal standard.

The 1-phenylethyl residue on the NHC is more efficient than the *t*-butyl group. This can be accounted for by the thermal rotation of the residues, which makes the 1-phenylethyl moiety appear much bigger than it looks in the crystal structure. Subtle differences in the mechanisms of the Suzuki–Miyaura, the Stille and the Mizoroki–Heck reaction are apparent by the change in the most efficient phosphine ligands. This observation shows that fine tuning of catalyst properties by the combination of different types of ligands on the same metal center can be very fruitful. The comparison of the activity of the bis(phosphine) complex **7b**, the bis(NHC) complex **8a** and the corresponding mixed complex **1i** in the Suzuki–Miyaura reaction shows that **1i** combines both activity and stability leading to maximized overall turnover numbers.

4. Conclusion

Mixed palladium(II) complexes of NHCs and phosphines have been characterized and one crystal structure was determined. A *trans*-coordinated complex was isolated and characterized. The structural details do not exhibit any unexpected features for NHC complexes.

The idea of mixing NHC and trialkyl- or triarylphosphines for catalysis was based on the idea to merge the strengths of both ligand systems: High stability of the NHC–palladium bond, combined with easy dissociation of the phosphine ligands. Mixed NHC–phosphine complexes of palladium(II) provide an excellent means of triggering both activity and stability of the catalytically active species in CC-coupling reactions. Our experiments demonstrate the applicability of these catalysts in the Suzuki–Miyaura and the Stille biaryl formations as well as in the Mizoroki–Heck olefination and the homocoupling of terminal alkynes. An important feature of the catalysts is the necessity of *bulky* NHC ligands whereas the phosphine ligand has to be optimized for each type of reaction separately. Until now, the additional involvement of bis(phosphine) complexes in catalysis cannot be ruled out.

5. Experimental

5.1. General comments

NMR spectra (^{1}H, ^{13}C, ^{31}P) were recorded on a Jeol JMX-GX 400 instrument. Chemical shifts are given in ppm. The spectra are calibrated to the residual protons of the solvent (^{1}H), to the 13-carbon signals of the solvent (^{13}C) or to 85% H_3PO_4 as the external standard (^{31}P). NMR multiplicities are abbreviated as follows: s = singlet, d = dublet, q = quartet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. GC-MS spectra were measured on a Hewlett–Packard gas chromatograph GC 5890 A equipped with a mass selective detector MS 5970 B. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. The CC-coupling products were identified by comparison of GC-MS data and retention times with authentical samples. The yields of catalysis experiments were generally determined by gas chromatography using diethyleneglycol-di-*n*-butylether as the internal standard.

Except for work-up of reaction mixtures and the preparation of diiodobis(NHC)palladium(II) complexes, all operations were carried out under nitrogen. DMSO, acetonitrile, triethylamine and pentane were used as purchased without further purification. Xylene and DMAc were degassed prior to use by distillation under nitrogen. Dichloromethane and toluene were carefully dried and degassed according to standard procedures [36].

5.2. Reagents

$Pd(OAc)_2$ and PPh_3 were obtained from Merck-Schuchardt. PdI_2 and tricyclohexylphosphine (PCy_3) were obtained from ABCR. P(*t*-Bu)$_3$ was purchased from Strem. Tri(*o*-tolyl)phosphine P(*o*-Tol)$_3$ was prepared from the corresponding Grignard reagent and PCl_3 by literature methods [37]. Other chemicals were bought from Fluka and Aldrich. All chemicals were used as received without any further treatment if not stated otherwise. Diiodobis(phosphino)palladium(II) complexes were prepared according to general literature methods starting from PdI_2 [38]. 1,3-Dimethylimidazolium iodide [39] and 1,3-di[1-(*R*)-phenylethyl]-imidazolium chloride [40] were prepared following published methods. Di-μ-iodobis{1,3-di[(*R*)-1-phenylethyl]imidazolin-2-ylidene}diiododipalladium(II) (**6c**) [9m] and diiodobis(1,3-dimethylimidazolin-2-ylidene)-palladium(II) were prepared according to the literature [11h].

5.3. Preparations

5.3.1. 1,3-Di-tert-butylimidazolium chloride

A total of 300 mg of formaldehyde (10 mmol) was dissolved in 10 ml of toluene and 1.06 ml of *tert*-butyl amine (731 mg, 10 mmol) were added dropwise. The mixture was stirred and heated until a clear solution formed. After cooling to 0°C another 1.06 ml of *tert*-butyl amine (731 mg, 10 mmol) was added. A total of 3.33 ml of a 3 M aqueous HCl (10 mmol) was added dropwise and after removal of the cooling

1.14 ml glyoxal (40% in water, 10 mmol) were added dropwise. The reaction mixture was stirred at 40°C for 15 h. After dilution with a saturated $NaHCO_3$(aq.) solution the aqueous phase was extracted three times with 2 ml of diethylether. The water of the aqueous phase was then removed in vacuo and the crude product obtained was extracted three times with 5 ml of CH_2Cl_2. After evaporation of the organic solvent in vacuo, 1.47 g (7 mmol, 68%) of the colorless salt was obtained. ^1H (400 MHz, [D_6]-DMSO): δ [ppm] = 9.37 (s, 1 H, NCHN), 8.11 (s, 2 H, NCHCHN), 1.60 (s, 18 H, CH_3). $^{13}C\{^1H\}$ (100 MHz, [D_6]-DMSO): δ [ppm] = 132.7 (NCHN), 120.4 (2 C, NCHCHN), 59.6 (2 C, $NCMe_3$), 29.1 (6 C, CH_3). Anal. Found: C, 61.04; H, 9.71; N, 12.75. Calc. for $C_{11}H_{21}N_2Cl$ (216.75): C, 60.95; H, 9.77; N, 12.92%.

5.3.2. 1,3-Di-tert-butylimidazolium tetrafluoroborate

A total of 300 mg of paraformaldehyde (10 mmol) was dissolved in 10 ml of toluene and 1.06 ml of *tert*-butyl amine (731 mg, 10 mmol) were added dropwise. The mixture was stirred and heated until a clear solution formed. After cooling to 0°C another 1.06 ml of *tert*-butyl amine (731 mg, 10 mmol) is added. A total of 2.04 ml of H[BF_4] (35% in water, 10 mmol) was added dropwise and after removal of the cooling 1.14 ml of glyoxal (40% in water, 10 mmol) was added dropwise. The reaction mixture was stirred at 40°C for 15 h while the colorless product precipitated. After filtration of the reaction and washing with 5 ml of water and 5 ml of diethylether, 2.33 g (9 mmol, 87%) of the colorless salt was obtained. ^1H (400 MHz, [D_6]-DMSO): δ [ppm] = 8.96 (t, $^4J_{HH}$ = 2.1 Hz, 1 H, NCHN), 8.02 (d, $^4J_{HH}$ = 2.1 Hz, 2 H, NCHCHN), 1.59 (s, 18 H, CH_3). $^{13}C\{^1H\}$ (100 MHz, [D_6]-DMSO): δ [ppm] = 132.1 (NCHN), 120.4 (2 C, NCHCHN), 59.7 (2 C, $NCMe_3$), 29.0 (6 C, CH_3). Anal. Found: C, 49.44; H, 7.71; N, 10.50. Calc. for $C_{11}H_{21}N_2BF_4$ (268.10): C, 49.28; H, 7.89; N, 10.45.

5.3.3. Di-μ-iodobis(1,3-dimethylimidazolin-2-ylidene)-diiododipalladium(II) (**6a**)

A total of 200 mg of $Pd(OAc)_2$ (0.89 mmol), 534 mg of NaI (3.56 mmol), 96 mg of K(O*t*-Bu) (1.00 mmol) and 199 mg of 1,3-dimethylimidazolium iodide (0.89 mmol) were dissolved in 30 ml of CH_3CN. The mixture was stirred for 24 h at room temperature (r.t.). The solvent was evaporated in vacuo and the brown crude product was isolated by soxhlet extraction. After column chromatography (silica, CH_3CN) the red product was obtained in 171 mg (0.19 mmol, 42%). ^1H (400 MHz, [D_6]-DMSO): δ [ppm] = 7.46 (s, 4 H, NCHCHN), 3.79 (s, 12 H, CH_3). $^{13}C\{^1H\}$ (100 MHz, [D_6]-DMSO): δ [ppm] = 122.3 (4 C, NCHCHN), 36.5 (4 C, CH_3), carbene signal not detected. Anal. Found: C, 13.5; H, 1.9; N, 5.8. Calc. for $C_{10}H_{16}N_4I_4Pd_2$ (912.72): C, 13.16; H, 1.77; N, 6.14.

5.3.4. Di-μ-iodobis(1,3-di-tert-butylimidazolin-2-ylidene)diiododipalladium(II) (**6b**)

A total of 112 mg of $Pd(OAc)_2$ (0.50 mmol), 300 mg of NaI (2.00 mmol), 66 mg of K(O*t*-Bu) (0.60 mmol) and 0.50 mmol of either 1,3-di-*tert*-butylimidazolium chloride or 1,3-di-*tert*-butylimidazolium tetrafluoroborate were dissolved in 40 ml of THF. The mixture was stirred for 5 h at r.t. The solvent was evaporated in vacuo and the product was separated by column chromatography (silica, diethylether–hexane, 1:1). The product was obtained in 243 mg (0.23 mmol, 90%). ^1H (400 MHz, CD_2Cl_2): δ [ppm] = 7.31 (s (br), 2 H, NCH=) 7.26 (s (br), 2 H, NCH=), 2.12 (s, 18 H, CH_3), 2.05 (s, 18 H, CH_3). $^{13}C\{^1H\}$ (100 MHz, CD_2Cl_2): δ [ppm] = 147.3 (2 C, NCH=), 146.7 (2 C, NCH=), 60.7(2 C, $NCMe_3$), 60.0 (2 C, $NCMe_3$), 33.9 (6 C, CH_3), 33.0 (6 C, CH_3), carbene signal not detected.

5.3.5. Diiodo(1,3-dimethylimidazolin-2-ylidene)(triphenylphosphino)palladium(II) (**1a**)

A total of 100 mg of di-μ-iodobis(1,3-dimethylimidazolin-2-ylidene)diiododipalladium(II) (**6a**) (0.22 mmol) was dissolved in 10 ml of CH_3CN. To the solution 58 mg of triphenylphosphine (0.22 mmol) was added. The yellow mixture was stirred at r.t. for 30 min. Evaporation of the solvent in vacuo and washing with hexane afforded the desired compound in 157 mg (0.22 mmol, 99%). ^1H (400 MHz, [D_6]-DMSO): δ [ppm] = 7.82–7.58 (m, 15 H, PPh_3), 7.18 (s, 2 H, NCHCHN), 3.58 (s, 6 H, CH_3). $^{13}C\{^1H\}$ (100 MHz, [D_6]-DMSO): δ [ppm] = 134.8 (d, J_{CP} = 11 Hz, Ar), 132.2 (Ar), 131.7 (d, J_{CP} = 13 Hz, Ar), 129.3 (d, J_{CP} = 10 Hz, Ar), 124.5 (NCHCHN), 37.9 (CH_3), carbene signal not detected. $^{31}P\{^1H\}$ (162 MHz, [D_6]-DMSO): [ppm] δ = 24.7. Anal. Found: C, 38.5; H, 3.2; N, 3.7; P, 4.3; Pd, 14.9. Calc. for $C_{23}H_{23}N_2I_2PPd$ (718.65): C, 38.44; H, 3.23; N, 3.90; P, 4.31; Pd, 14.81%.

5.3.6. Diiodo[1,3-di(tert-butyl)imidazolin-2-ylidene](triphenylphosphino)palladium(II) (**1e**)

A total of 216 mg di-μ-iodobis(1,3-di-*tert*-butylimidazolin-2-ylidene)diiododipalladium(II) (**6b**) (0.2 mmol) was dissolved in 10 ml of CH_3CN. To the solution 105 mg of triphenylphosphine (0.4 mmol) was added. The red mixture was stirred at r.t. for 30 min. Slow evaporation of the solvent over night and washing with hexane afforded the analytically pure compound as yellow crystals in 313 mg (0.39 mmol,

98%). ^{1}H (270 MHz, CD_2Cl_2): δ [ppm] = 7.76–7.69 (m, 6 H, PPh_3), 7.40–7.38 (m, 9 H, PPh_3), 7.31 (d, $^5J_{PH}$ = 1.5 Hz, 2 H, NCHCHN), 1.92 (s, 18 H, CH_3). $^{13}C\{^1H\}$ (68 MHz, CD_2Cl_2): δ [ppm] = 134.7 (d, J_{CP} = 10.2 Hz, Ar), 133.0 (d, $^1J_{CP}$ = 44.1 Hz, 3 C, *ipso*-C PPh_3), 129.8 (Ar), 127.7 (d, J_{CP} = 10.2 Hz, Ar), 121.1 (d, $^4J_{CP}$ = 5.4 Hz, NCHCHN), 59.5 ($NCMe_3$), 32.3 (CH_3), carbene signal not detected. $^{31}P\{^1H\}$ (109 MHz, CD_2Cl_2): δ [ppm] = 15.9. Anal. Found: C, 43.56; H, 4.60; N, 3.64. Calc. for $C_{29}H_{35}N_2I_2PPd$ (802.81): C, 43.39; H, 4.39; N, 3.49%.

5.3.7. Diiodo{1,3-di[(R)-1-phenylethyl]imidazolin-2-ylidene}(triphenylphosphino)palladium(II) (**1i**) [12]

A total of 209 mg of di-μ-iodobis{1,3-di[(*R*)-1-phenylethyl]imidazolin-2-ylidene]}diiododipalladium(II) (**6c**) (0.20 mmol) was dissolved in 10 ml of CH_2Cl_2. To the red solution, 105 mg of triphenylphosphine (0.40 mmol) was added. The yellow mixture was stirred at r.t. for 10 min. Slow evaporation of the solvent over night and washing with hexane afforded the analytically pure compound as yellow–orange crystals in 170 mg (0.38 mmol, 95%). ^{1}H (400 MHz, CD_2Cl_2): δ [ppm] = 7.76–7.35 (m, 25 H, Ar), 7.08 (d, $^5J_{PH}$ = 1.5 Hz, 2 H, NCHCHN), 6.34 (q, $^3J_{HH}$ = 7.3 Hz, 2 H, NCH(Me)Ph), 1.93 (d, $^3J_{HH}$ = 7.3 Hz, 6 H, CH_3). $^{13}C\{^1H\}$ (100 MHz, CD_2Cl_2): δ [ppm] = 155.9 (C–Pd), 140.2 (Ar), 135.6 (d, J_{PC} = 10.0 Hz, Ar), 133.1 (d, $^1J_{PC}$ = 44.6 Hz, Ar), 130.5 (d, $^4J_{PC}$ = 2.3 Hz, Ar), 128.8 (Ar), 128.4 (Ar), 128.3 (Ar), 128.1 (d, J_{PC} = 10.0 Hz, Ar), 120.0 (d, $^4J_{PC}$ = 6.1 Hz, NCHCHN), 59.2 (NCH(Me)Ph), 20.4 (CH_3). $^{31}P\{^1H\}$ (162 MHz, CD_2Cl_2): δ [ppm] = 16.5. Anal. Found: C, 49.55; H, 3.69; N, 3.32. Calc. for $C_{37}H_{35}N_2I_2PPd$ (898.90): C, 49.44; H, 3.92; N, 3.12%.

5.3.8. Diiodobis{1,3-di[(R)-1-phenylethyl]imidazolin-2-ylidene}palladium(II) (**8a**)

Orange crystals of the complex **8a** were obtained by column chromatography in the preparation [9m] of di-μ-iodobis{1,3-di[(*R*)-1-phenylethyl]imidazolin-2-ylidene}diiododipalladium(II) (**6c**) in 32 mg (0.04 mmol, 7%). ^{1}H (400 MHz, [D_6]-DMSO): δ [ppm] = 7.28–7.65 (m, 20 H, Ar), 7.27 (s, 4 H, NCHCHN), 6.48 [q, 4 H, $^3J_{HH}$ = 6.6 Hz, NCH(Me)Ph], 1.93 (d, 12 H, $^3J_{HH}$ = 6.6 Hz, CH_3). $^{13}C\{^1H\}$ (100 MHz, [D_6]-DMSO): δ [ppm] = 165.4 (C–Pd), 140.9 (Ar), 128.9 (Ar), 128.3 (Ar), 128.1 (Ar), 120.1 (NCHCHN), 59.1 [NCH(Me)Ph], 20.4 (CH_3).

5.4. Catalysis

5.4.1. Suzuki–Miyaura cross-coupling reaction

A total of 1.2 equivalents of phenylboronic acid (146 mg, 1.2 mmol) and 1.5 equivalents of potassium carbonate (207 mg, 1.5 mmol) were placed in a Schlenk tube equipped with a stirring bar. The vessel was put under an atmosphere of nitrogen and one equivalent of aryl halide (1.0 mmol; e.g. 187 mg of 4-bromoanisole, 125 μl), 50 mg of diethyleneglycol-di-*n*-butylether and 2 ml of degassed xylene were added. After thermostating at 130°C for 10 min the catalyst solution prepared in xylene (by mixing the phosphine and the complex **6** in an 1:1 ratio of P:Pd in 0.5 ml xylene and stirring for 10 min at r.t.) was added against a positive stream of nitrogen. To finish the reaction, the mixture was allowed to cool to r.t. and 3 ml of water was added. The aqueous phase was extracted three times with 2 ml of diethylether and the combined organic phases were dried over $MgSO_4$.

5.4.2. Stille cross-coupling reaction

A total of 1.2 equivalents of phenyltributylstannane (440 mg, 390 μl, 1.2 mmol), one equivalent of aryl halide (1.0 mmol; e.g. 199 mg of 4-bromoacetophenone), 50 mg of diethyleneglycol-di-*n*-butylether and 2 ml of dry toluene were placed in a Schlenk tube equipped with a stirring bar under an atmosphere of nitrogen. After thermostating at 95°C for 10 min the catalyst solution prepared in toluene (by mixing the phosphine and the complex **6** in an 1:1 ratio of P:Pd in 0.5 ml toluene and stirring for 10 min at r.t.) was added against a positive stream of nitrogen and the reaction was put into an oil bath at 110°C. To finish the reaction, the mixture was allowed to cool to r.t. and 3 ml of water and a small amount of $[NBu_4]F$ were added. The aqueous phase was extracted three times with 2 ml of diethylether and the combined organic phases were dried over $MgSO_4$.

5.4.3. Heck–Mizoroki reaction

A total of 1.5 equivalents of sodium acetate (123 mg, 1.5 mmol) were placed in a Schlenk tube equipped with a stirring bar. The vessel was put under an atmosphere of nitrogen and 1.0 equivalents of aryl halide (1.0 mmol; e.g. 187 mg of 4-bromoanisole, 125 μl), 1.5 equivalents of styrene (156 mg, 170 μl, 1.5 mmol), 50 mg of diethyleneglycol-di-*n*-butylether and 2 ml of degassed DMAc (dimethylacetamide) were added. After thermostating at 130°C for 10 min the catalyst solution prepared in DMAc (by mixing the phosphine and the complex **6** in an 1:1 ratio of P:Pd in 0.5 ml DMAc and stirring for 10 min at r.t.) was added against a positive stream of nitrogen. To finish the reaction, the mixture was allowed to cool to r.t. and 3 ml of 1 M HCl(aq.) was added. The aqueous phase was extracted three times with 2 ml of diethylether and the combined organic phases were dried over $MgSO_4$.

5.4.4. Dimerization of phenylacetylene; formation of *9* and *10*

One equivalent of phenylacetylene (102 mg, 110 μl, 1.0 mmol), 50 mg of diethyleneglycol-di-*n*-butylether and 2 ml of degassed triethylamine were placed in a Schlenk tube equipped with a stirring bar under an atmosphere of nitrogen. In the case of the formation of diyne **9**, 0.05 equivalents of CuI (10 mg, 0.05 mmol) were added for optimized yield of **9**. After thermostating at 75°C for 10 min the catalyst solution prepared in triethylamine (by mixing the phosphine and the complex **6** in an 1:1 ratio of P:Pd in 0.5 ml triethylamine and stirring for 10 min at r.t.) was added against a positive stream of nitrogen and the reaction was put into an oil bath at 90°C. To finish the reaction, the mixture was allowed to cool to r.t. and 3 ml of 1 M HCl(aq.) was added. The aqueous phase was extracted three times with 2 ml of diethylether and the combined organic phases were dried over $MgSO_4$.

5.5. X-ray crystal structure determination

Crystals of the complex **1e** suitable for X-ray diffraction were grown from CH_2Cl_2. All X-ray data were collected on a Nonius Kappa CCD detection system at 153 K with graphite-monochromated Mo–K_α irradiation. A total number of 9100 reflections were measured and 6626 unique reflection (R_{int} = 0.025) were used in the full matrix least squares refinement. The intensities of the reflections were corrected for absorption effects [41]. The structure was solved by direct methods [42] and refined by full-matrix least-squares calculations employing SHELXL-97 [43]. All heavy atoms of the compound were refined with anisotropic temperature factors. All hydrogen atoms were calculated. Crystallographic data and experimental details of compound **1e** are given in Table 1.

6. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153169 for complex **1e**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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