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Journal of Organometallic Chemistry 622 (2001) 6–18

Journal of Organometallic Chemistry

N-Acyl-*N*,*N*-dipyridyl and *N*-acyl-*N*-pyridyl-*N*-quinoyl amine based palladium complexes. Synthesis, X-ray structures, heterogenization and use in Heck couplings

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Received 11 July 2000; received in revised form 7 September 2000

Abstract

A series of homogeneous and heterogeneous palladium(II)-catalysts and their use in Heck-couplings is described. Starting from four different amines, *N*-pyrid-2-yl-*N*-(3-methylpyrid-2-yl)amine (**1**), *N*-pyrid-2-yl-*N*-(6-methylpyrid-2-yl)amine (**2**), *N*-(6-methylpyrid-2-yl)-*N*-(4-methylquinolin-2-yl)amine (**3**) and *N*-bis(6-methylpyrid-2-yl)amine (**4**), the corresponding acetyl- and norbornene derivatives, *N*-pyrid-2-yl-*N*-(3-methylpyrid-2-yl) acetamide (**5**), *N*-pyrid-2-yl-*N*-(6-methylpyrid-2-yl) acetamide (**6**), *N*-(6-methylpyrid-2-yl)-*N*-(4-methylquinolin-2-yl) acetamide (**7**), *N*-bis(6-methylpyrid-2-yl)acetamide (**8**) and *N*-pyrid-2-yl-*N*-(3-methylpyrid-2-yl)-*endo*-norborn-2-ene-5-carbamide (**9**), *N*-pyrid-2-yl-*N*-(6-methylpyrid-2-yl)-*endo*-norborn-2-ene-5-carbamide (**10**) and *N*-(6-methylpyrid-2-yl)-*N*-(4-methylquinolin-2-yl)-*endo*-norborn-2-ene-5-carbamide (**11**), respectively, have been prepared. The acetyl derivatives **5**–**8** have been used for the preparation of the homogeneous Heck catalysts *N*-acetyl-*N*-pyrid-2-yl-*N*-(3-methylpyrid-2-yl)amine palladium dichloride (**13**), *N*-acetyl-*N*-pyrid-2-yl-*N*-(6-methylpyrid-2-yl)amine palladium dichloride (**14**), *N*-acetyl-*N*-(6-methylpyrid-2-yl)-*N*-(4-methylquinolin-2-yl)amine palladium dichloride (**15**) and *N*-acetyl-*N*-bis(6-methylpyrid-2-yl)amine palladium dichloride (**16**). X-ray data were obtained for compounds **9**, **11**, **13** and **14**. Polymer supports **17**–**19** were prepared via ring-opening metathesis copolymerization of the norbornene derivatives **9**–**11** with 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo*-*endo*-dimethano-naphthalene (HDMN-6) and subsequently loaded with palladium(II) chloride. Both the homogeneous catalysts **13**–**16** and the heterogeneous catalysts are active in the vinylation of aryl iodides and aryl bromides with turn-over numbers (TONs) of up to 220 000. Comparably low yields (= 34%) and TONs (= 2100) are achieved in the tetrabutylammonium bromide- (TBAB-) assisted vinylation of aryl chlorides as well as in the amination of aryl bromides. Structural data of compounds **9**, **11**, **13** and **14** were compared with those of the parent systems, *N*-acetyldipyridylamine palladiumdichloride (**20**) and the poly(*N*,*N*-dipyrid-2-yl-*endo*-norborn-2-ene-5-carbamide)based resin (**21**), respectively. Thus, methyl-substitution leads to a significant perturbation of the almost perfect square planar coordination of Pd found in **20** resulting in lowered stabilities of the corresponding Pd-complexes **13**–**16** and consequently lowered coupling yields compared to **20** and **21**.

Keywords: Palladium(II)-catalysts; Heck-couplings; Polymerizations; X-ray structures

1. Introduction

Palladium-mediated reactions such as polymerizations, C–C coupling reactions, aminations and hydrophosphorylations have attracted significant interest during the last years [1–8]. Nevertheless, 'classical' reactions such as the vinylation of aryl halides — commonly called the Heck reaction — are still the

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0022-328X/01/$ - see front matter
PII: S0022-328X(00)00783-X

center of interest [6]. In view of the significant progress in homogeneous catalysis [9,10] including asymmetric reactions [11–14], the demand for highly active and stable heterogeneous systems [15–19] is still high. Only few reports exist on the synthesis of heterogeneous palladium catalysts, e.g. based on palladium-loaded carbon or alumina, palladium-loaded porous glass, zeolite- (NaY-type) entrapped Pd-complexes, palladium colloids, Pd-grafted MCM-41 or triazene-functionalized Merrifield polymers [18–21]. Despite the high coupling activity of systems that may be generated from phosphine- or aminophosphine-based ligands [22], these are transformed easily into the corresponding phosphine oxides. This reaction results in a slow but permanent release of palladium (catalyst bleeding) which significantly restricts their industrial use. In order to circumvent this problem, more stable catalytic systems have been elaborated for homogeneous catalysis [19,23–25] including phospha-palladacyles [25,26], homoleptic chelating *N*-heterocyclic carbene complexes [27,28] as well as dipyridylamide based systems [29]. Ligands solely based on nitrogen [30], e.g. dipyridyl amide-based Heck coupling systems are relatively rare, yet turned out to be suitable for the synthesis of highly temperature stable and active Heck catalysts [29]. If incorporated into suitable monomers, ring-opening metathesis polymerization (ROMP) may be used for the preparation of well-defined heterogeneous Heck systems based on such ligands [29]. Generally speaking, heterogeneous polymer supports prepared by this approach are characterized by an exact knowledge about the chemical structure of the corresponding catalytic sites. Based on the encouraging results obtained with *N*-acyl-*N*,*N*-dipyridylamine-based Pd-complexes, we extended this type of *N*,*N*-ligands to other pyridine homologues. In this contribution, the use of methyl-substituted dipyridyl amide and pyridyl–quinoyl amide ligands for homogeneous and heterogeneous Heck couplings as well as the structural features that influence reactivity will be presented.

2. Results and discussion

2.1. Synthesis of amines

Palladium-catalyzed aryl–X activation (X = I, Br or Cl) reactions are an efficient tool for the synthesis of amines via C–N-bonds formation [31,32]. If 2-X–pyridines are used X can be Cl since the systems are activated, but the formation of catalyst deactivating palladium pyridine complexes has to be avoided. Thus, the palladium catalyst has to be stabilized by chelating bisphosphine ligands. Reactions of 2-aminopyridines with one equivalent of the corresponding 2-halogenpyridine and 1.25 equivalents of sodium-*tert*-butylate in the presence of 1 mol% bis-diphenylphosphinopropane and 0.5 mol% Pd_2dba_3 in toluene at 80°C leads usually after less than 1 h to a color change to yellow. After stirring additional 12 h, workup with dichloromethane and water, the compounds were purified via chromatography or crystallization. The reactions are highly selective, almost no formation of doubly arylated amines has been found. Compound **1** was prepared from 3-methylpyrid-2-yl-amine and 2-bromopyridine, compound **2** from 6-methylpyrid-2-yl-amine and 2-bromopyridine, compound **3** from 6-methylpyrid-2-yl-amine and 2-chloro-4-methylquinoline and compound **4** from 6-methyl-2-yl-amine and 2-chloro-6-methylpyridine (Fig. 1). All starting materials are commercially available.

2.2. Homogeneous Heck catalysts

In order to obtain structural information about geometry and binding, homogeneous analogues were prepared by reaction of the amines **1**–**4** with acetyl chloride and acetic anhydride, respectively (Scheme 1). Reaction of the resulting acetyl derivatives **5**–**8** with H_2PdCl_4 in methanol/water at pH 5 yields the corresponding palladium complexes **13**–**16**. Complexes **13** and **14** were characterized by X-ray analysis and show the expected yet distorted square planar conformation of the palladium center (Figs. 2 and 3). A summary of the relevant structural data is given in Table 1. A comparison between compounds **13** and **14**, *N*-acetyl-*N*,*N*-dipyrid-2-ylamine palladium dichloride (**20**) [29], the free ligands **7**, **9** (Figs. 4 and 5) and norborn-2-ene-5-(*N*,*N*-dipyrid-2-yl)carbamide [33] reveals no significant differences between the angles defined by C3–N3–C8 (C_α–N3–C'_α, 115.5–119.4°). The same applies to the distances Pd–N1, which were found to lie in the range of 142.2–144.4 pm. Nevertheless, the dihedral angle defined by PdN(1)N(2)–PdCl(1)Cl(2) turned out

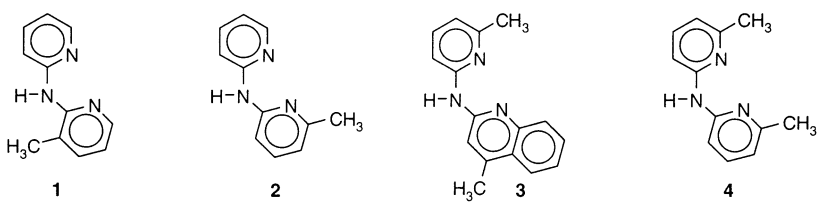
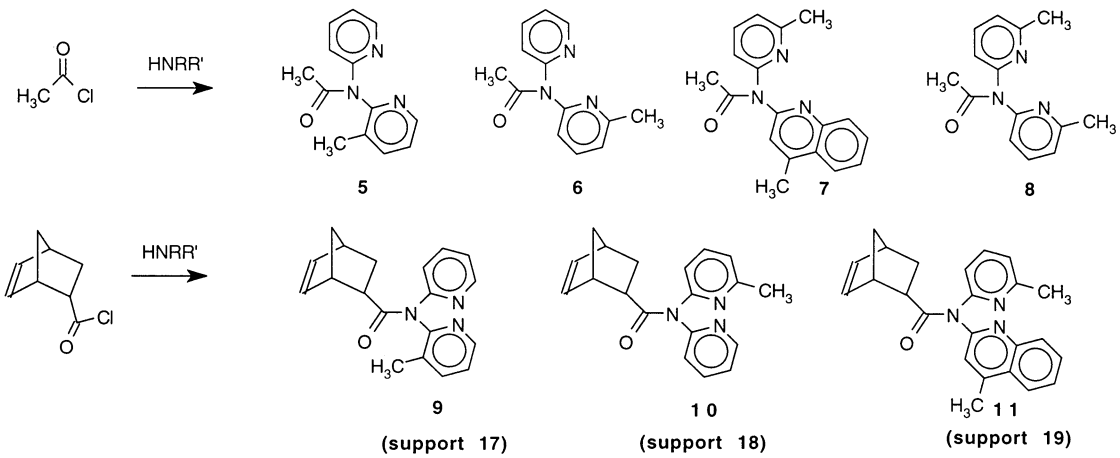


Fig. 1. Structure of compounds **1**–**4**.



Scheme 1. Synthesis of acetyl- and norbornene derivatives of compounds **1**–**4**.

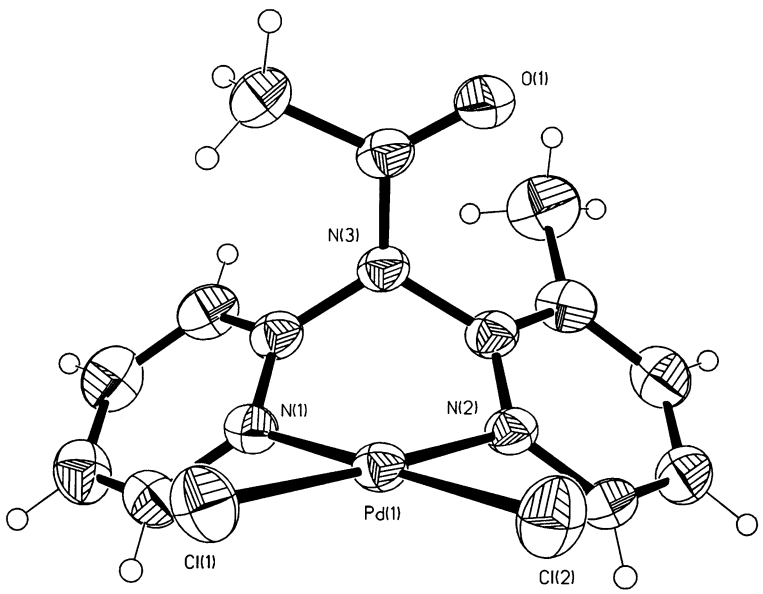


Fig. 2. X-ray structure of compound **13**.

to be an appropriate probe for the steric situation at the palladium. Thus, this angle is almost zero in the case of compounds **20** or **13** (2.8(1) and 1.1(1)°, respectively), yet is increased to 10.5(8)° in the case of compound **14**. Obviously, the steric repulsion between the methyl group and one chlorine atom results in the formation of such distorted square planar complexes. As might be expected, this unfavorable change in conformation is also reflected on the stability of the resulting Pd complexes. While the high stability of **20** basically impedes any quantitative NMR measurements, the dissociation constants (K_D) for complexes **13**–**16** may be obtained easily by ^{1}H-NMR in dmso-d_6. Thus, K_D increases in the order **13** (9×10^{-5}) < **14** (2.7×10^{-3}) < **16** (2.3×10^{-2}) < **15** (4.8×10^{-2} mol l^{-1}). The reactivity of compounds **13**–**16** and supports **17**–**19**, respectively (Table 3) is directly related to these geometric and thermodynamic features. While the methyl group in 3-position (compounds **13** and support **17**, respectively) basically has no influence on the reactivity, the methyl group in position six (compounds **14**–**16** and supports **18**–**19**, respectively) drastically reduces the stability of these catalytic systems. Consequently, coupling results obtained with these compounds are similar to those of $Pd(OAc)_2$ (vide infra).

2.3. Heterogeneous Heck catalysts

Ring-opening metathesis polymerization (ROMP) has been demonstrated to present a powerful tool in the preparation of functionalized polymer supports [29,33–40]. Even complex functionalities may be introduced with high reproducibility and without any change in the chemical nature, geometry and even chirality of the corresponding functional group. The norborn-2-ene-

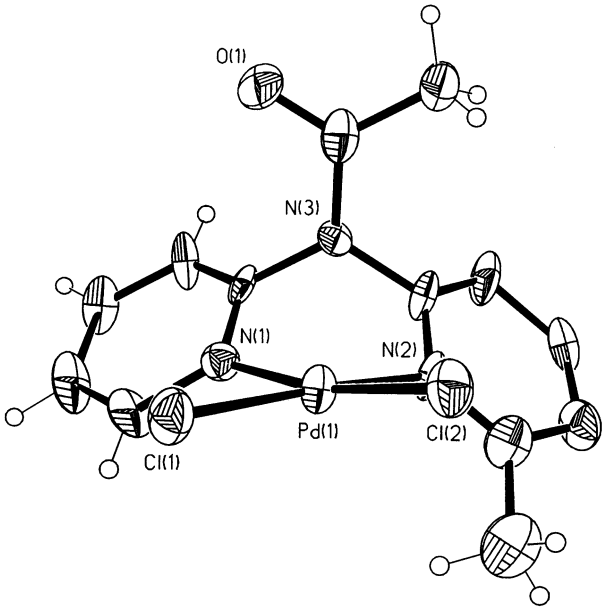


Fig. 3. X-ray structure of compound **14**.

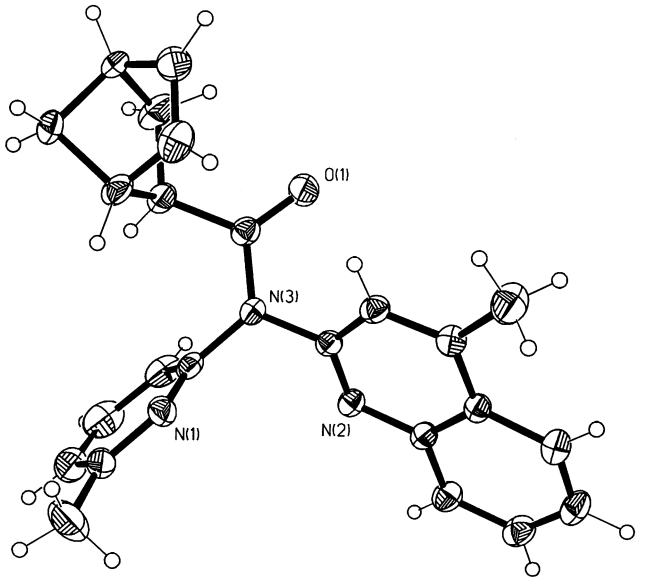


Fig. 4. X-ray structure of compound **7**.

derivatives **9**–**11** are conveniently prepared from norborn-2-ene-5-carboxylic chloride and the corresponding amine (Scheme 1) and may be polymerized in a living manner using the Schrock-catalyst Mo(*N*-2,6-*i*-Pr_2-C_6H_3)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$. Similar procedures for the synthesis of functional supports and subsequent loading of the resin have been reported previously [29]. Briefly, living polymers of compounds **9**–**11** were cross-linked using DMNH-6 (Scheme 2, Table 2). As a consequence of the polymerization order, the linear polymer chains bearing the functional groups form tentacles that are attached to the surface of the cross-linked carrier. The use of a Mo-based system is essential, since Ru-based Grubbs systems generally fail to polymerize such strongly chelating systems [41]. In contrast to the parent dipyridylamide-based ligands, significantly lowered Pd-loadings (0.03–0.05 mmol g^{-1}, Table 2) may be achieved. The palladium-loaded chelating groups are located exclusively at the surface of the particle [33,42], are easily accessible, diffusion plays a minor role and coupling reactions may proceed within the interphase [43,44].

Table 1
Selected X-ray data for compounds **9**, **11**, **13** and **14**

	9	**11**	**13**	**14**
Molecular formula	$C_{19}H_{19}N_3O$	$C_{24}H_{23}N_3O$	$C_{13}H_{13}Cl_2N_3OPd{\cdot}C_4H_8O$	$C_{13}H_{13}Cl_2N_3OPd$
Formula weight	305.37	369.45	476.67	404.56
Crystal system	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	$Pna2_1$ (no. 33)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)
a (pm)	1861.5(5)	975.5(2)	778.63(2)	1485.9(2)
b (pm)	1443.3(4)	1816.4(3)	916.75(2)	1509.0(2)
c (pm)	602.2(4)	1195.3(2)	1449.77(4)	1496.7(2)
α (°)	90	90	88.005	90
β (°)	90	112.79(2)	76.030	117.95(1)
γ (°)	90	90	71.236	90
V (nm^3)	1.6179(12)	1.9526(6)	0.94984(4)	2.9645(7)
Z	4	4	2	8
T (K)	218.2	293(2)	213(2)	218(2)
D_{calc} (mg m^{-3})	1.254	1.257	1.667	1.813
Absorption coefficient (mm^{-1})	0.080	0.078	1.274	1.610
Color, habit	Colorless prism	Colorless prism	Yellow prism	Light yellow prism
No. of reflections with $I>2\sigma(I)$	1358	2124	3505	1967
Goodness-of-fit on F^2	1.098	1.071	1.096	1.126
R indices $I>2\sigma(I)$	$R_1 = 0.0400$, $\omega R_2 = 0.0984$	$R_1 = 0.0435$, $\omega R_2 = 0.1019$	$R_1 = 0.0266$, $\omega R_2 = 0.0735$	$R_1 = 0.1057$, $\omega R^2 = 0.2002$

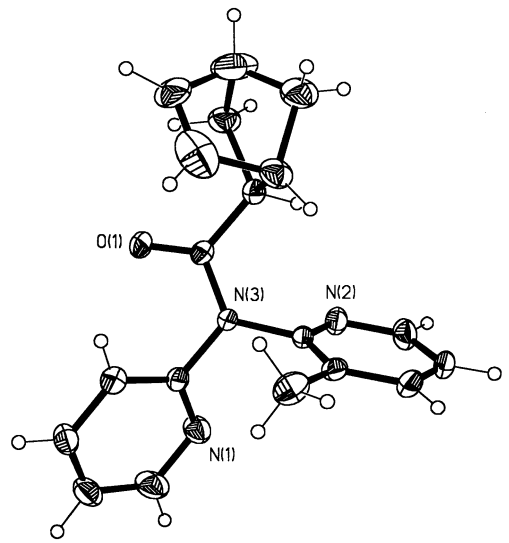


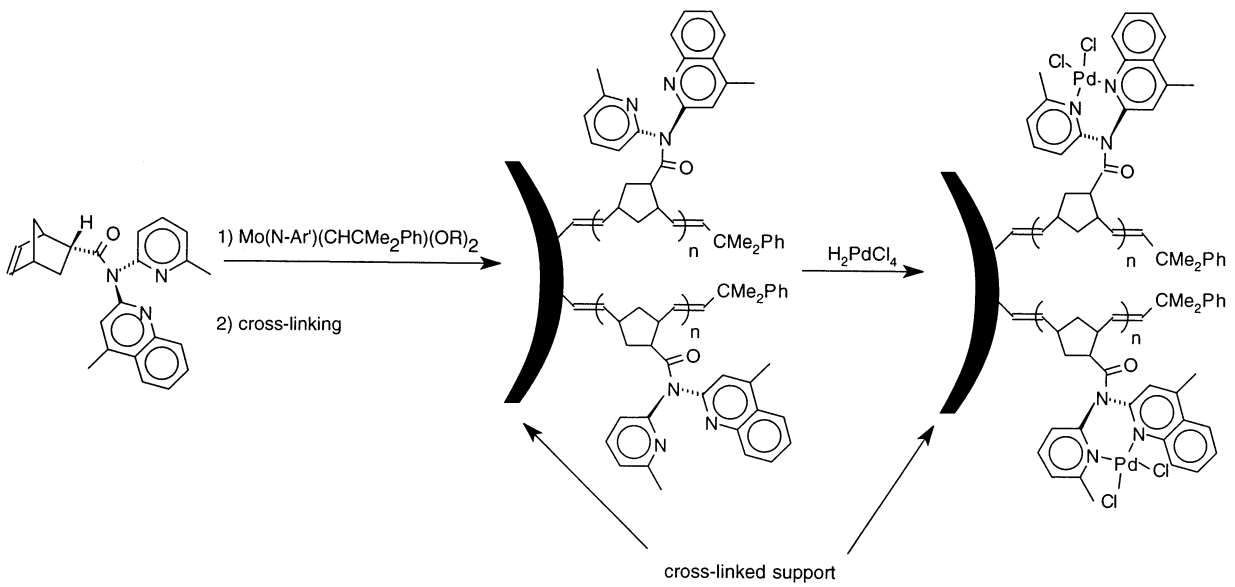
Fig. 5. X-ray structure of compound **9**.

2.4. Heck couplings

Heck couplings were carried out with compounds **13**–**16** as well as with the corresponding heterogeneous systems **17**–**19** between aryl iodides, bromides as well as chlorides and styrene and ethyl acrylate, respectively. A summary of the results is given in Table 3.

2.4.1. Aryliodides

A comparison of the data reveals no significant differences between the four different homogenous catalysts **13**–**16** (Table 3). In terms of the maximum achievable TONs, similar numbers (66 000–80 000) are obtained. Heterogenization requires a careful choice of the solvent, since it influences strongly the chemistry at the interphase [43,45]. Despite these similar results that are obtained with compounds **13**–**16**, some interesting data may be deduced from the kinetics that have been recorded for the corresponding heterogeneous systems **17**–**19**. Generally speaking DMAc/NBu_3 turned out to be the best system for this type of coupling, resulting in almost quantitative yields (91–96%) and acceptable TONs (32 000). Interestingly, the use of sodium/potassium carbonate did not give comparable results. Tetrabutylammonium bromide (TBAB) is known to promote Pd-mediated couplings [46] and may additionally be used as a non-aqueous ionic solvent [47–49]. Conse-



Scheme 2. Preparation and loading of polymer supports (e.g. resin **19**).

Table 2
Summary of cross-linked polymers

Resin	Monomer			Cross-linker		Initiator		Yield		Nitrogen		Pd-loading
	No.	mg	mmol	mg	mmol	mg	mmol	mg	%	%	mmol g^{-1}	mmol g^{-1}
17	9	120	0.39	480	3.03	17.8	0.023	320	53	2.90	2.1	0.03
18	10	74	0.24	296	1.87	11.0	0.014	368	98	2.71	1.9	0.05
19	11	109	0.30	438	2.77	16.4	0.021	286	52	4.15	3.0	0.05

Table 3
Summary of Heck-couplings [a]

No.	Ar–X	H_2C=CHR	Product	Catalyst	Pd (mol%)	Solvent	Yield (%)	TON $\times 10^{-3}$
1	Iodobenzene	Styrene	*trans*-Stilbene	13	0.001	DMF [b]	66	
2	Iodobenzene	Styrene	*trans*-Stilbene	14	0.001	DMF [b]	80	80.0
3	Iodobenzene	Styrene	*trans*-Stilbene	15	0.001	DMF [b]	75	75.0
4	Iodobenzene	Styrene	*trans*-Stilbene	16	0.001	DMAC [b]	67	75.8
5	Iodobenzene	Styrene	*trans*-Stilbene	17	0.003	DMAC [b]	91	31.9
6	Iodobenzene	Styrene	*trans*-Stilbene	18	0.003	DMAC [b]	96	33.6
7	Iodobenzene	Styrene	*trans*-Stilbene	19	0.003	DMAC [b]	92	32.2
8	Iodobenzene	Styrene	*trans*-Stilbene	21	0.0008	DMAC [b]	99	111.0
9	Iodobenzene/TBAB	Styrene	*trans*-Stilbene	17	0.003	DMAC [b]	80	28.0
10	Iodobenzene/TBAB	Styrene	*trans*-Stilbene	18	0.003	DMF [b]	81	28.4
11	Iodobenzene/TBAB	Styrene	*trans*-Stilbene	19	0.003	DMF [b]	87	30.5
12	Iodobenzene/TBAB	Styrene	*trans*-Stilbene	21	0.0014	DMF [b]	98	93.2
13	Iodobenzene	Styrene	*trans*-Stilbene	17	0.001	DMF [b]	47	54.2
14	Iodobenzene	Styrene	*trans*-Stilbene	18	0.001	DMF [b]	39	45.0
15	Iodobenzene	Styrene	*trans*-Stilbene	19	0.001	DMF [b]	45	52.9
16	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	13	0.002	DMF [b]	97	49.3
17	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	14	0.002	DMF [b]	97	49.3
18	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	15	0.002	DMF [b]	97	49.3
19	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	17	0.0004	DMF [b]	87	213.2
20	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	18	0.0004	DMF [b]	91	223.0
21	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	18	0.0004	DMF [b]	89	218.1
22	Iodobenzene	Ethyl acrylate	Ethyl cinnamate	21	0.0006	DMF [b]	75	175.1
23	Bromobenzene	Styrene	*trans*-Stilbene	17	0.002	DMAC [b]	6	2.5
24	Bromobenzene	Styrene	*trans*-Stilbene	18	0.002	DMAC [b]	35	14.4
25	Bromobenzene	Styrene	*trans*-Stilbene	19	0.002	DMAC [b]	31	12.8
26	Bromobenzene	Styrene	*trans*-Stilbene	21	0.002	DMAC [c]	90	40.0
27	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	13	0.004	DMF [b]	45	10.3
28	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	14	0.004	DMF [b]	88	20.1
29	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	15	0.004	DMF [b]	87	19.8
30	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	17	0.0005	DMF [b]	36	67.6
31	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	18	0.0005	DMF [b]	34	63.8
32	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	19	0.0005	DMF [b]	33	62.0
33	4-Bromobenzonitrile	Styrene	4-cyano-*trans*-Stilbene	21	0.0004	DMF [b]	83	157.7
34	4-Bromo-1-fluorobenzene	Styrene	4-fluoro-*trans*-Stilbene	17	0.002	DMAC [b]	38	22.2
35	4-Bromo-1-fluorobenzene	Styrene	4-fluoro-*trans*-Stilbene	18	0.002	DMAC [b]	41	23.9
36	4-Bromo-1-fluorobenzene	Styrene	4-fluoro-*trans*-Stilbene	19	0.002	DMAC [b]	21	12.3
37	4-Bromo-1-fluorobenzene	Styrene	4-fluoro-*trans*-Stilbene	21	0.0014	DMAC [c]	58	34.4
38	Chlorobenzene/TBAB	Styrene	*trans*-Stilbene	17	0.003	DMAC [c]	0	0
39	Chlorobenzene/TBAB	Styrene	*trans*-Stilbene	18	0.003	DMAC [c]	0	0
40	Chlorobenzene/TBAB	Styrene	*trans*-Stilbene	19	0.003	DMAC [c]	0	0
41	Chlorobenzene/TBAB	Styrene	*trans*-Stilbene	21	0.007	DMAC [c]	89	23.6
42	4-Chloroacetophenone/TBAB	Styrene	4-acetyl-*trans*-Stilbene	17	0.02	DMAC [b]	18	1.1
43	4-Chloroacetophenone/TBAB	Styrene	4-acetyl-*trans*-Stilbene	18	0.02	DMAC [b]	34	2.1
44	4-Chloroacetophenone/TBAB	Styrene	4-acetyl-*trans*-Stilbene	19	0.02	DMAC [b]	20	1.2
45	4-Chloroacetophenone/TBAB	Styrene	4-acetyl-*trans*-Stilbene	21	0.014	DMAC [c]	95	6.1
46	Bromobenzene/KO-t-Bu	*N*-methylaniline	*N*-methyldiphenylamine	18	0.003	THF [d]	14	4.7
47	Bromobenzene/KO-t-Bu	*N*-methylaniline	*N*-methyldiphenylamine	21	0.017	[d]	45	3.8

[a] TBAB = tetrabutylammonium bromide. Yields were determined by ^{1}H-NMR. Heck-couplings were carried out at $T = 140$°C, $t = 90$ h.
[b] tri-*n*-Butylamine.
[c] K_2CO_3/Na_2CO_3.
[d] KO-*t*-Bu/NaO-*t*-Bu (1:1), reflux.

quently, its influence on the reactivity was investigated. Interestingly, significantly different kinetics were observed for **17**–**19** in DMF (Fig. 6), these differences basically vanished in the case of DMF/TBAB (Fig. 7) or pure DMAc. Nevertheless, such drastic changes in kinetics as found for the parent dipyridyl syste [29] were not observed. Finally, as expected, rather high TONs ($>200\,000$) are obtained with electron deficient vinyl compounds such as ethyl acrylate (Table 3). In summary, these results are comparable

with those obtained with the parent, unsubstituted system **21** [29].

2.4.2. Arylbromides and arylchlorides

In contrast to aryliodides, the successful coupling of arylbromides and in particular arylchlorides requires the presence of a stabilizing ligand. Consequently, such couplings may be used as a probe for the effectiveness of a coupling system. In the present system, changing from aryliodides to the less reactive aryl bromides leads to lower coupling yields and TONs both in the homogeneous and heterogeneous case. Thus, coupling yields for bromobenzene and the more activated 4-fluoro- and 4-cyano-substituted analogues were in the range of 33–41%, TONs of 21 000–68 000 were achieved. For comparison, the use of the parent heterogeneous system **21** resulted in significantly elevated coupling yields (58–90%) and TONs (34 000–160 000) [29]. Interestingly, comparatively results in terms of TONs (4700 for **18** vs. 3800 for **21**) are obtained in the Pd-mediated arylation of arylamines. As expected, chlorobenzene may not be coupled even if TBAB is used. Finally, even activated arylchlorides such as 4-chloroacetophenone in the presence of TBAB give lower yields (18–34%) compared to the parent system **21** (95%) [29].

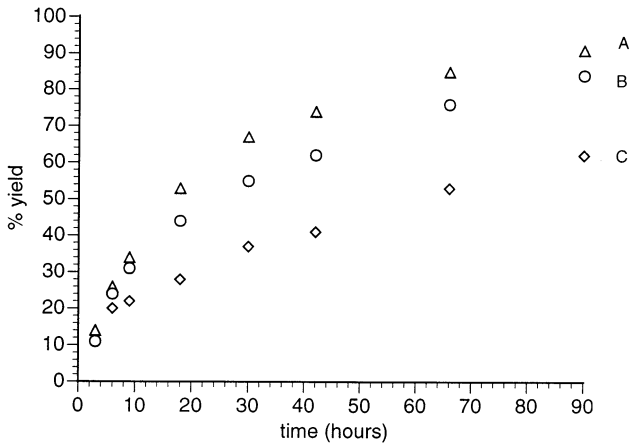


Fig. 6. Time profile for the formation of *trans*-stilbene in DMF ($T = 140$°C). (A) Using **18**; (B) using **19**, (C) using **17**.

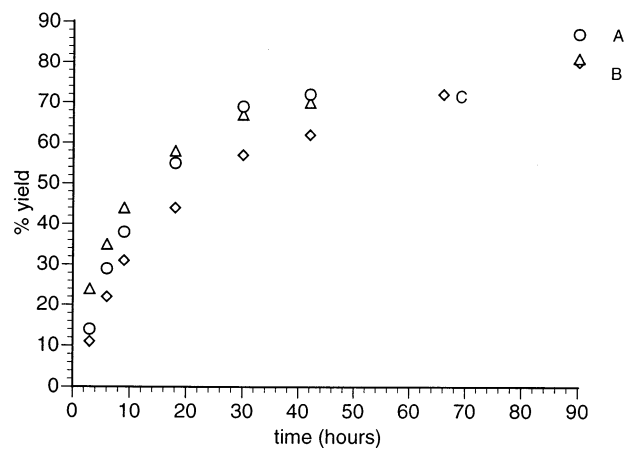


Fig. 7. Time profile for the formation of *trans*-stilbene in DMF/TBAB ($T = 140$°C). (A) Using **19**; (B) using **18**, (C) using **17**.

2.4.3. Active species

Neutral or anionic palladium(0) species are widely accepted to represent the active species in phosphane-based Heck couplings [50,51]. They are generated by a redox-reaction [52], e.g. via oxidation of a phosphine to the corresponding phosphine oxide [53,54]. Recently, Arai et al. proposed that Pd(0) that leached into a suitable solvent from a support essentially catalyzes the reaction. Both the base and the solvent influence the kinetics of the reaction, yet do not affect the overall rate of the reaction much. Based on the comparably large dissociation constants (K_D) of the Pd-complexes **13**–**16** (vide supra) and on the observed coupling activities in the current systems we believe that such dissolved Pd species may play a certain role in the present systems. Consequently, these differ from the parent, unsubstituted dipyridylamide-based system, which was found to form stable Pd-complexes and is highly active in the homogeneous and heterogeneous coupling of aryl halides, including aryl chlorides. To provide some data for this hypothesis, heterogeneous supports were checked for their initial and final Pd-content prior to and after an iodobenzene/styrene coupling reaction by means of ICP-OES. No change in the Pd-content was detected within experimental error (10%). This indicates, that (at least major amounts) of the Pd are still on the carrier. The organic reaction mixture was not found to be active in a consecutive coupling reaction. Nevertheless, in contrast to the parent heterogeneous dipyridyl system, the coupling activity of such a support was drastically diminished. This suggests that the polymer supported palladium exists in form of rather large, free Pd-clusters and not in form of ligated, well-defined organometallic compounds. So far, this hypothesis is in accordance with the reports of Arai et al., who found that dissolved Pd-species may 'reprecipitate' onto a support [55,56].

3. Experimental

3.1. General details

NMR data were obtained in the indicated solvent at 30°C on a Bruker AM 300 and 400, unless stated otherwise and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are given in Hertz. IR-spectra were

recorded on a Nicolet FT-IR. Further instrumentation for GPC and ICP-OES experiments, is described elsewhere [33]. Purchased starting materials were used without any further purification. Reagent grade tetrahydrofuran and toluene were distilled from sodium benzophenone ketyl under nitrogen. *endo*-Norborn-2-ene-5-carboxylic acid chloride [33] and Mo(*N*-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)(OCMe$(CF_3)_2)_2$ [57] were synthesized as described in the literature. Polymerizations were carried out in a nitrogen-mediated dry-box (Braun, Germany). Column chromatography was performed on silica gel 60 (0.063–0.200 mm) from Merck.

3.2. Preparation of amines

All operations are performed under argon. In a Schlenk vessel, 15 mmol of a 2-aminopyridine and one molar equivalent of a 2-halogenpyridine (2-bromopyridine, 2-chlorolepidine or 2-chloro-6-methylpyridine) are mixed with 62 mg (1 mol%) bis-diphenylphosphinopropane, 69 mg (0.5 mol%) dipalladium-tris(benzylideneacetone) Pd_2dba_3 and 1.80 g (1.25 equivalents) sodium-*t*-butylate. To this mixture 15 ml of dry toluene is added and heated to 80°C with stirring. For reasons of safety, pressure should be released after reaching this temperature by briefly opening the Schlenk valve. After 1 h, usually earlier, the contents of the Schlenk turns yellow and a solid precipitates. The reaction mixture is stirred over night for completion and cooled to room temperature. Depending on the viscosity of the mixture the solvent is removed in a rotary evaporator or condensed into a dry ice trap under vacuum. For work up, dichloromethane and water are added to the reaction mixture, the organic phase is washed once with water, the aqueous phase re-extracted once with a small amount of dichloromethane. The combined organic phase is dried over sodium sulfate and the solvents evaporated to yield the crude product, which is purified by the method given in detail below.

3.3. Preparation of acetyl derivatives

Method A: the reaction was performed under an argon atmosphere by standard Schlenk techniques. A solution of the corresponding amine in 15 ml dry methylene chloride was cooled to -40°C. Acetyl chloride was added to the well-stirred solution. The mixture was slowly warmed to room temperature, and stirred for an additional 19 h. For work up, the mixture was extracted with saturated aqueous sodium bicarbonate solution (until the aqueous layer was alkaline). The organic layers were dried over sodium sulfate, and the solvent was removed in vacuo. The formerly oily product was purified by repeated crystallization from diethyl ether.

Method B: 300–370 mg of the corresponding amine were dissolved in 4 ml of acetic anhydride. The solution was stirred at 110°C for 4 h. For work-up, 50 ml of saturated aqueous sodium bicarbonate solution was added and the mixture was stirred until no more carbon dioxide developed. The alkaline solution was extracted with diethyl ether. The combined organic layers were dried over sodium sulfate and the solvent was removed in vacuo. The oily product was purified by column chromatography (silica G-60, 2.5×25 cm, diethyl ether) and repeated crystallization from diethyl ether.

3.3.1. N-Pyrid-2-yl-N-(3-methylpyrid-2-yl)amine (**1**)

Compound **1** was prepared from 3-methylpyrid-2-ylamine (1.62 g, 15 mmol) and 2-bromopyridine (1.46 ml, 2.37 g, 15 mmol). Chromatography of the crude product over silica gel (eluent: petroleum ether (b.p. 40–60°C)/ethyl acetate 2:1) gave a yellow viscous oil, which did not solidify even after prolonged standing, in 2.66 g (95%) yield. ^{1}H-NMR (C_6D_6): δ 8.94 (d, 1H, $J = 8.4$); 8.31 (m, 1H); 8.20 (d, 1H, $J = 4.9$); 7.36 (m, 1H); 7.24 (s, broad, 1H, NH); 6.81 (m, 1H); 6.57 (m, 1H); 6.44 (dd, 1H, $J = 7.2$, $J = 4.9$); 1.57 (s, 3H, Ar–CH_3). ^{13}C-NMR (C_6D_6): δ 154.9; 153.5; 148.5; 145.6; 138.0; 137.8; 119.0; 117.3; 116.2; 113.1; 16.8 (Ar–*C*H_3). Elemental Anal. Calc. for $C_{11}H_{11}N_3$ ($M_w = 185.23$ g mol^{-1}): C, 71.33; H, 5.99; N, 22.69. Found: C, 71.70; H, 6.15; N, 22.42%.

3.3.2. N-Pyrid-2-yl-N-(6-methylpyrid-2-yl)amine (**2**)

Compound **2** was prepared from 6-methylpyrid-2-ylamine (1.62 g, 15 mmol) and 2-bromopyridine (1.46 ml, 2.37 g, 15 mmol). Chromatography of the crude product over silica gel (eluent: petroleum ether (b.p. 40–60°C)/ethyl acetate 3:1) gave a yellow viscous oil, which did not solidify even after prolonged standing, in 2.67 g (96%) yield. MS (CI, 70eV): 185 (60) [M$^+$]; 184 (100) [M$^+ -$ H]; 170 (3) [M$^+ -$ CH$_3$]; 78 (15). ^{1}H-NMR (C_6D_6): δ 8.27 (m, 1H); 7.60 (s, broad, 1H, N*H*); 7.39 (m, 1H); 7.26 (d, 1H, $J = 8.2$); 7.13 (m, 2H) 6.46 (d $\times$ d $\times$ d, 1H, $J_1 = 1.2$, $J_2 = 5.2$, $J_3 = 7.5$); 6.42 (d, 1H, $J = 7.4$), 2.40 (s, 3H, Ar–*C*H_3). ^{13}C-NMR (C_6D_6): δ 157.0; 155.1; 154.3; 148.3; 138.1; 137.6; 116.3; 115.7; 112.1; 109.1; 24.6 (Ar–*C*H_3). Elemental Anal. Calc. for $C_{11}H_{11}N_3$ ($M_w = 185.23$ g mol^{-1}): C, 71.33; H, 5.99; N, 22.69. Found: C, 71.21; H, 6.19; N, 21.98%.

3.3.3. N-(6-Methylpyrid-2-yl)-N-(4-methylquinolin-2-yl)amine (**3**)

Compound **3** was prepared from 6-methylpyrid-2-ylamine (1.62 g, 15 mmol) and 2-chloro-4-methylquinoline (2.67 g, 15 mmol). The crude product was dissolved in a minimum amount of dichloromethane, layering

with the double amount of *n*-pentane and standing for a few days yields yellow blocky crystals in 2.59 g (69%) yield. The yield can be improved by treating the mother liquor again in the same way or by chromatography of the crude product over silica gel (eluent: petroleum ether (b.p. 40–60°C)/ethyl acetate 1:1). ^{1}H-NMR ($CDCl_3$): δ 8.25 (d, 1H, $J = 8.3$); 7.84 (m, 2H); 7.58 (m, 2H); 7.50 (s, 1H, N*H*); 7.34 (m, 1H); 7.00 (s, 1H); 6.76 (d, 1H, $J = 7.5$); 2.60 (s, 3H, quin-CH_3); 2.46 (s, 3H, py-CH_3). ^{13}C-NMR ($CDCl_3$): δ 157.0; 153.4; 153.0; 147.6; 146.0; 138.8; 136.1; 129.8; 128.1; 125.2; 124.0; 123.8; 117.0; 114.1; 109.8; 24.6; 19.3. Elemental Anal. Calc. for $C_{16}H_{15}N_3$ ($M_w = 249.31$ g mol^{-1}): C, 77.08; H, 6.06; N, 16.85. Found: C, 77.01; H, 6.05; N, 16.73%.

3.3.4. N-bis(6-Methylpyrid-2-yl)amine (4)

Compound **4** was prepared from 6-methylpyrid-2-ylamine (1.62 g, 15 mmol) and 2-chloro-6-methylpyridine (1.64 ml, 1.91 g, 15 mmol). The crude oily product solidifies on standing over night. Melting in vacuum (1 mbar) and cooling gives after resolidification a brownish solid, 2.99 g (quantitative), which is sufficiently pure for further work. For elemental analysis an analytical sample was purified by chromatography over silica gel (eluent: petroleum ether (b.p. 40–60°C)/ethyl acetate 2:1). ^{1}H-NMR δ (C_6D_6, Bruker 400MHz): 8.25 (s, broad, 1H, N*H*); 7.37 (d, 2H, $J = 8.3$); 7.14 (t, 2H, $J = 7.5$); 6.42 (d, 2H, $J = 7.1$); 2.40 (s, 6H, *CH*$_3$). ^{13}C-NMR (C_6D_6): δ 156.7; 154.4; 137.8; 115.3; 108.8; 24.3. Elemental Anal. Calc. for $C_{12}H_{13}N_3$ ($M_w = 199.25$ g mol^{-1}): C, 72.33; H, 6.58; N, 21.09. Found C, 72.10; H, 6.62; N, 20.88%.

3.3.5. N-Pyrid-2-yl-N-(3-methylpyrid-2-yl) acetamide (5)

Compound **5** was prepared according to method A from acetyl chloride (1 ml, 14 mmol) and *N*-pyrid-2-yl-*N*-(3-methylpyrid-2-yl)amine (460 mg, 2.5 mmol) in 36% yield (100 mg). IR (KBr, cm^{-1}): 3066w, 2985w, 2954w, 1692vs ($\nu_{C=O}$),1576s, 1466s, 1438s, 1370s, 1328s, 1302vs, 1264s, 1156s, 1123m, 1023m, 1007m, 985w, 816m, 780s, 743m, 656m, 602s, 525m. ^{1}H-NMR ($CDCl_3$): δ 8.41 (m, 1H), 8.28 (d, broad, 1H, $J = 4.5$), 7.68 (m, 3H), 7.25 (m, 1H), 7.04 (m, 1H), 2.20 (s, 3H, Ar–CH_3), 2.03 (s, 3H, CH_3CO). ^{13}C-NMR ($CDCl_3$): δ 170.6 (CO), 153.8, 148.2, 147.3, 140.0, 137.7, 132.2, 123.7, 120.6, 119.5, 24.3 (*C*H$_3$CO), 17.5 (*C*H$_3$Ar). Elemental Anal. Calc. for $C_{13}H_{13}N_3O$ ($M_w = 227.27$ g mol^{-1}): C, 68.71; H, 5.77; N, 18.49. Found: C, 68.95; H, 5.76; N, 18.47%.

3.3.6. N-Pyrid-2-yl-N-(6-methylpyrid-2-yl) acetamide (6)

Compound **6** was prepared according to method A from acetyl chloride (1 ml, 14 mmol) and *N*-pyrid-2-yl-*N*-(6-methylpyrid-2-yl) amine (340 mg, 1.8 mmol) in 70% yield (147 mg). IR (KBr, cm^{-1}): 3109m, 3053m, 3001m, 2928m, 1688vs ($\nu_{C=O}$), 1587s, 1575s, 1457s, 1433s, 1365s, 1305s, 1272s, 1219s, 1150s, 1098m, 1021m, 993m, 807m, 779s, 625m, 554m, 525m, 410m; ^{1}H-NMR ($CDCl_3$): δ 8.40 (m, broad, 1H), 7.62 (m, 3H), 7.08 (m, 3H), 2.49 (s, 3H, Ar–CH_3), 2.12 (s, 3H, CH_3CO); ^{13}C-NMR ($CDCl_3$): δ 170.9 (CO), 158.4, 154.6, 154.0, 148.6, 138.3, 137.8, 121.8, 121.5, 119.4, 24.6 (*C*H$_3$CO), 24.2 (Ar–*C*H$_3$). Elemental Anal. Calc. for $C_{13}H_{13}N_3O$ ($M_w = 227.27$ g mol^{-1}): C, 68.71; H, 5.77; N, 18.49. Found: C, 68.53; H, 5.75; N, 18.40%.

3.3.7. N-(6-Methylpyrid-2-yl)-N-(4-methylquinolin-2-yl) acetamide (7)

Compound **7** was prepared according to method B from *N*-(6-methylpyrid-2-yl)-*N*-(4-methylquinolin-2-yl) amine (370 mg, 1.5 mmol) in 72% yield (309 mg). IR (KBr, cm^{-1}): ^{1}H-NMR ($CDCl_3$): δ 7.95 (m, 2H), 7.65 (m, 2H), 7.54 (m, 1H), 7.34 (s, 1H), 7.25 (d, 1H, $J = 7.9$), 7.08 (d, 1H, $J = 7.5$), 2.68 (s, 3H, quin-CH_3), 2.50 (s, 3H, py-CH_3), 2.24 (s, 3H, CH_3CO). ^{13}C-NMR ($CDCl_3$): δ 171.4 (CO), 158.3, 153.9, 153.7, 146.9, 146.4, 138.2, 129.6, 129.3, 126.9, 126.3, 123.6, 121.7, 120.4, 119.3, 24.7 (*C*H$_3$CO), 24.2 (py-*C*H$_3$), 18.8 (quin-*C*H$_3$).

3.3.8. N,N-Bis-(6-methylpyrid-2-yl) acetamide (8)

Compound **8** was prepared according to method B from bis-(6-methylpyrid-2-yl) amine (327 mg, 1.6 mmol) in 90% yield (358 mg). IR (KBr, cm^{-1}): 1688vs ($\nu_{C=O}$), 1594s, 1566s, 1457s, 1364s, 1304s, 11261m, 1169m, 1032m, 1001m, 820m, 789m, 746m, 654m, 629m, 558m, 546m, 407m. ^{1}H-NMR ($CDCl_3$): δ 7.59 (d × d, 2H, $J_1 = 7.9$, $J_2 = 7.5$), 7.19 (d, 2H, $J = 7.9$), 7.02 (d, 2H, $J = 7.5$), 2.47 (s, 6H, Ar–CH_3), 2.14 (s, 3H, CH_3CO). ^{13}C-NMR ($CDCl_3$): δ 171.0 (CO), 158.1, 154.0, 138.1, 121.4, 118.9, 24.5 (*C*H$_3$CO), 24.2 (Ar–*C*H$_3$). Elemental Anal. Calc. for $C_{14}H_{15}N_3O$ ($M_w = 241.29$ g mol^{-1}): C, 69.69; H, 6.27; N, 17.41; found: C, 69.35, H, 6.13, N, 17.35%.

3.4. Preparation of homogenous Pd-catalysts

A solution of sodium hydroxide (15%) was added to a solution of palladium(II) chloride in conc. hydrochloric acid (1 ml) to adjust to a pH of roughly 5. A solution of the corresponding acetyl-derivative in methanol (3 ml) was added to the well-stirred solution. A yellow crystalline solid formed which was filtered off, washed with methanol and diethyl ether and dried in vacuo.

3.4.1. N-Acetyl-N-pyrid-2-yl-N-(3-methylpyrid-2-yl)amine palladium dichloride (13)

Compound **13** was synthesized from **5** (62 mg, 0.27 mmol) and palladium(II) chloride (48 mg, 0.27 mmol)

in 58% yield (64 mg). IR (KBr, cm^{-1}): 3099w, 2962w, 2913w, 1700vs ($\nu_{C=O}$), 1603s, 1461, 1372s, 1302s, 1279s, 1229m, 1135m, 1040m, 1023m, 795s, 595m; ^{1}H-NMR (DMSO-d_6): δ 8.82 (d, 1H, J 0 5.3), 8.62 (d, 1H, $J = 5.6$), 8.29 (m, 2H), 8.11 (d, 1H, $J = 7.5$), 7.72 (m, 1H), 7.59 (m, 1H), 2.41 (s, 3H, Ar–CH_3), 2.28 (s, 3H, CH_3CO); ^{13}C-NMR (DMSO-d_6): δ 168.3 (CO), 153.3, 150.5, 148.5, 146.9, 143.4, 143.3, 135.1, 126.3, 126.1, 125.6, 22.6 (*C*H_3CO), 17.0 (Ar–*C*H_3). Elemental Anal. Calc. for $C_{13}H_{13}N_3OPdCl_2$ ($M_w = 404.59$ g mol^{-1}): C, 38.59; H, 3.24; N, 10.39. Found: C, 38.79; H, 3.27; N, 10.26%. Single crystals suitable for X-ray analysis were obtained by crystallization from methylene chloride/THF.

3.4.2. *N-Acetyl-N-pyrid-2-yl-N-(6-methylpyrid-2-yl)amine palladium dichloride* (**14**)

Compound **14** was synthesized from **6** (57 mg, 0.32 mmol) and palladium(II) chloride (56.8 mg, 0.32 mmol) in 89% yield (115 mg). IR (KBr, cm^{-1}): 3073w, 2925m, 1712vs ($\nu_{C=O}$), 1604s, 1572m, 1469vs, 1444m, 1371s, 1283s, 1252s, 1168m, 1158m, 1035m, 803m, 774m, 757m, 670m, 615m, 602m, 558m. ^{1}H-NMR (DMSO-d_6): δ 8.65 (d, 1H, $J = 5.7$), 8.25 (m, 1H, $J = 7.5$), 8.16 (m, 1H), 7.93 (m, broad, 2H), 7.65 (m, 1H), 7.55 (d, 1H, $J = 8.3$), 3.11 (s, 3H, Ar–CH_3), 2.36 (s, 3H, CH_3CO). ^{13}C-NMR (DMSO-d_6): δ 168.4 (CO), 162.3, 152.7, 148.7, 148.5, 142.3, 141.9, 126.3, 125.6, 125.3, 122.4, 26.5 (Ar–*C*H_3), 22.8 (*C*H_3CO). Elemental Anal. Calc. for $C_{13}H_{13}N_3OPdCl_2$ ($M_w = 404.59$ g mol^{-1}): C, 38.59; H, 3.24; N, 10.39. Found: C, 38.36; H, 3.19; N, 10.17%. Single crystals suitable for X-ray analysis were obtained by crystallization from methylene chloride/THF.

3.4.3. *N-Acetyl-N-(6-methylpyrid-2-yl)-N-(4-methylquinolin-2-yl)amine palladium dichloride* (**15**)

Compound **15** was synthesized from **7** (105 mg, 0.36 mmol) and palladium(II) chloride (64 mg, 0.36 mmol) in 83% yield (146 mg). IR (KBr, cm^{-1}): 1707vs ($\nu_{C=O}$), 1594s, 1565s, 1512m, 1469s, 1414m, 1367s, 1341s, 1311m, 1278m, 1251m, 1171m, 1033m, 982m, 798m, 762s, 634m, 607m. ^{1}H-NMR (DMSO-d_6): δ 9.04 (d (b), 1H, $J = 8.7$), 7.99 (m, 4H), 7.75 (m, 2H), 7.49 (d (b), 1H, $J = 7.9$), 3.10 (s, 3H, py-CH_3), 2.81 (s, 3H, quin-CH_3), 2.49 (s, 3H, CH_3CO). ^{13}C-NMR (DMSO-d_6): δ 168.4 (CO), 162.0, 149.9, 148.4, 144.4, 141.9, 131.2, 128.7, 127.8, 126.4 (2 C), 124.7, 124.1, 122.2, 26.3 (py-*C*H_3), 23.3 (*C*H_3CO), 18.2 (quin -*C*H_3).

3.4.4. *N-Acetyl-N,N-bis(6-methylpyrid-2-yl)amine palladium dichloride* (**16**)

Compound **16** was synthesized from **8** (29.5 mg, 0.17 mmol) and palladium(II) chloride (40.0 mg, 0.17 mmol) in 90% yield (63 mg). IR (KBr, cm^{-1}): 1711 ($\nu_{C=O}$), 1606s, 1565m, 1467s, 1371s, 1296s, 1262s, 1248s, 1167m, 1096m, 1032m, 951m, 866m, 808m, 754m, 626m, 607m. ^{1}H-NMR (DMSO-d_6): δ 8.11 (d × d, 2H, $J_1 = 7.9$, $J_2 = 7.9$), 8.03–7.86 (s, broad, 2H), 7.55 (d, broad, 2H, $J = 7.1$), 3.07 (s, 6H, Ar–CH_3), 2.41 (s, 3H, COCH_3). ^{13}C-NMR (DMSO-d_6): δ 168.3 (CO), 162.0, 133.7, 126.1, 122.3, 26.1 (Ar–*C*H_3), 23.0 (CO*C*H_3). Elemental Anal. Calc. for $C_{14}H_{15}N_3OPdCl_2$ ($M_w = 418.62$g mol^{-1}): C, 40.17, H, 3.61, N, 10.04. Found: C, 40.09, H, 3.56, N, 9.89%.

3.5. Preparation of norbornene-based monomers

Reactions were performed under an argon atmosphere by standard Schlenk techniques. A solution of the corresponding amine in 10 ml of dry methylene chloride was cooled to −40°C. *endo*-Norborn-2-ene-5-carboxylic acid chloride was added to the well-stirred solution. The mixture was warmed slowly to room temperature and stirred for additional 18 h. For work up, 20 ml of saturated aqueous sodium bicarbonate solution were added and the mixture was stirred until no more carbon dioxide was developed. The alkaline solution was extracted with methylene chloride. The combined organic layers were dried over sodium sulfate, and the solvent was removed in vacuo. The remaining brown residue was dissolved in diethyl ether and the product was isolated by column chromatography (silica G-60, 2.5 × 25 cm, diethyl ether) and purified by repeated crystallization from diethyl ether.

3.5.1. *N-Pyrid-2-yl-N-(3-methylpyrid-2-yl)-endo-norborn-2-ene-5-carbamide* (**9**)

Compound **9** was prepared from **1** (377 mg, 2.0 mmol) and norborn-2-ene carboxylic chloride (1 ml, 7 mol) in 80% yield (251 mg). IR (KBr, cm^{-1}): 3050m, 2979m, 2932m, 2864m, 1680vs ($\nu_{C=O}$), 1572s, 1434s, 1357s, 1310s, 1248s, 1204s, 1119m, 1025m, 990m, 794m, 768m, 768s, 712s, 641m. ^{1}H-NMR ($CDCl_3$): δ 8.44 (d × d, 1H, $J_1 = 4.9$, $J_2 = 1.5$), 8.29 (d (broad), 1H, $J = 4.9$), 7.63 (m, 3H), 7.23 (m, 1H), 7.03 (m, 1H), 6.21 (d × d, 1H, $J_1 = 5.7$, $J_2 = 3.0$, H_2), 6.11 (d × d, 1H, $J_1 = 5.7$, $J_2 = 3.0$, H_3), 3.11 (m (broad), 2H, $H_{4,5}$), 2.80 (s (broad), 1H, H_1), 2.16 (s, 3H, CH_3), 1.50 (m (broad), 2H, $H_{6a,b}$), 1.29 (m, 1H, H_{7a}), 1.04 (d (broad), 1H, $J = 8.3$, H_{7b}). ^{13}C-NMR ($CDCl_3$): δ 174.9 (CO), 154.3, 153.8, 148.3, 147.1, 139.8, 137.4, 137.1, 132.6, 132.2, 123.4, 120.5, 120.4, 49.6, 45.9, 44.4, 42.7, 30.4, 17.8 (CH_3). Elemental Anal. Calc. for $C_{19}H_{19}N_3O$ ($M_w = 305.38$ g mol^{-1}): C, 74.73; H, 6.27; N, 13.76. Found: C, 74.59; H, 6.31; N, 13.79%. Single crystals suitable for X-ray analysis may be obtained by crystallization from diethyl ether.

3.5.2. N-Pyrid-2-yl-N-(6-methylpyrid-2-yl)-endo-norborn-2-ene-5-carbamide (**10**)

Compound **10** was prepared from **2** (500 mg, 2.7 mmol) and norborn-2-ene carboxylic chloride (0.4 ml, 4 mol) in 38% yield (157 mg). IR (KBr, cm^{-1}): 3063m, 2979m, 2938w, 2872m, 1673vs ($\nu_{C=O}$), 1657s, 1589s, 1574s, 1565s, 1455s, 1432s, 1377s, 1338s, 1313s, 1264s, 1223s, 1153s, 1093m, 996m, 910m, 836m, 790s, 760s, 714s, 695m. ^{1}H-NMR ($CDCl_3$): δ 8.41 (m, 1H), 7.66 (m, 2H), 7.50 (d (broad), 1H, $J = 8.3$), 7.11 (m, 3H), 6.22 (d × d, 1H, $J_1 = 5.7$, $J_2 = 3.0$, H_2), 6.13 (d × d, $J_1 = 5.7$, $J_2 = 3.0$, H_3), 3.26 (m, 1H, H_5), 2.94 (s (broad), 1H, H_4), 2.82 (s (broad), 1H, H_1), 2.51 (s, 3H, CH_3), 1.54 (m, 2H, $H_{6a,b}$), 1.30 (m, 1H, H_{7a}), 1.08 (m, 1H, $J = 8.3$, H_{7b}). ^{13}C-NMR ($CDCl_3$): δ 175.1 (CO), 158.3, 155.0, 154.1, 148.6, 138.0, 137.5, 137.0, 132.6, 122.0, 121.5, 121.2, 119.8, 49.6, 46.1, 44.4, 42.8, 30.9, 24.3 (CH_3). Elemental Anal. Calc. for $C_{19}H_{19}N_3O$ ($M_w = 305.38$ g mol^{-1}): C, 74.73; H, 6.27; N, 13.76. Found: C, 74.60; H, 6.24; N, 13.79%.

3.5.3. N-(6-Methylpyrid-2-yl)-N-(4-methylquinolin-2-yl)-endo-norborn-2-ene-5-carbamide (**11**)

Compound **11** was prepared from **3** (500 mg, 2.0 mmol) and norborn-2-ene carboxylic chloride (2.0 ml, 13 mol) in 60% yield (220 mg). IR (KBr, cm^{-1}): 3072m, 2966m, 2931m, 2854m, 1673vs ($\nu_{C=O}$), 1595s, 1569s, 1509s, 1455s, 1343s, 1278s, 1245s, 1220s, 1187m, 1016m, 837m, 769s, 719s, 616w. ^{1}H-NMR ($CDCl_3$): δ 7.92 (m, 2H), 7.61 (m, 2H), 7.51 (m, 1H), 7.26 (d (broad), 1H, $J = 8.3$), 7.19 (d (broad), 1H, $J = 7.9$), 7.03 (d (broad), 1H, $J = 7.5$), 6.22 (d × d, 1H, $J_1 = 5.7$, $J_2 = 3.0$, H_2), 6.15 (d × d, $J_1 = 5.7$, $J_2 = 3.0$, H_3), 3.42 (m, 1H, H_5), 3.01 (s (broad), 1H, H_4), 2.79 (s (broad), 1H, H_1), 2.66 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 1.54 (m, 2H, $H_{6a,b}$), 1.28 (m, 1H, H_{7a}), 1.06 (m, 1H, $J = 7.9$, H_{7b}). ^{13}C-NMR ($CDCl_3$): δ 175.7 (CO), 158.1, 154.0, 146.9, 145.8, 137.8, 137.0, 132.7, 129.6, 129.1, 126.8, 126.0, 123.5, 121.3, 120.7, 119.7, 49.6, 46.2, 44.5, 42.8, 31.0, 24.2 (CH_3), 18.8 (CH_3). Elemental Anal. Calc. for $C_{24}H_{23}N_3O$ ($M_w = 369.47$ g mol^{-1}): C, 78.02; H, 6.27; N, 11.37. Found: C, 77.86; H, 6.31; N, 11.28%. Single crystals suitable for X-ray analysis may be obtained by crystallization from diethyl ether.

3.6. Preparation of linear polymers

The corresponding monomer (20 mg) was dissolved in dry methylene chloride. The initiator (Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$, 3 mg, 3.9 μmol, dissolved in 1 ml of methylene chloride) was added to the well-stirred solution. After stirring for 3 h, ferrocene carboxaldehyde (about tenfold excess based on initiator) was added, and stirring was continued for 1 h. Finally, the polymer was precipitated by an excess of diethyl ether, filtered off and dried in vacuo. The obtained yields were > 80%.

3.6.1. Poly-**9**

$M_w = 6400$, PDI = 1.16; ^{1}H-NMR ($CDCl_3$): δ 8.33 (broad, 1H), 8.25 (broad, 1H), 7.66 (broad, 1H), 7.57(broad, 2H), 7.18 (broad, 1H), 7.66 (d, broad, 1H, $J = 7.5$), 5.62 (broad, 1H), 5.40 (broad, 1H), 4.13 (m), 4.04 (s) (Cp), 2.79 (broad, 1H), 2.61 (broad, 2H), 2.06 (broad, 3H), 1.89 (broad, 2H), 1.46 (broad, 1H), 1.26 (d, $J = 6.8$) ($CHCMe_2Ph$) (90% *cis*). ^{13}C-NMR ($CDCl_3$): δ 175.1 (CO), 154.1, 148.2, 146.9, 139.9, 137.5, 134.3, 132.0, 130.2, 127.8, 126.3, 123.3, 122.7, 120.8, 69.0 (Cp), 47.7, 41.8, 40.5, 37.4, 27.9, 18.0 (CH_3).

3.6.2. Poly-**10**

$M_w = 7500$, PDI = 1.19; ^{1}H-NMR ($CDCl_3$): δ 8.34 (broad, 1H), 7.58 (m, broad, 3H), 7.57(broad, 2H), 7.01 (m, broad, 1H), 5.54 (broad, 1H), 5.40 (broad, 1H), 4.13 (m), 4.02 (s) (Cp), 3.10 (broad, 1H), 2.76 (broad, 1H), 2.54 (broad, 1H), 2.40 (broad, 3H), 1.92 (broad, 2H), 1.81 (broad, 1H), 1.37 (broad, 1H), 1.26 (d, $J =$ 6.8) ($CHCMe_2Ph$) (80% *cis*). ^{13}C-NMR ($CDCl_3$): δ 174.8(CO), 158.2, 154.8, 154.1, 148.6, 138.2, 137.6, 133.9, 130.6, 122.2, 121.6, 119.8, 47.6, 41.8, 37.8, 37.4, 27.9, 24.3 (CH_3).

3.6.3. Poly-**11**

$M_w = 14300$, PDI = 1.38; ^{1}H-NMR ($CDCl_3$): δ 7.85 (broad, 1H), 7.72 (m, broad, 1H), 7.53(broad, 1H), 7.44 (broad, 2H), 7.44 (m, broad, 3H), 5.58 (broad, 1H), 5.41 (broad, 1H), 4.02 (s) (Cp), 3.27 (broad, 1H), 2.75 (broad, 1H), 2.55 (s, broad, 3H) (CH_3), 2.31 (s, broad, 3H) (CH_3), 2.00 (broad, 2H), 1.79 (broad, 2H), 1.32 (broad, 1H), 1.25 (d, $J = 6.8$) ($CHCMe_2Ph$) (80% *cis*). ^{13}C-NMR ($CDCl_3$): δ 175.3 (CO), 158.0, 154.0, 146.9, 146.0, 138.0, 137.5, 134.1, 130.7, 129.4, 129.1, 126.9, 126.1, 123.7, 121.4, 120.8, 119.8, 47.9, 41.8, 40.2, 37.4, 24.2(CH_3), 18.9(CH_3).

3.7. Preparation of the resins

Resins were synthesized according to a previously published procedure [29,33].

3.8. Loading of heterogeneous Pd-catalysts

Water (5 ml) was added to a solution of palladium(II) chloride (1.5-fold excess based on the total amount of ligand attached to the support) in conc. hydrochloric acid (1 ml). A solution of sodium hydroxide (15%) was carefully added to adjust to a pH of 5. After addition of ca. 5 ml of methanol, the cross-linked polymer was added and the suspension was stirred for 20 h. The resin was filtered off, washed with water and

dried in vacuo. The actual amount of palladium(II) sorbed onto the resin was determined by ICP-OES.

3.9. Heck-couplings/aminations

Unless stated otherwise, couplings were carried out at $T = 140$°C on a 2–4-g scale in the solvent indicated in Table 3. Solvents and reagents were used as purchased. The educts were dissolved in 10–30 ml of solvent and the base (tri-*n*-butylamine, K_2CO_3, Na_2CO_3) as well as the catalyst were added. For aminations, the aryl halide and the amine were dissolved in dry THF, the base as well as the catalyst were added. Reactions were carried out at 65°C. The reaction time was 90 h throughout. Reaction times as well as a summary of the experiments including the corresponding scales and molar ratios are given in Table 3. Yields were determined from the educts: product ratio that was determined by ^{1}H-NMR-spectroscopy via integration of the *o*-H signals of the stilbene derivative and the aryliodide, respectively. For work-up, the reaction mixture was poured on water, acidified with hydrochloric acid (2 N) and extracted with diethyl ether (4×50 ml). The combined organic phases were dried over sodium sulfate. 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.

3.10. Time profiles for the formation of trans-stilbene

(A) Standard procedure: a mixture of iodobenzene (1.5 g), styrene (0.77 g), Bu_3N (3 ml) and the Pd catalyst (0.0027 mol% Pd(II) based on styrene) in dimethyl formamide (DMF) was stirred at 140°C. The time-dependent yield was calculated from the educt:product ratio which was determined by ^{1}H-NMR spectroscopy. (B) Tetrabutylammonium bromide (Bu_4NBr, 0.5 g) was added to the standard mixture. (C) Reaction was performed in dimethyl acetamide (DMAC).

3.11. Dissociation constants

Values for K_D (equilibrium constant for dissociation, defined as $L_2PdCl_2 \rightarrow L_2 + PdCl_2$) were determined by NMR spectroscopy in dmso-d_6 via integration of the signals for the methyl groups of the complex and the free ligand and comparison with an internal standard (Me_4Si).

3.12. X-ray measurement and structure determination of compounds *9*, *11*, *13*, *14*

Data for compounds **9** and **11** were collected on a Bruker P4 diffractometer with graphite-monochromatized Mo–Kα radiation ($\lambda = 71.073$ pm). Intensities were measured via ω-scans and corrected for Lorentz and polarization effects. Compounds **13** and **14** were measured on a Nonius Kappa CCD area-detector diffractometer ($\lambda = 71.073$ pm) with the CCD detector placed 36 mm from the crystal via a mixture of 2 (**13**) or 1.3° (**14**) ϕ and ω-scans. The raw data were processed with the program DENZO-SMN [58] to obtain conventional data. Structures were solved by direct methods (SHELXS-86) [59] and refined by full matrix least-squares against F^2 (SHELXL-93) [60]. 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. All hydrogen atoms were located by difference Fourier methods, but in the refinement they were generated geometrically and refined with isotropic displacement parameters 1.2 times and 1.5 (for the methyl-group) higher than U_{eq} of the attached carbon atoms. In compound **11**, the norborn-2-enyl-group was distorted in ratio 0.7:0.3 by replacement of the enantiomeric group at the same position; for **13**, the solvent molecules (THF) were disordered in three, partially overlaying positions in the ratio 0.6:0.2:0.2. Single crystals of **14** were characterized by high mosaicity and had two molecules in the asymmetric unit. The well-ordered molecule was used to discuss bond distances and angles. The second molecule was disordered 1:1 by the position of the methyl group in a way that each pyridyl-group had half a methyl-group. The carbon atom at this disordered position had to be refined isotropically. The relevant crystallographic data are summarized in Table 1.

4. Summary

A series of methyl-substituted pyridyl and quinoyl-based ligands have been synthesized. Heterogeneous catalytic systems have been prepared therefrom via ring-opening metathesis precipitation polymerization. Subsequent loading with palladium(II) resulted in polymer-immobilized palladium catalysts. The high affinity of the dipyridyl amides for Pd was found to be reduced by the presence of additional methyl groups which leads to a less favorable distorted square planar ligand sphere around Pd. Consequently, compared to the parent dipyridylamide-based supports, Pd-loadings of the methyl-substituted pyridyl and quinoyl-based supports were lowered by almost a factor of 10. Nevertheless, these systems may still be used in Heck-type couplings of aryliodides and bromides as well as for the amination of arylbromides.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 142885–142888. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support provided by ESPE, Germany is greatfully acknowledged. R. K. thanks the Deutsche Forschungsgemeinschaft, the Bundesministerium für Bildung und Forschung, the Fonds der Chemischen Industrie, the Max-Planck-Gesellschaft, the Karl-Winnacker-Stiftung, the Aventis R & D GmbH, Degussa-Hüls AG, the SKW Trostberg AG, the Grünenthal GmbH, the SynTec Wolfen GmbH and Organica Wolfen GmbH for financial support.

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