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Bis(pyrimidine)-based palladium catalysts: synthesis, X-ray structure and applications in Heck–, Suzuki–, Sonogashira–Hagihara couplings and amination reactions

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Abstract

The synthesis of *N*,*N*-bis(pyrimid-2-yl)amine (**1**), *N*-acetyl-*N*,*N*-bis(pyrimid-2-yl)amide (**2**), *N*-norborn-2-ene-5-ylbis(pyrimid-2-yl)carbamide (**4**) is described. The Pd-complex *N*-acetyl-*N*,*N*-bis(pyrimid-2-yl)amine palladium dichloride (**3**) has been prepared from compound **2** and its X-ray structure has been determined. A polymer supported catalytic system (**6**) was prepared via ring-opening metathesis copolymerization of **4** with 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphthalene (HDMN-6) and subsequent loading with $PdCl_2$. Both the homogeneous and heterogeneous catalysts **3** and **6** were active in Heck–, Suzuki–, Sonogashira–Hagihara-type couplings and amination reactions using aryl iodides, bromides and chlorides. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aminations reactions; Palladium catalysts; Coupling; ROMP; Heterogeneous catalysis

1. Introduction

Palladium-mediated reactions including polymerizations, C–C coupling reactions, aminations and hydrophosphorylations have attracted significant interest during the last years [1–8]. In course of our search for non-phosphorous-based ligands, we already reported on the use of bidentate *N*,*N*-based analogues. So far, these systems have been based on (substituted) *N*,*N*-dipyridylcarbamides [9,10]. They are completely air-stable, show high activities in various coupling reactions of aryl iodides and bromides and may—with some restrictions—also be used for C–C coupling reactions of aryl chlorides [11]. In order to obtain even more stable and active systems we already investigated homologous methyl-substituted and benzo-anelated derivatives [11]. Since these systems generally suffered from steric interactions of the methyl groups with either the palladium chloride or the carbonyl moiety, we moved to similar electron-rich, yet unsubstituted systems. In this contribution, we report on the synthesis, the properties and use of monomeric and polymer-supported bis(pyrimidyl)-based palladium complexes.

2. Results and discussion

2.1. Synthesis of bis(pyrimid-2-yl)amine (1)

Palladium catalyzed aryl-X activation (X = I, Br or Cl) reactions are an efficient tool for the synthesis of bi- and triaryl amines via C–N-bond formation [12,13]. In analogy to 2-X-pyridines [11], 2-X-pyrimidine was used. X can be Cl since the systems are activated, but the formation of catalyst deactivating palladium pyrimidine complexes has to be avoided. In order to prevent this, the palladium catalyst has to be stabilized by chelating bisphosphine ligands [12]. Reaction of 2-aminopyrimidine with one equivalent of 2-chloropyrimidine and

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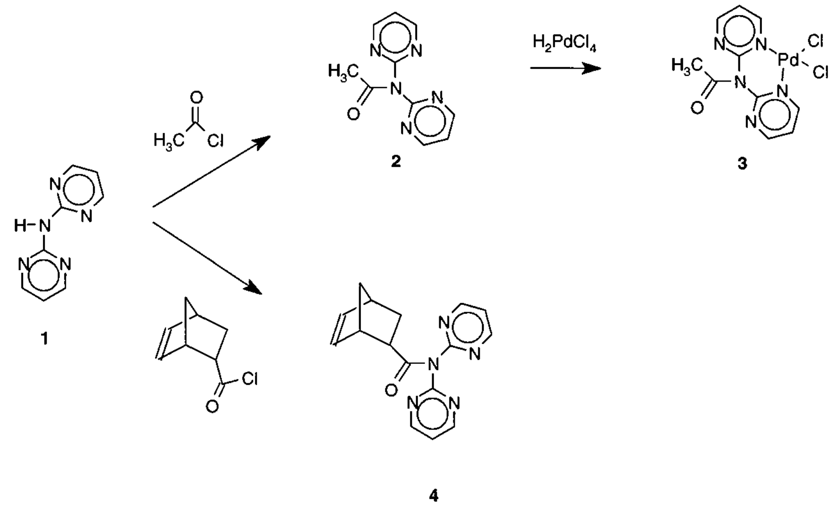


Scheme 1. Synthesis of compounds **1**–**4**.

1.15 equivalents of sodium-*tert*-butylate in the presence of 0.65 mol% bis-diphenylphosphinopropane and 0.32 mol% Pd_2dba_3 in toluene at 80 °C yields **1** overnight. Workup is a bit tedious because of the low solubility of the bis(pyrimid-2-yl)amine in standard solvents, but by extraction and recrystallization from water, followed by drying, the product was obtained in reasonable yields.

2.2. Synthesis of monomeric palladium complex *3*

Compound **2** was prepared according to a previously published procedure [11] from **1** and acetyl chloride. The synthesis of the palladium (II) complex **3** was accomplished by reaction of a methanolic solution of compound **2** with an aqueous solution of H_2PdCl_4, freshly prepared from $PdCl_2$ and HCl (Scheme 1). The resulting palladium compound is only soluble in highly polar organic solvents such as DMSO or DMF. In order to obtain information on structural features of this compound, complex **3** was characterized by X-ray analysis. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ and shows the expected almost perfect square planar conformation around the palladium center (Fig. 1). The angle formed by the two pyrimidines was found to be 56.1(1)°, thus being similar to the one found in the related dipyrid-2-yl-analogue (54.8(1)°) [10]. Analogous similarities are found in the angle defined by C2–N1–C2′ (117.3(2) vs. 116.5(3)°). A detailed summary of the relevant structural data is given in Tables 1 and 2.

2.3. Synthesis of polymer supported Pd-catalysts and their use in coupling reactions

2.3.1. Synthesis of support

Compound **4** was prepared in an analogous way as described for compound **2** (Scheme 1). For the synthesis of the support, the polymerization of **4** was initiated by $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$. Subsequent cross-linking with 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphthalene (DMN-H6) results in the formation of the ligand containing support (Scheme 2). The entire setup results in the formation of irregularly shaped particles with an average size of 20–40 μm. This size guarantees the convenient removal of the catalyst at the end of the reaction by means of filtration. Due to the living character of the polymerization, a quantitative incorporation of **4** into the subsequently formed support is guaranteed. As already described earlier for similar systems [14], this allows the synthesis of tailor-made supports in terms of catalyst loading simply by stoichiometry of the reactants. The reaction sequence itself results in the formation of a highly cross-linked matrix with the linear, ligand carrying polymer chains attached to its surface.

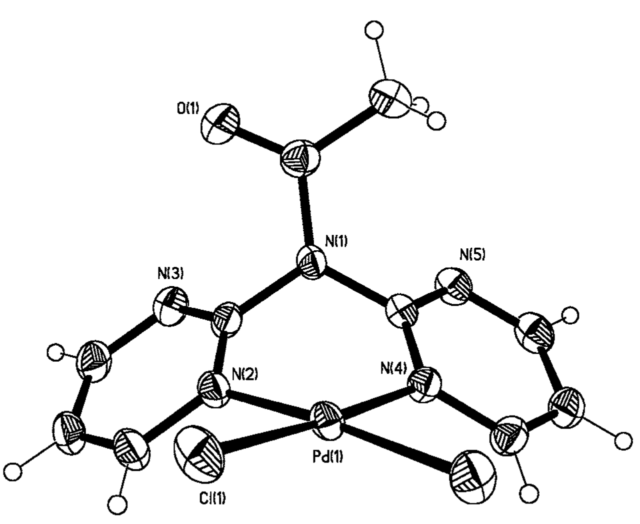


Fig. 1. Structure of compound **3**.

Table 1
Selected X-ray data for **3**

	3
Molecular formula	$C_{10}H_9Cl_2N_5OPd$
Formula weight	392.52
Temperature (K)	223(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	1208.71
b (Å)	1423.69
c (Å)	744.49
α (°)	90
β (°)	90.158(2)
γ (°)	90
V (nm^3)	1.28113(7)
Z	4
D_{calc} (mg m^{-3})	2.035
Absorption coefficient (mm^{-1})	1.863
Color, habit	Yellow prism
Reflections with $I>2\sigma(I)$	2035
Goodness-of-fit on F^2	1.068
R indices [$I>2\sigma(I)$])	$R_1=0.022$, $wR_2=0.051$

Table 2
Selected bond lengths (Å) and angles (°) for **3**

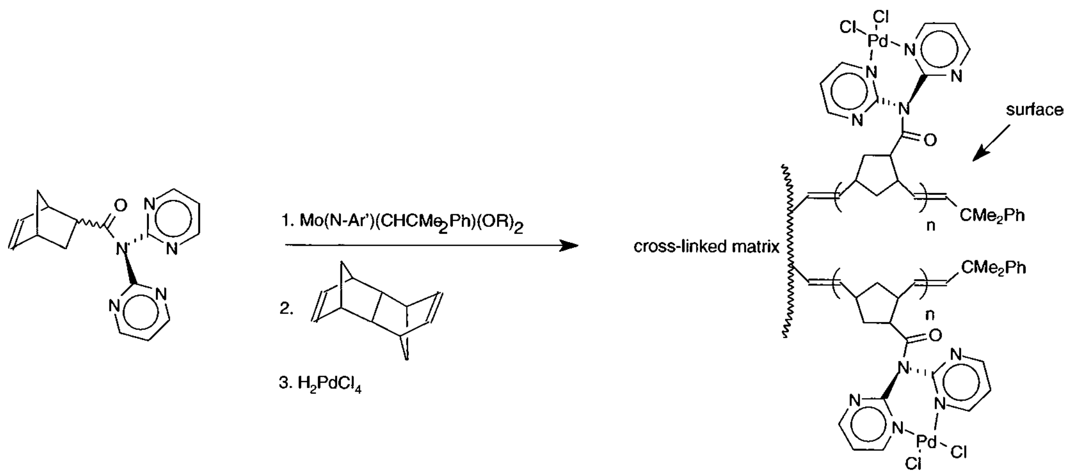
Bond lengths	
Pd(1)–N(2)	203.1(2)
Pd(1)–N(4)	204.8(2)
Pd(1)–Cl(1)	227.76(7)
Pd(1)–Cl(2)	228.17(7)
Bond angles	
N(2)–Pd(1)–N(4)	87.13(8)
N(2)–Pd(1)–Cl(1)	91.13(6)
N(4)–Pd(1)–Cl(1)	176.24(6)
N(2)–Pd(1)–Cl(2)	174.30(6)
N(4)–Pd(1)–Cl(2)	91.65(6)
Cl(1)–Pd(1)–Cl(2)	90.40(3)
C(3)–N(2)–Pd(1)	121.5(2)
C(4)–N(2)–Pd(1)	121.0(2)
C(7)–N(4)–Pd(1)	120.7(2)
C(8)–N(4)–Pd(1)	122.3(2)

Subsequent reaction of this support with H_2PdCl_4 gives the desired heterogeneous Pd catalysts. One significant difference to the parent dipyridylamide-based system needs to be addressed. Thus, the Pd-content of the Pd-loaded support as determined by ICP-OES was found to be roughly twice as much as the bis(pyrimidine) content of the unloaded support as determined by elemental analysis would let expect. Apparently, complexation of the Pd-units does not only occur as observed in **3** but also between the repetitive units and polymer chains, respectively, as illustrated in Fig. 2. The deep orange color of the supports as well as a comparably reduced softness of the support further indicate some cross-linking between the surface bound, ligand-containing polymer chains. This extensive sorption capacity for Pd leads to the favorable situation, were comparably high Pd loadings may be achieved with a comparably low amount of ligand. Despite the two different binding sites in this support, no leaching of Pd was observed during any type of coupling reaction. In all cases, the reduced (presumably Pd(0)) species remains virtually quantitatively attached to the support at the end of the reaction.

2.3.2. Heck couplings (entries 1–9, Table 3)

Heck couplings were carried out with compounds **3** and **6** between aryl iodides, bromides as well as chlorides and styrene and ethyl acrylate, respectively. A summary of the results is given in Table 3. All three systems were found to be highly active in the vinylation of aryl iodides and bromides. Generally speaking reactions carried out in DMAc using NBu_3 as this base turned out to be the best system for this type of couplings, resulting in almost quantitative yields (91–96%) and high TONs (up to 11 000). As for the parent dipyridylamide-based catalyst [10], no significant differences between the homogeneous system **3** and the heterogeneous analogue **6** were observed. Therefore, we carried out all further coupling reactions with the heterogeneous catalyst **6**.

Tetrabutylammonium bromide (TBAB) is known to promote Pd-mediated couplings [15] and may additionally be used as a non-aqueous ionic solvent [16–18]. Consequently, its influence on the reactivity was investigated. In contrast to aryliodides, the successful coupling of arylchlorides requires the presence of a stabilizing ligand. Thus, such couplings may be used as a probe for the effectiveness of a coupling system. Chlorobenzene does not react under standard conditions. Nevertheless, as observed for dipyridylamide-based systems, coupling of activated chloroarenes may successfully be accomplished in the presence of TBAB. While these coupling results are quite similar to those obtained previously with dipyridyl-based ligands [10], one difference was found in the reactions kinetics. Thus, pyrimidyl-based ligands exceed the dipyridylamide-based analogues in terms of turn-over frequency. A comparison of these two systems is shown in Fig. 3. As may be deduced therefrom, coupling reactions between bromobenzene and styrene catalyzed by **6** proceed at about the same rate as the reaction between the even more reactive iodobenzene and styrene catalyzed by the parent dipyridylamide system. Obviously, the enhanced electron density in pyrimidyl-based systems accelerates these reactions. This strongly indicates that the concept of electron rich N-based ligands, which should mimic the phosphine analogues in terms of basicity and electron density, gives access to more reactive coupling systems. Such systems are superior to alkyl-substituted



Scheme 2. Synthesis of resin **6**.

dipyrid-2-ylamines, since these suffer from unfavorable steric interactions between the alkyl groups and the carbonyl and chlorine moieties, respectively, thus resulting in distorted and consequently unstable catalysts [11].

2.3.3. Suzuki-couplings (entries 10–14, Table 4)

Suzuki couplings [4,19–21] represent an interesting yet still comparably expensive alternative to Heck couplings. With the present system (**6**), reaction of aryl boronic acids with iodoarenes in THF proceeds smoothly with yields $>80\%$. Coupling reactions with bromoarenes require comparably high amounts of Pd (up to 0.2 mol%) in order to obtain acceptable yields. Chloroarenes basically do not react under standard conditions (refluxing THF), yields are less than 5%. In light of recent results published on the Suzuki coupling of even deactivated aryl chlorides [22], the use of the present system for this type of C–C coupling reaction definitely appears less attractive.

2.3.4. Aminations and α-arylations (entries 15–20 Table 4) [23]

The combination of strong, sterically non-hindered bases and activated alkenes such as ethyl acrylate allows to run α-aminations in comparably high yields (up to 90%). Weaker bases such as ammonia result in the formation of the corresponding mono and dialkylated species in acceptable yields (60%). Interestingly, even non-activated chloroarenes may be converted into the corresponding *N*-aryl derivatives with comparably high TONs (up to 4400) and yields (up to 80%). Additionally, no transcomplexation is observed even with strong amines, thus underlining the high stability of the bispyrimidyl complexes. Finally, the catalytic system also provides access to α-arylations, yet yields are too low ($<45\%$) to be of any significant synthetic value.

2.3.5. Sonogashira–Hagihara couplings (entries 21–25, Table 5)

The heterogeneous system **6** is highly active in alkyne coupling reactions, in particular if aryl iodides are used. Virtually quantitative yields are obtained without the presence of additional Cu (I). The use of the less active aryl bromides results in satisfactory yields of up to 85% even with Pd amounts as low as 0.006 mol%. Again, the reaction of aryl chlorides may be accelerated effectively by TBAB to give yields similar to those obtained with aryl bromides. Unfortunately, we were not able to perform any alkyne couplings with *N*-containing substrates, e.g. between iodobenzene and 2-ethynylpyridine.

3. Experimental

3.1. Instrumentation

NMR data were obtained in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and on a Bruker AM400, respectively, and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hertz. IR spectra were recorded on a Nicolet 510 FT-IR. Titrations were performed using a 686 Titroprocessor (Metrohm, Switzerland). Eluents were degassed with He 5.0. Ele-

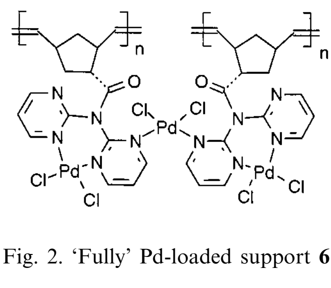


Fig. 2. 'Fully' Pd-loaded support **6**.

Table 3
Summary of Heck-type couplings

#	Ar–X	H_2C=CHR	Product	Catalyst	Yield [a] (%)	TON × 10^3
1	Bromobenzene	Styrene	Stilbene	**3**	96	8.6
2	4-Bromobenzonitrile	Styrene	4-Cyanostilbene	**6**	98	2.3a
3	4-Bromo-1-fluorobenzene	Styrene	4-Fluorostilbene	**3**	98	7.3
4	4-Bromo-1-fluorobenzene	Ethylacrylate	4-Fluorocinnamate	**3**	98	7.3
5	4-Methoxybromobenzene	Ethylacrylate	4-Methoxycinnamate	**3**	65	6.6
6	Chlorobenzene	Styrene	Stilbene	**3**	0	0
7	Chlorobenzene/TBAB	Styrene	Stilbene	**3**	30	1.0
8	4-Chloroacetophenone	Styrene	4-Acetylstilbene	**3**	0	0
9	4-Chloroacetophenone/TBAB	Styrene	4-Acetylstilbene	**6**	70	10.8
9	4-Chloroacetophenone/TBAB	Styrene	4-Acetyistilbene	**3**	63	4.2

Reactions were carried out in DMAc/N-Bu_3N at $T = 150$ °C. TBAB, tetrabutylammonium bromide.

[a] Isolated yields. The amount of Pd added was in the range of 0.006–0.03 mol%.

mental analyses were carried out at the Institute of Physical Chemistry, University of Vienna. Further instrumentation for ICP-OES experiments and for the determination of the specific surface area (σ) by means of GPC, is described elsewhere [9].

3.2. Reagents and standards

Synthesis of the ligands and polymerizations were performed under an argon atmosphere by standard Schlenk techniques or in an Ar-mediated dry-box (Braun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, tetrahydrofurane and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane, 1,2-dichioroethane were distilled from CaH under argon. Other solvents and reagents were used as purchased. *N*,*N*-Dimethylformamide (DMF) was dried over molecular sieves. Deionized water was used throughout. *endo*-Norborn-2-ene-5-carboxylic acid chloride [9], 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethanonaphthalene (DMN-H6), the initiators, $Mo(N\text{-}2,6\text{-}(i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2)$ [24], were prepared according to literature procedures and checked for purity by means of NMR.

3.3. Bis(pyrimid-2-yl)amine (**1**)

2-Aminopyrimidine (1.90 g, 20 mmol)), 2.29 g (20 mmol) 2-chloropyrimidine, 54 mg (1.3×10^{-4} mol) bis-diphenylphoshinopropane, 60 mg (6.5×10^{-4} mol) dipalladium-trisbenzylideneacetone, 2.23 g (23.2 mmol) sodium-*tert*-butylate and 20 ml toluene are combined in a Schlenk vessel under Argon. The mixture, which colorizes yellow and warms already while mixing the compounds, is kept at 80 °C for 16 h. After cooling, 20 ml water are added and a yellowish solid is collected by filtration over a sintered glass filter. The solid is washed twice with toluene and once with *n*-pentane, then dried in vacuum for a short time. The raw material is continuously extracted with boiling water (e.g. in a soxhlet) for some hours; most of the material dissolves, until only black or brown solids remain. Upon cooling, colorless to yellow needles precipitate from the extraction solution. Recrystallization from water can be repeated. These crystals contain 2 mol of water, which can be removed by drying in a vacuum desiccator over KOH for 24 h. Yield: 1.34 g (39% of theory) of fine, colorless needles.^1H (dmso-d_6,): δ 10.03 (s, 1H, NH); 8.57 (d, 4H, H_{meta}); 7.03 (t, 2H, H_{para}) ^{13}C (dmso-d_6): δ 159.2; 158.4; 115.4. Elemental Anal. Calc. for $C_8H_7N_5$ ($M_w = 173.17$ g mol^{-1}): C, 55.48; H, 4.07; N, 40.44. Found: C, 55.79; H, 4.01; N, 40.53%.

3.4. N-Acetyl-bis(pyrimid-2-yl)amide (**2**)

Compound **1** (250 mg, 1.4 mmol) was dissolved in a mixture of 0.15 ml of acetic anhydride and 0.15 ml of acetylchloride. The reaction mixture was refluxed for 12 h. The volatiles were removed in vacuo and **2** was

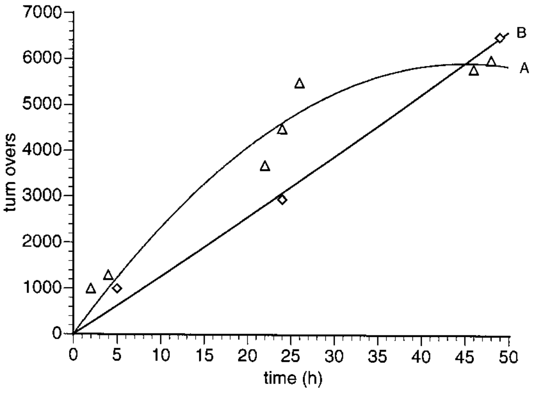


Fig. 3. Comparison of reaction rates (expressed in turn overs). (A) Bis(pyrimidyl)-catalyzed Heck reaction of styrene with C_6H_5Br; (B) parent dipyridylamide-catalyzed Heck reaction of styrene with C_6H_5I.

Table 4
Summary of Suzuki couplings, aminations and α-arylations

#		Ar–X	Product	Catalyst	Yield [a] (%)	TON × 10^3
Ar–B(OH)$_2$, Ar=						
10	4-MeC$_6$H$_4$-	Iodobenzene	4-Methylbiphenyl	**6**	83	6.5
11	4-MeOC$_6$H$_4$-	Bromobenzene	4-Methoxybiphenyl	**6**	35	2.9
12	4-MeC$_6$H$_4$-	Bromobenzene	4-Methylybiphenyl	**6**	74	0.7
13	4-MeOC$_6$H$_4$-	4-Bromoanisole	4,4′-Bis(methoxy)biphenyl	**6**	32	2.6
14	4-MeC$_6$H$_4$-	Chlorobenzene	4-Methylybiphenyl	**6**	<5	0.46
Amine						
15	Piperidine	Chlorobenzene	*N*-Phenylpipendine [b]	**6**	24	4.4
16	Piperidine	Chiorobenzene	*N*-Phenylpipefldine [b]	**6**	80	1.4
17	Diethylamine	Ethylacrylate	β-(*N*,*N*-Diethylamino)-ethylpropionate	**6**	79	10
18	Ammonia (30%)	Ethylacrylate	(β-Amino)E/*N*,*N*-bis-(1-ethoxy-carbonyleth-2-yl)amine	**6**	60 (1:2 mixture)	7
19	Morpholine	Ethylacrylate	β-(*N*-Morpholino)ethylpropionate	**6**	90	11.5
CH-acidic compound						
20	CH$_2$(CO$_2$Et)$_2$	Bromobenzene	PhCH(CO$_2$Et)$_2$	**6**	43	13.4

Reactions were carried out in THF at $T = 65$ °C, reaction time = 6 h. T = $NBu_4^+Br^-$.

[a] Isolated yields.

[b] Reaction was carried out in dioxane at 100 °C. The amount of Pd added was 0.005–0.2 mol-%, base = Cs$_2$CO.

Table 5
Summary of Sonogashira–Hagihara couplings

#	R–CCH	Ar–X	Product	Catalyst	Yield [a]	TON × 10^3
21	Ph–CCH	Iodobenzene	Diphenylacetylene	**6**	98	22.3
22	Ph–CCH	Bromobenzene	Diphenylacetylene	**6**	68	15.5
23	Ph–CCH/TBAB	Chlorobenzene	Diphenylacetylene	**6**	65	14.8
24	Tris(2-propyl)silylethyne	Dibromobenzene	Diethynylbenzene	**6**	85	12.4
25	Tris(2-propyl)silylethyne	Dichlorobenzene	Diethynylbenzene	**6**	50	7.3

Reactions were carried out in THF at $T = 65$ °C. Reaction time = 72 h. The amount of Pd added was in the range of 0.007–0.004 mol%, base = Bu$_3$N.

[a] Isolated yields.

purified by column chromatography (silica G 60, 220–400 mesh, THF). Yield: 217 mg (70%). IR (KBr): 1705 (C=O), 1686, 1563 (Ar), 1391, 1374 (CH$_3$), 1310, 1038, 814, 697, 608, 594. ^{1}H-NMR (dmso-d_6) δ 8.58 (d, 4H, $J = 3.0$), 7.14 (t, 2H, $J = 3.0$), 2.52 (s, 3H). ^{13}C-NMR (dmso-d_6) δ 172.3 (C=O), 160.5 (C$_{ipso}$), 158.6, 118.4, 25.8 (CH$_3$).

3.5. *N-Acetyl-bis(pyrimid-2-yl)-aminopalladium(II)dichloride (**3**)*

Compound **2** (50 mg, 0.23 mmol) was dissolved in methanol and an aq. solution of H$_2$PdCl$_4$ (prepared from 50 mg PdCl$_2$ and HCl, pH adjusted with NaOH to approximately 6) was added. The slightly cloudy solution was allowed to stand overnight, after which crystals of **3** suitable for X-ray analysis were filtered off. Yield: 72 mg (80%). IR (KBr): 1733 (C=O), 1590 (Ar), 1526, 1438, 1300, 1223 (CO), 826, 818, 809, 660. ^{1}H-NMR (dmso-d_6) δ 8.78 (d, 4H, $J = 4.9$), 7.42 (t, 2H, $J = 4.9$), 2.45 (s, 3H). ^{13}C-NMR (dmso-d_6) δ 171.5 (CO), 161.3, 158.8, 121.8, 118.9, 25.3 (CH$_3$). For X-ray data refer to Tables 1 and 2.

3.6. *N,N,-Bis(pyrimid-2-yl) (**4**)*

Norborn-2-ene-5-ylcarboxylic chloride 0.5 ml, 3.2 mmol) was added to a solution of **1** (0.25 g, 1.4 mmol) in dichloroethane (4 ml). The reaction mixture was refluxed for 24 h and poured on saturated aq. NaHCO$_3$ solution. Extraction was performed with methylene chloride. The combined organic layers were dried over sodium sulfate. After evaporation of the solvent, the residue was recrystallized from diethyl ether. Yield: 250 mg (61%). ^{1}H-NMR (dmso-d_6) δ 8.68 (d, 4H, $J = 4.9$), 713 (t, 2H, $J = 4.9$), 5.30 (m, 2H), 4.00 (m, 1H, C*H*CON), 3.01 (bs, 1H, C*H*), 2.84 (bs, 1H, C*H*), 1.81 (m, 1H, C*H*), 1.56 (m, 2H, 2 C*H*). ^{13}C-NMR (dmso-d$_6$) δ 177 (CO), 161.1, 158.6, 137.3, 132.7, 118.2, 49.5, 46.0, 45.5, 42.8, 30.3. Elemental Anal. Calc. for C$_{16}$H$_{15}$N$_5$O ($M_w = 293.328$ g mol^{-1}) C, 65.52; H, 5.15; N, 23.88. Found: C, 65.70; H, 5.22; N, 23.52%.

*3.7. Preparation of the resin **6***

The preparation and characterization of the resin (40 ± 10 μm, 0.19 mmol bis(pyrimidylamide) was performed under an argon atmosphere by standard Schlenk techniques according to previously published procedures [9,11]. Loading with palladium (II) was achieved by stirring the resin in an aq. solution of H_2PdCl_4 (1000 μg ml^{-1} in 5% HCl, pH adjusted to 5.0 with NaOH) at room temperature (r.t.) for 12 h. The actual amount of palladium (II) sorbed onto the resin as determined by ICP-OES was 0.4 mmol g^{-1}.

3.8. Heck-couplings

The educts (1:1 ratio, 1–2 g) were dissolved in 70–100 ml of solvent (used as purchased), then the base (1.2 equivalents) and the catalyst were added. Couplings were carried out at $T = 140$ °C in DMAc. Reaction times were 72 h unless stated otherwise. For work-up, the reaction mixture was poured on water, acidified with HCl (2 N) and extracted with diethyl ether (3–5 × 50 ml). The combined organic phases were dried over Na_2SO_4. Finally, the solvent and (where applicable) the reactants were evaporated in vacuo. The coupling products were isolated by flash chromatography (silica G-60, 4 × 30 cm, pentane–diethyl ether = 90:10) and repeated crystallization. Purity of the corresponding crops was determined by ^{1}H-NMR.

3.9. Suzuki-couplings, aminations and α-arylations

The educts (1:1 ratio, 1–2 g) were dissolved in 10–20 ml of THF, the base as well as the catalyst were added. Reactions were carried out in THF at $T = 65$ °C for 72 h. Cs_2CO_3 (1.5 equivalents) was used for Suzuki couplings and α-arylations, aminations were carried out in the absence of a base. For work-up, the reaction mixture was poured on water and the aq. phase was extracted with diethyl ether. After drying over Na_2SO_4, the solvent was evaporated. The corresponding products were purified by crystallization from diethyl ether–pentane.

3.10. Sonogashira–Hagihara couplings

The educts (1:1 ratio, 1–2 g) were dissolved in 10–20 ml of THF (used as purchased), then the base (tri-*n*-butylamine, 1.5 equivalents) and the catalyst were added. Reactions were carried out at $T = 65$ °C for 72 h. For work-up, the reaction mixture was poured on water and the aq. phase was extracted with diethyl ether. After drying over Na_2SO_4, the solvent was evaporated. The corresponding products were purified by crystallization from diethyl ether/pentane.

*3.11. X-ray measurement and structure determination of **3***

Compound **3** was measured on a Nonius Kappa CCD area-detector diffractometer with graphite-monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å) via a mixture of 2° ϕ and ω-scans, placing the CCD detector 36 mm from the crystal. The raw data were processed with the program DENZO-SMN [25] to obtain conventional data. The structure was solved by direct methods (SHELXS-86) [26] and refined by full matrix least-squares against F^2 (SHELXL-93) [27]. The function minimized was $\Sigma[w(F_O^2 - F_C^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_O^2) + (xP)^2 + yP]$ and $P = (F_O^2 + 2F_C^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were located by difference Fourier methods, but in the refinement they were generated geometrically and refined with isotropic displacement parameters 1.2 and 1.5 (methyl group) times higher than U_{eq} of the attached carbon atoms. Selected crystallographic data are summarized in Tables 1 and 2.

4. Summary

N-acyl substituted bispyrimidylamines form stable Pd complexes which may be used as highly active catalysts in a large variety of C–C and C–N coupling reactions. Similar to the parent *N*-acyldipyridylamines, bispyrimidylamines may be incorporated into a polymeric matrix via ROMP. The pyrimidyl-based systems exceed the parent system in terms of reactivity and additionally allow the extensive Pd-loading of the heterogeneous support by virtually quantitative complexation of all pyrimidine nitrogens.

5. Supplementary material

Further details are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) on quoting the depository numbers CCDC-161925, the names of the authors, and the journal citations.

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