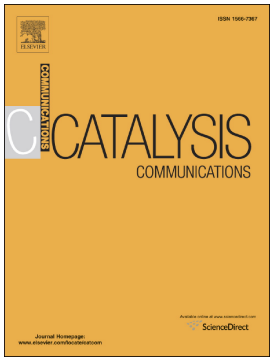

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Cationic Acetylacetonate Palladium Complexes/Boron Trifluoride Etherate Catalyst Systems for Hydroamination of Vinylarenes Using Arylamines

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Abstract

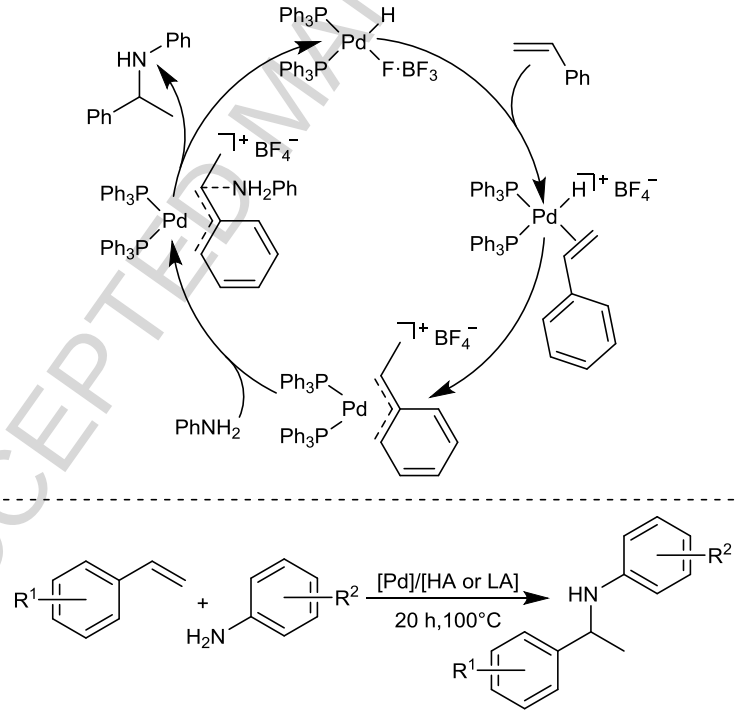
A simple and solvent-free protocol using cationic acetylacetonate palladium complexes with mono-/bidentate phosphine ligands activated with $BF_3{\cdot}OEt_2$ as *in situ*-formed catalyst for hydroamination of vinylarenes with arylamines have been developed. Excellent catalytic activities were obtained using $[Pd(acac)(PPh_3)_2][BF_4]$/$BF_3{\cdot}OEt_2$/*i*-PrOH catalyst system with the addition of a small amount of palladium (0.2-0.05 mol%) to the reaction mixture. Furthermore, the novel unexpected diphosphine-bridged palladium complexes have been prepared and characterized: $[Pd(acac)(dpppt)]_2[BF_4]_2$ and $[Pd(acac)(dpph)]_2[BF_4]_2$ (dpppt – 1,5-*bis*(diphenylphosphino)pentane, dpph – 1,6-*bis*(diphenylphosphino)hexane)

Keywords

Palladium; acetylacetonate; aniline; hydroamination; styrene

Introduction

Transition-metal-catalyzed hydroamination of olefins is an efficient route to alkyl- and benzylamines from readily available reagents [1–3]. Compared to the significant progress in the intramolecular hydroamination of alkenes by rare earth metals, group 4 metals, and main-group metal complexes, the intermolecular hydroamination reactions are less explored [1,4]. One promising approach to the hydroamination of olefins, reported by Hartwig and coworkers [5–7], is the addition of anilines to vinylarenes catalyzed by a combination of $Pd(OCOCF_3)_2$, phosphine (PPh_3 or dppf), and an acid with weakly coordinating anion such as TfOH. Further Pd-catalyzed hydroamination with modified reaction conditions was reported by Takahashi, Lin and coworkers [8]. In contrast to Rh- and Ru-catalyzed intermolecular hydroaminations of vinylarenes [1] palladium-catalyzed transformations exhibit high Markovnikov selectivity and high yields, but suffers from large palladium loadings. Mechanistic and DFT studies indicated that these transformations involve an insertion of the styrene double bond into a Pd–H species, followed by an external nucleophilic attack of the aniline to a η^3-benzyl complex [6,9] (Scheme 1).



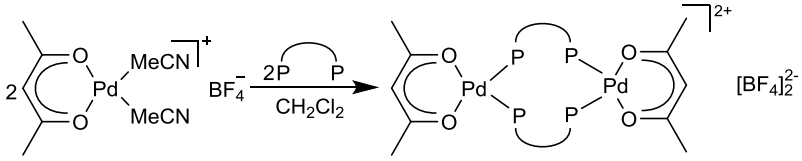
[Pd]:
$[Pd(acac)(PR_3)_2]BF_4$ (R = Ph (**1**), Cy (**2**)),
$[Pd(acac)(P\text{^}P)]BF_4$ (P^P = dppm (**3**), dppp (**4**), dppb (**5**), dppf (**6**)),
$[Pd(acac)(\mu\text{-}P\text{^}P)]_2[BF_4]_2$ (μ-P^P = dpppt (**7**), dpph (**8**)).
[**HA**]: $[H{\cdot}OEt_2]BF_4$; [**LA**]: $BF_3{\cdot}OEt_2$

Scheme 1. Pd(II)-catalyzed hydroamination of styrene ($[BF_4]$ as weakly coordinating anion) and catalysts used in this work (below dashed line).

Recently, our group showed that acetylacetonate-based cationic palladium complexes with di-/monophosphine ligands, [Pd(acac)(P^P)]BF_4 or [Pd(acac)$(PR_3)_2$]BF_4, can be used as very efficient precursors (in combination with $BF_3{\cdot}OEt_2$) for the selective dimerization of styrene [10] and telomerization of 1,3-dienes with diethylamine [11]. In the case of styrene dimerization, one can assume that in these catalyst systems Pd–H species are generated *in situ* as well [12]. Herein, we report our recent study on the acetylacetonate cationic palladium complexes catalyzed intermolecular hydroamination of styrenes with anilines.

Results and discussion

Cationic acetylacetonate monophosphine/diphosphine-ligated palladium complexes **1**-**8** were prepared combining the corresponding [Pd(acac)$(MeCN)_2$]BF_4 with an slight excess of phosphine ligand in CH_2Cl_2 or Et_2O at room temperature. This approach requires complex [Pd(acac)$(MeCN)_2$]BF_4, which can be easily prepared starting from $Pd(acac)_2$, MeCN, and $BF_3{\cdot}OEt_2$ [12]. Syntheses of **1**-**6** using the same or other methodologies have been already reported [11,13–16]. The structures of new compounds **7** and **8** have been confirmed by the usual techniques (NMR, FTIR, EA). Instead of the expected monocationic complexes their dicationic μ-bonded analogues were obtained (Scheme 2). Single crystals of **8** suitable for X-ray crystallographic analysis were prepared from a Et_2O solution of **8** diffused by toluene at 20°C. The crystal structure, selected bond lengths, and angles of the complex **8** are presented in Figure 1. The palladium atom has a distorted square-planar coordination environment, created by the two phosphorus atoms and the two oxygen atoms of the acac ligand. The crystallographic data, and structure refinement summary data for **8** are listed in Table S1 [17] (see Electronic Supplementary Information). The ^{31}P NMR chemical shifts of complexes **7** and **8** are 19.9 ppm and 28.1 ppm assuming similar structural features for complex **7** (literature data for binuclear palladium complexes with μ-bonded diphosphines: 31.51 ppm (dpppt) [18], 13.5 ppm (dpph) [19]). For comparison, in P^P-chelate monocationic **4**, **5**, and **6** the ^{31}P NMR chemical shifts are 37.3, 40.3, and 43.5 ppm respectively [11].



Scheme 2. Syntheses of Acetylacetonate Palladium Complexes **7** and **8**.

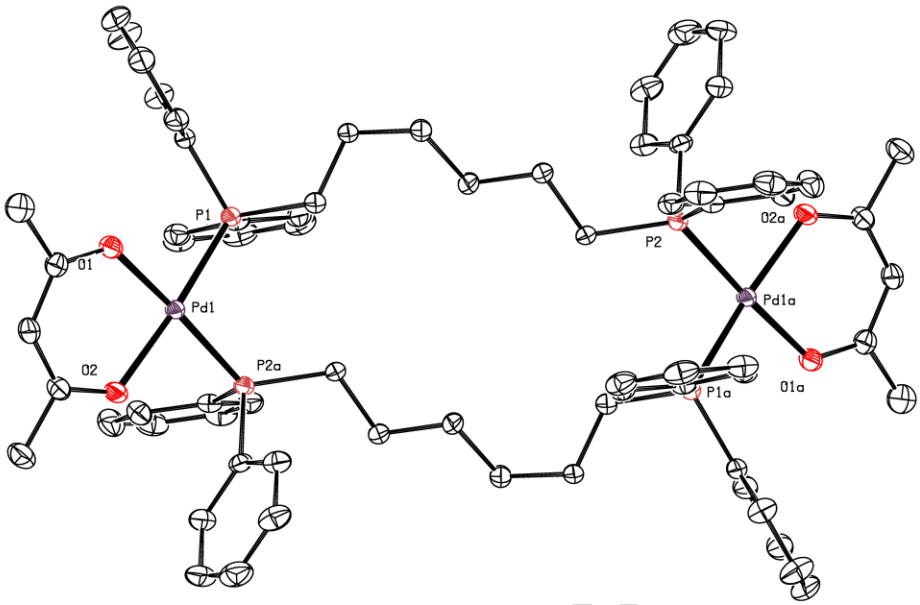


Figure 1. ORTEP drawing of **8** (all hydrogen atoms, anion, and solvent molecules are omitted for clarity). Selected Bond Distances (Å) and Angles (°): Pd1-O1 = 2.027 (2), Pd1-O2 = 2.059 (2), Pd1^{i}-P2 = 2.2714 (8), Pd1—P2^{i} = 2.2714 (8), Pd1-P1 = 2.2551 (8), O1-Pd1-O2 = 90.23 (9), P2-Pd1-P1 = 94.97 (3). Symmetry code(s): (i) -*x*+1, -*y*+1, -*z*+1.

Based on the results of Hartwig et al. [5], we investigated the hydroamination reaction using complexes **1**, **2**, and **6** by employing similar reaction conditions (Table 1, entries 1–10). The reaction of aniline with styrene occurred to give the Markovnikov addition product in high selectivity after 20h at 100°C when catalyzed by a mixture of **6** and [H·OEt$_2$][BF$_4$] co-catalyst (entry 1). No reaction was observed without acid co-catalyst. We investigated several more polar solvents for this process and found that reaction conducted in the presence of nitromethane did not occur, but reactions in the presence of *i*-PrOH were slightly faster than those conducted with toluene. The same trend was observed in [20]: reactions of the η^3-allyl and η^3-benzyl palladium complexes with aniline were faster in DMSO-d_8 than in THF-d_8/CD_2Cl_2 mixture. When simple PPh_3 ligand was used (entry 7), the reaction did give the desired product, but unfortunately with lower selectivity. Very interestingly, the sterically bulkier ligand PCy_3 exhibited high selectivity (99%) to 1,3-diphenylbuten-1-ne, but hydroamination products were not found in the reaction mixture. Electronic effects, not ligand bulkiness, must account for this difference in selectivity because the hydroamination product is formed by external nucleophilic attack of amine on the η^3 complex [9,20]. Thus the PCy_3 ligand basicity can dramatically change the degree of positive charge at the site of nucleophilic attack.

Table 1 Optimization studies

Entry	Complex	n_{Pd}, μmol	$[B]_0$:$[Pd]_0$	Co-catalyst	Solvent	TON[a]	Selectivity[b] [%]
1[c]	dppf	20	10	$[H{\cdot}OEt_2][BF_4]$	Toluene	32	99
2[c]	dppf	20	10	$[H{\cdot}OEt_2][BF_4]$	$MeNO_2$	52.5	0
3[c]	dppf	20	10	$[H{\cdot}OEt_2][BF_4]$	DMF	12	99
4[c]	dppf	20	10	$[H{\cdot}OEt_2][BF_4]$	1,2,4-TCB	9	99
5[c]	dppf	20	10	$[H{\cdot}OEt_2][BF_4]$	*i*-PrOH	42	99
6[c]	$2PCy_3$	20	10	$[H{\cdot}OEt_2][BF_4]$	Toluene	74	0
7[c]	$2PPh_3$	20	10	$[H{\cdot}OEt_2][BF_4]$	Toluene	38	94
8[d]	dppf	10	10	$[H{\cdot}OEt_2][BF_4]$	*i*-PrOH	45	99
9[e]	dppf	5	10	$[H{\cdot}OEt_2][BF_4]$	*i*-PrOH	36	99
10[f]	dppf	2	10	$[H{\cdot}OEt_2][BF_4]$	*i*-PrOH	24	99
11[c]	$2PPh_3$	20	10	$BF_3{\cdot}OEt_2$	Toluene	20	91
12[c]	$2PPh_3$	20	10	$BF_3{\cdot}OEt_2$	*i*-PrOH	41	92
13[c]	$2PPh_3$	20	20	$BF_3{\cdot}OEt_2$	*i*-PrOH	43	83
14[c]	$2PPh_3$	20	30	$BF_3{\cdot}OEt_2$	*i*-PrOH	50	40
15[c]	$2PPh_3$	20	40	$BF_3{\cdot}OEt_2$	*i*-PrOH	49	31
16[c]	$2PPh_3$	20	50	$BF_3{\cdot}OEt_2$	*i*-PrOH	48	12
17[g]	$2PPh_3$	16	20	$BF_3{\cdot}OEt_2$[l]	—	242	59
18[h]	$2PPh_3$	8	20	$BF_3{\cdot}OEt_2$[l]	—	430	80
19[i]	$2PPh_3$	4	20	$BF_3{\cdot}OEt_2$[l]	—	550	81
20[j]	$2PPh_3$	2	20	$BF_3{\cdot}OEt_2$[l]	—	780	84
21[i]	$2PPh_3$	4	10	$BF_3{\cdot}OEt_2$[l]	—	520	81
22[i]	$2PPh_3$	4	50	$BF_3{\cdot}OEt_2$[l]	—	780	48
23[i]	$2PPh_3$	4	100	$BF_3{\cdot}OEt_2$[l]	—	850	43
24[k]	$2PPh_3$	4	20	$BF_3{\cdot}OEt_2$[l]	—	298	93

[a] mol_{St}/mol_{Pd}. Reaction conditions: 20 h, t = 100°C, V_0 = 1.5 mL [b] Towards *N*-(1-phenylethyl)aniline. The crude products were analyzed by GC-FID. 1,3-diphenylbut-1-ene was detected as main by-product (GC-MS). [c] $[Pd]_0:[St]_0:[An]_0$ = 1:75:50, [d] $[Pd]_0:[St]_0:[An]_0$ = 1:150:100 [e] $[Pd]_0:[St]_0:[An]_0$ = 1:300:200 [f] $[Pd]_0:[St]_0:[An]_0$ = 1:600:400 [g] $[Pd]_0:[St]_0:[An]_0$ = 1:250:250 [h] $[Pd]_0:[St]_0:[An]_0$ = 1:500:500 [i] $[Pd]_0:[St]_0:[An]_0$ = 1:1000:1000 [j] $[Pd]_0:[St]_0:[An]_0$ = 1:2000:2000 [k] $[Pd]_0:[St]_0:[An]_0$ = 1:350:500 [l] As 20%vol. solution in *i*-PrOH

When $BF_3{\cdot}OEt_2$ was applied as co-catalyst in the reaction, TON was substantially better in *i*-PrOH than in toluene (entries 11 and 12) due to formation of Brønsted acid according to eq. (1).

$$BF_3{\cdot}OEt_2 + i\text{-PrOH} \underset{+OEt_2}{\overset{-OEt_2}{\rightleftharpoons}} i\text{-PrOH}{\cdot}BF_3 \rightleftharpoons H^+(BF_3{\cdot}i\text{-PrO})^- \quad (1)$$

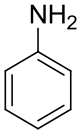
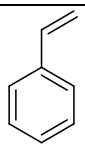
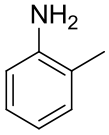
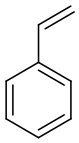
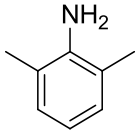
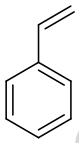
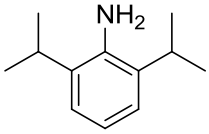
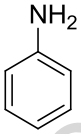
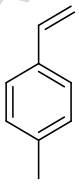
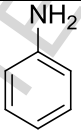
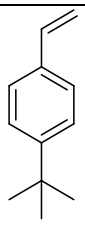
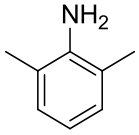
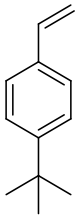
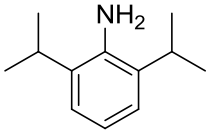
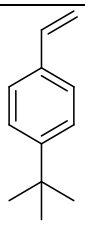
To investigate the effect of the amount of co-catalyst, a set of runs was carried out with the B/Pd ratios from 10 to 50 at 100°C. As one may see in Table 1 (entries 12-16), the selectivity to *N*-(1-phenylethyl)aniline decreased from 92 to 12 %, while the B/Pd molar ratio changed from 10 to 50, and formation of styrene dimers as well as higher oligomer were detected. In contrast to $[H{\cdot}OEt_2]BF_4$, usage of $BF_3{\cdot}OEt_2$/6.5*i*-PrOH as co-catalyst allows to improve catalyst productivity (to the best of our knowledge the highest catalyst turnover number ever reported for this reaction was achieved) (entries 18-23). Moreover, this protocol does not require solvents (5–10%vol. of *i*-PrOH is added as catalyst system component) and the reaction selectivity can be increased by aniline excess in the reaction medium (entry 24).

With the optimized reaction conditions, the scope of substrates was examined. As shown in Table 2, the aniline with methyl at the ortho positions afforded the corresponding amines, but selectivity decrease with increasing steric hindrance in anilines (entries 1-4). For the para-substituted styrenes, the electron-rich substrates gave slightly lower selectivity values to generate products (entries 5-7).

In general, the phosphine ligand has a profound influence on both the activity and selectivity of transition-metal catalyst systems. The influence of the phosphine on the conversion and selectivity of (**1**–**8**)/$BF_3{\cdot}OEt_2$/*i*-PrOH catalyst system is shown in Table 3. When complexes **1** and **4** with PPh_3 and dppp ligands were used to catalyze the reaction, good selectivities were obtained (entries 2, 4). However, **2**, **5**, **7**, and **8** with PCy_3 and bis(diphenylphosphino)alkane ligands exhibited poor selectivity, which decrease with increasing ligand basicity (entries 1, 5–7). Finally, compared with the above complexes, **6** with the dppf ligand presented the best selectivity (99%) to afford amine with good TON (860 mol_{St}/mol_{Pd}, entry 8). Complexes with dppm and nitrogen ligands exhibited practically no activity under tested reaction conditions (entries 3, 9–12).

Table 2

Scope of the substrates

Entry	Aniline	Vinylarene	TON[a]	Selectivity[b] [%]
1			430	80
2			430	53
3			345	30
4			—	—
5			480	45
6			455	88
7			290	44
8			—	—

[a] mol_{St}/mol_{Pd}. Reaction conditions:$\{[Pd(acac)(PPh_3)_2]BF_4\}_0$:$[St]_0$:$[An]_0$:$[B]_0$= 1:500:500:20, co-catalyst: $BF_3{\cdot}OEt_2$ as 20%vol. solution in *i*-PrOH, 20 h, t = 100°C. [b] Towards *N*-(1-arylethyl)anilines. The crude products were analyzed by GC-FID. 1,3-diarylbut-1-ene were detected as main by-products (GC-MS).

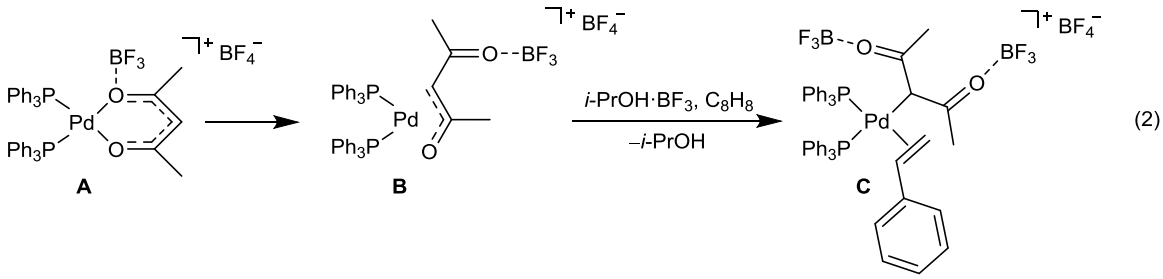
Table 3

Ligand screening

Entry	Complex	n_{Pd}, μmol	$[B]_0$:$[Pd]_0$	TON[a]	Selectivity[b] [%]
1	**2**	4	20	990	0
2	**1**	4	20	560	81
3	**3**	4	20	traces	—
4	**4**	4	20	440	86
5	**5**	4	20	340	77
6	**7**	4	20	850	58
7	**8**	4	20	750	28
8	**6**	4	20	860	99
9	$[Pd(acac)(bipy)]BF_4$	4	20	traces	—
10	$[Pd(acac)(MeCN)_2]BF_4$	4	20	traces	—
11	$[Pd(acac)(morpholine)_2]BF_4$	4	20	traces	—
12	$[Pd(acac)(N^N)]BF_4$[c]	4	20	traces	—

[a] mol_{St}/mol_{Pd}. Reaction conditions: $[Pd]_0$:$[St]_0$:$[An]_0$ = 1:1000:1000, 20 h, t = 100°C, co-catalyst: $BF_3{\cdot}OEt_2$ as 20%vol. solution in *i*-PrOH . [b] Towards *N*-(1-phenylethyl)aniline. The crude products were analyzed by GC-FID. 1,3-diphenylbut-1-ene was detected as main by-product (GC-MS). [c] N^N = $(2,6\text{-}^iPr_2Ph)_2$-DAB-Me_2, DAB = 1,4-diazabutadiene.

Although we have not carried out detailed mechanistic studies of the interaction of **1**–**8** and $BF_3{\cdot}OEt_2$/*i*-PrOH in the presence of styrene and aniline, we favor a mechanism that involves a palladium hydride species (Scheme 1) [5,6,9,20]. We assume that in the case of cationic acetylacetonate palladium complexes as precursors, the first step of the catalytic reaction involves BF_3-promoted transformation of κ^2-O,O-acetylacetonate **A** to η^3-oxoallyl intermediate **B** , which leads to the formation of π-complex **C** with γ-bonded acetylacetonate ligand [12] (eq. 2).



(2)

Insertion of styrene into Pd-C bond in **C** followed by β-hydride elimination leads to a coordinately unsaturated $[Pd\text{-}H]^+$ species. The product is then formed by external nucleophilic attack of amine on the η^3-complex (Scheme 1). Most likely, on that step formation of inactive Pd(0) species can occur via reductive elimination [9]. Regeneration of a palladium hydride by protonation of Pd(0) by $H[BF_3{\cdot}i\text{-PrO}]$ (or the corresponding ammonium salt) and reinsertion of vinylarene would regenerate the η^3-aryl intermediate.

Conclusions

We have described a Pd-catalyzed intermolecular selective hydroamination of styrenes using cationic acetylacetonate palladium complexes with mono-/bidentate phosphine ligands activated by $BF_3{\cdot}OEt_2/i\text{-PrOH}$. Compared to known catalysts $[Pd(acac)(PPh_3)_2][BF_4]/BF_3{\cdot}OEt_2/i\text{-PrOH}$ catalyst system showed higher activity and productivity. However, influence of the ligand structure on the catalyst selectivity still needs to be studied. The related investigation is in progress in our laboratory.

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Supporting Information. Electronic Supplementary Information available: Experimental procedures, spectral data, and crystallographic data for **8** (in CIF format).

Author Contributions

Chemical Experiments: BMV, SDS, PMV; XRD Experiments: APA; NMR Experiments: UIA; Writing – original draft: SDS; Writing – review & editing: BMV, SDS, APA, TVS.

References

[1] L.J. Goossen, L. Huang, M. Arndt, K. Goossen, H. Heydt, Late transition metal-catalyzed hydroamination and hydroamidation, Chem. Rev. 115 (2015) 2596–2697.

[2] A.L. Reznichenko, A.J. Nawara-Hultzsch, K.C. Hultzsch, Asymmetric Hydroamination, in: Top Curr Chem, 2013: pp. 191–260.

[3] T.E. Müller, M. Beller, Metal-Initiated Amination of Alkenes and Alkynes, Chem. Rev. 98 (1998) 675–704.

[4] F. Yu, P. Chen, G. Liu, Pd(II)-catalyzed intermolecular enantioselective hydroamination of styrenes, Org. Chem. Front. 2 (2015) 819–822.

[5] M. Kawatsura, J.F. Hartwig, Palladium-catalyzed intermolecular hydroamination of vinylarenes using arylamines [5], J. Am. Chem. Soc. 122 (2000) 9546–9547.

[6] U. Nettekoven, J.F. Hartwig, A new pathway for hydroamination. Mechanism of palladium-catalyzed addition of anilines to vinylarenes, J. Am. Chem. Soc. 124 (2002)

1166–1167.

[7] J.F. Hartwig, Development of catalysts for the hydroamination of olefins, Pure Appl. Chem. 76 (2004) 507–516.

[8] A. Hu, M. Ogasawara, T. Sakamoto, A. Okada, K. Nakajima, T. Takahashi, et al., Palladium-Catalyzed Intermolecular Asymmetric Hydroamination with 4,4′-Disubstituted BINAP and SEGPHOS, Adv. Synth. Catal. 348 (2006) 2051–2056.

[9] L.K. Vo, D.A. Singleton, Isotope effects and the nature of stereo- and regioselectivity in hydroaminations of vinylarenes catalyzed by palladium(II)-diphosphine complexes, Org. Lett. 6 (2004) 2469–2472.

[10] D.S. Suslov, V.S. Tkach, M. V. Bykov, M. V. Belova, Selective dimerization of styrene to 1,3-diphenylbutene-1 in the presence of [(acac)Pd(PAr3)2]BF4/BF3OEt2 catalytic systems, Pet. Chem. 51 (2011) 157–163.

[11] D.S. Suslov, M. V. Bykov, M. V. Belova, P.A. Abramov, V.S. Tkach, Palladium(II)–acetylacetonate complexes containing phosphine and diphosphine ligands and their catalytic activities in telomerization of 1,3-dienes with diethylamine, J. Organomet. Chem. 752 (2014) 37–43.

[12] D.S. Suslov, M. V. Bykov, P.A. Abramov, M. V. Pahomova, I.A. Ushakov, V.K. Voronov, et al., Pd(acac)(MeCN)2]BF4: air-tolerant, activator-free catalyst for alkenes dimerization and polymerization, RSC Adv. 5 (2015) 104467–104471.

[13] B.F.G. Johnson, J. Lewis, D. White, Cationic transition metal-olefin complexes, J. Am. Chem. Soc. 91 (1969) 5186–5187.

[14] M. Basato, B. Corain, P. De Roni, R. Jaforte, G. Favero, Michael addition of alpha-dicarbonyls to alpha,beta-unsaturates ketones catalyzes by mixed sphere beta-carbonylenolate diphosphino metal complexes, J. Mol. Catal. 42 (1987) 115–125.

[15] J. Vicente, A. Arcas, D. Bautista, A. Tiripicchio, M. Tiripicchio-Camellini, Isolation of a postulated intermediate in the Stille reaction. Synthesis of 2-arylazoarylphosphonium salts via C-P coupling. Synthesis of acetone complexes of palladium(II). Crystal and molecular structure of [Pd(C6H4N=NPh-2)(PPh3)(acetone)], [Ph3P{C6H3(N2C6H4Me-4')-2-Me-5}]ClO4 and [Pd(O,O-acac)(PPh3)2]ClO4, New J. Chem. 20 (1996) 345–356.

[16] V.S. Tkach, D.S. Suslov, G. Myagmarsuren, G. V. Ratovskii, A. V. Rohin, T. Felix, et al., An effective route for the synthesis of cationic palladium complexes of general formula [(Acac)PdL1L2]+A−, J. Organomet. Chem. 693 (2008) 2069–2073.

[17] Crystallographic data and refinement details for

$[Pd(acac)((Ph_2P)_2C_6H_{12})]_2(BF_4)_2 \cdot 0.7C_7H_8$ are given in Table S1. The diffraction data were collected on a New Xcalibur (Agilent Technologies) diffractometer with MoK_α. Structure was solved by direct method and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELX 2014/7 [21] in ShelXle program [22]. The crystallographic data have been deposed in the CCDC under the deposition code 1523552.

[18] S.W. Lai, T.C. Cheung, M.C.W. Chan, K.K. Cheung, S.M. Peng, C.M. Che, Luminescent mononuclear and binuclear cyclometalated palladium(II) complexes of 6-Phenyl-2,2'-bipyridines: Spectroscopic and structural comparisons with platinum(II) analogues1,2, Inorg. Chem. 39 (2000) 255–262.

[19] J. Yang, P. Li, Y. Zhang, L. Wang, Dinuclear NHC-palladium complexes containing phosphine spacers: synthesis, X-ray structures and their catalytic activities towards the Hiyama coupling reaction, Dalt. Trans. 43 (2014) 7166–7175.

[20] A.M. Johns, J.W. Tye, J.F. Hartwig, Relative rates for the amination of η^3-allyl and η^3-benzyl complexes of palladium., J. Am. Chem. Soc. 128 (2006) 16010–16011.

[21] G.M. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr. Sect. C Struct. Chem. 71 (2015) 3–8.

[22] C.B. Hübschle, G.M. Sheldrick, B. Dittrich, ShelXle : a Qt graphical user interface for SHELXL, J. Appl. Crystallogr. 44 (2011) 1281–1284.

Highlights

- Novel Pd-catalyst for hydroamination of vinylarenes with arylamines
- A simple and solvent-free protocol have been developed
- Diphosphine-bridged Pd complexes have been prepared and characterized