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Simple, efficient and reusable Pd–NHC catalysts for hydroamination†

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A series of chelating NHC–palladium complexes with different alkane-bridges of the type Pd[NHC–$(CH_2)_n$–NHC]X_2 (X = Br or Cl, n = 2–4) were synthesized, where NHC is a triazolyl-*N*-heterocyclic carbene donor ligand. The bromide complexes with n = 2 and 3 were characterized by X-ray crystallography. The effects of the length of the bridge and halide ligand on the catalytic reactivity in the hydroamination reaction were investigated. The best catalytic performance was observed with the propylene-bridged Pd–NHC bromide complex **2**. The hydroamination of phenylacetylene or 4-methylphenylacetylene with various substituted anilines catalyzed by **2** yielded only Markovnikov addition products in good yield. Interestingly, this homogenous catalyst can be reused three times without significant loss in activity.

Introduction

Amines and their derivatives are widely found in biologically active and industrially useful molecules. One of the most attractive routes for C–N bond formation is the transition metal catalyzed hydroamination reaction, which involves the atom-economic addition of N–H bonds across unsaturated C–C multiple bonds.[1] However, diverse thermodynamic and kinetic effects hinder the direct nucleophilic addition of this transformation, and the reaction requires that a catalyst activates the amine and/or the carbon–carbon bond for the coupling process.[2] A plethora of catalytic systems have been developed to overcome the high activation barrier during the last two decades, including a number of early- and late-transition-metal complexes.[3,4] Recently, much effort has been focused on the use of late transition metal complexes because they are easily accessible, simple to handle, and can tolerate more functional groups. Nevertheless, it must be pointed out that most of the hydroamination reactions catalyzed by late transition metals suffer from problems due to sensitive ligands and metal complexes, the high catalyst loadings, the high cost of the expensive precious metal, such as Rh, Ir and Au, and patented phosphine ligands.[5] Consequently, it is necessary to develop air-stable, robust and well-defined late metal complexes with inexpensive ligands. In addition, none of these homogeneous catalysts are recyclable, which make these methods more expensive from an economic point of view. As recyclability is of great importance for applying a catalyst in industrial processes, making the catalyst recyclable is of particular value.

Owing to their wide application as potentially useful catalysts in organic synthesis, the chemistry of palladium–NHC (*N*-heterocyclic carbene) complexes has become an area of great interest and has been extensively studied.[6] Although Pd–NHC complexes have been successfully used in many organic transformations, very little work has been reported on hydroamination using NHC palladium complexes.[7] Herein, we report on an easily synthesized, air- and moisture-stable Pd(II) complex supported by an inexpensive chelating di-carbene ligand based on 1,2,4-triazoles with varying bridge length. The hydroamination of phenylacetylene can be efficiently catalyzed by the palladium complexes under mild reaction conditions, and we demonstrated in one example that the catalyst is reusable in the process of hydroamination.

Results and discussion

Synthesis and characterization of the palladium complexes

The preparation of the $(CH_2)_n$-linked (n = 2–4) bis-triazolium salts as ligand precursors was straightforward and high-yielding.[8] Palladation of triazolium bromides or chlorides was routinely carried out with $Pd(OAc)_2$ in DMSO at elevated temperature as shown in Scheme 1. The yield of the complex changes significantly with varying bridge length. Complexes **2** and **5** with a propylene bridge were achieved in good yield (85% and 77%), and complexes **1** and **4** with an ethylene

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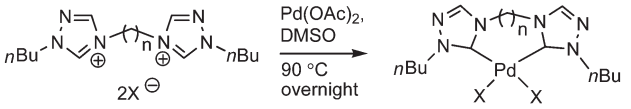


1: n = 2, X = Br; **2**: n = 3, X = Br;
3: n = 4, X = Br; **4**: n = 2, X = Cl;
5: n = 3, X = Cl;

Scheme 1 Synthesis of compounds **1–5**.

bridge were in moderate yield, whereas a yield of only 36% for complex **3** with a butylene bridge was isolated. The Pd complex bearing chloride ligands with a butylene-bridge cannot be isolated in a pure form at all. Furthermore, the bridge length has an effect on the color and solubility of palladium complexes too. The complexes with ethylene and propylene spacers are white powders; however, complex **3** with butylene spacer is a light yellow solid. All complexes have poor solubility in common solvents and the solubility is in the order of **2**, **5** (n = 3) > **1**, **4** (n = 2) > **3** (n = 4). The complexes **1–2** and **4–5** are slightly soluble in DMSO, MeOH and CH_3CN, whereas, complex **3** is only slightly soluble in DMSO. All the complexes are air- and moisture-stable and can be stored in an air atmosphere for more than 6 months without any noticeable decomposition.

The proton signal of NC*H*N from the triazolium salts was absent in the ^{1}H NMR of the palladium complexes, confirming carbene generation. In addition, the ^{13}C NMR of the Pd complexes provide direct evidence of the metalation of the ligand, as seen by the signal in the typical range of 158–164 ppm. The ^{1}H NMR spectra reflect the rigidity of the dicarbene complexes. For example, two different multiplets of the linker protons are present in the ^{1}H NMR spectrum for **1**, indicating that these protons are chemically but not magnetically equivalent. This splitting can be explained as an AA′XX′ spin system caused by a fixed C1-symmetric arrangement of ligands.

The molecular structures of **1** and **2** were determined by means of X-ray diffraction studies. Single crystals for the solid-state structure determination of **1** could be obtained by slow evaporation of a DMSO saturated solution, and for **2** were obtained by a CH_3CN solution. The molecular diagrams of **1** and **2** are shown in Fig. 1 and Fig. 2, respectively. Selected

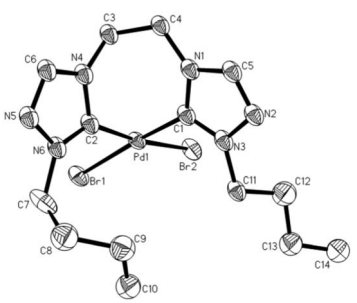


Fig. 1 ORTEP structural drawing of **1**. Ellipsoids are drawn at 30% probability level, and hydrogen atoms are omitted for clarity.

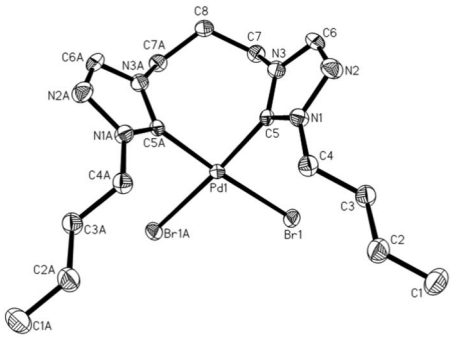


Fig. 2 ORTEP structual drawing of **2**. Ellipsoids are draw at 30% probability level, and hydrogen atoms and solvent are omitted for clarity.

crystallographic data for complexes **1** and **2** are given in Table 1. Selected bond lengths and angles are given in Table 2. In both compounds, the geometry at the palladium is square planar with the triazole rings of the chelating ligand at a dihedral angle of *ca.* 88°. Complex **1** contains a seven-membered metallacycle, and complex **2** contains an eight-membered metallacycle. The coordination plane of the two bromides was twisted out of the C_2Pd plane by 8.14° for **1**, which is much larger than that for **2** (1.55°). The C1–Pd–C2 bite angle increased slightly from 83.6(9)° for **1** with the ethyl bridge to 87.0(4)° for **2** with the propyl bridge, however, these bite angles are less than 90° due to a chelate effect. The distortions of the Pd–C(carbene)–N bond angles are reflected in the yaw distortion angle θ (Table 2). The angle is decreased with increasing bridge length (θ = 8.8 or 2.2 for **1**; θ = 1.35 for **2**), which was proposed to be a consequence of the ring strain. It can also be seen from complex **1** that the yaw distortion mainly affects one of the two Pd–NHC bonds, which appears to be energetically favorable. The length of the Pd–C bonds is slightly shorter than those in a similar iodide complex,[9a] thus reflecting the lower *trans* influence of bromide *versus* iodide, and are comparable with analogue dibromide complexes.[9b] All other distances and angles lie in the expected range.

Catalysis in hydroamination

Initial studies for hydroamination were conducted with the intermolecular hydroamination reaction of phenylacetylene with aniline and the results are summarized in Table 3. The influence of the bridge length on the activity can be seen for complexes **1–3** containing identical heterocycles, wingtip and bromide ligands, differing only in bridge length.

In all cases, the production of the imine was clean and efficient at 2 mol% of Pd complex loading in the presence of 4 mol% silver triflate as an additive, and only the Markovnikov product was obtained in 99% yield within 2 h. Therefore, the amount of Pd catalyst and silver triflate was reduced by a factor of 2 in two additional experiments. With 1 mol% of loading of the catalyst, 99% yield was still observed for all three complexes within 2 h. However, when the amount was lowered to 0.5 mol%, only complex **2** with the propene bridge was found to be still very efficient. Even though it required an increased reaction time to achieve the same level of yield, it is still significant that the reaction was carried out with only 0.5

Table 1 Selected crystallographic data for complexes **1** and **2**

Complexes	**1**	**2**
Formula[a]	$C_{14}H_{24}Br_2N_6Pd$	$C_{15}H_{26}Br_2N_6Pd{\cdot}C_2H_3N$
M/g mol^{-1} [a]	542.61	597.67
T/K	298(2)	296(2)
Wavelength[b]/Å	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P21/c$	$Pnma$
a/Å	16.0644(18)	8.1484(11)
b/Å	9.4857(11)	18.284(2)
c/Å	13.3115(16)	15.475(2)
α/°	90	90
β/°	100.765(3)	90
γ/°	90	90
V/Å^3	1992.7(4)	2305.6(5)
Z	4	4
ρ/g cm^{-3}	1.809	1.722
F(000)	1064	1184
Crystal size/mm	0.40 × 0.30 × 0.20	0.33 × 0.27 × 0.08
θ range/°	2.51 to 24.99°	1.72 to 25.00°
Limiting indices	$-19 \leqslant h \leqslant 18$	$-9 \leqslant h \leqslant 9$
	$-11 \leqslant k \leqslant 11$	$-21 \leqslant k \leqslant 20$
	$-14 \leqslant l \leqslant 15$	$-18 \leqslant l \leqslant 18$
Reflections collected/unique	16 867/3314	22 406/2099
Data/restraints/parameters	3314/0/210	2091/2/133
GOF	1.245	1.025
R_1, wR_2 [$I > 2\sigma(I)$]	R_1 = 0.1349, wR_2 = 0.3353	R_1 = 0.0421, wR_2 = 0.1361
R_1[c], wR_2[d,e] (all data)	R_1 = 0.1493, wR_2 = 0.3444	R_1 = 0.0497, wR_2 = 0.1536
Largest diff. peak and hole/e Å^3	1.988 and −3.076	0.704 and −1.139

[a] Including solvate molecules. [b] Mo-Kα radiation. [c] $R_1 = \sum(|F_o| - |F_c|)/\sum(|F_o|)$ for observed reflections. [d] $w = 1/[\sigma^2(F_o^2) + (\alpha P)^2 + bP]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$. [e] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ for all data.

mol% of catalyst. The yield was decreased dramatically to 52% for **1** (n = 2) and only 28% for **3** (n = 4). These results indicate that the highest yield of the hydroamination product was achieved using the propene-bridged complex, and no clear trend is found with regard to the bridge length.

The influence of halide ligands on the reactivity of the palladium complex was investigated by comparing complexes **1** and **2** bearing bromides *vs.* complexes **4** and **5** bearing chlorides. Both of the complexes with chlorides were not as good as their analogues with bromides. For example, an

Table 2 Selected bond lengths (Å) and angles (°) for **1** and **2**

1

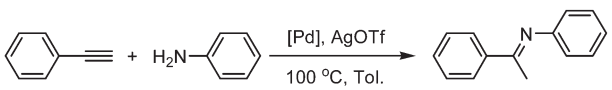
Pd(1)–C(1)	2.00(2)	N(6)–C(2)–Pd(1)	136.4(19)
Pd(1)–C(2)	1.99(2)	N(4)–C(2)–Pd(1)	118.8(16)
Pd (1)–Br(1)	2.476(3)	N(1)–C(1)–Pd(1)	129.4(19)
Pd (1)–Br(2)	2.477(3)	N(3)–C(1)–Pd(1)	125.0(17)
N(4)–C(2)	1.38(3)	C(2)–Pd(1)–C(1)	83.6(9)
N(6)–C(2)	1.29(3)	C(2)–Pd(1)–Br(2)	172.7(7)
N(1)–C(1)	1.36(3)	C(1)–Pd(1)–Br(1)	172.8(7)
N(3)–C(1)	1.31(3)	triazole dihedral angle[a]	88.21
		θ	8.8 or 2.2

2

Pd (1)–C(5)	1.974(7)	C(5)–Pd(1)–Br(1A)	176.39(18)
Pd (1)–Br(1)	2.4797(8)	C(5A)–Pd(1)–Br(1)	176.39(19)
N(1)–C(5)	1.328(9)	N(3)–C(5)–Pd(1)	126.6(5)
N(3)–C(5)	1.348(9)	N(1)–C(5)–Pd(1)	129.3(5)
C(5A)–Pd(1)–C(5)	87.0(4)	triazole dihedral angle[b]	88.39
		θ	1.35

[a] Triazole dihedral angle = angle between LS planes: one through the C1 triazole ring; one through the C2 triazole ring. θ = 1/2[∠N(1)–C(1)–Pd(1)−∠N(3)–C(1)–Pd(1)] or 1/2[∠N(6)–C(2)–Pd(1)−∠N(4)–C(2)–Pd(1)]. [b] Triazole dihedral angle = angle between LS planes: one through the C5 triazole ring; one through the C5A triazole ring. θ = 1/2[∠N(1)–C(5)–Pd(1)−∠N(3)–C(5)–Pd(1)].

Table 3 The hydroamination of phenylacetylene with anilines with Pd complexes **1–5**



Entry[a]	Pd catalyst (mol%)	AgOTf (mol%)	Time (h)	Yield[b] (%)
1	**1** (2)	4	2	99
2	**2** (2)	4	2	99
3	**3** (2)	4	2	99
4	**1** (1)	2	2	99
5	**2** (1)	2	2	99
6	**3** (1)	2	2	99
7	**1** (0.5)	1	12	52
8	**2** (0.5)	1	12	99
9	**3** (0.5)	1	12	28
10	**4** (0.5)	1	12	42
11	**5** (0.5)	1	12	65

[a] Reaction conditions: phenylacetylene (0.6 mmol), aniline (0.5 mmol), Pd complex (0.5–2 mol%) and AgOTf (1–4 mol%) in toluene (1 mL) at 100 °C. [b] GC yield measured with dodecane as internal standards.

excellent yield of 99% was achieved when the reaction was catalyzed by **2**, while a markedly lower yield of 65% was obtained for **5** under the same conditions (Table 3, entry 11).

Based on the results in Table 3, 0.5 mol% loading of complex **2** was chosen in the addition reaction of phenylacetylene and 4-methylphenylacetylene with various anilines, and the results are depicted in Table 4. Good results were obtained for the anilines containing either electron-withdrawing or electron-donating substituents, and corresponding amines from the reduction of the hydroamination products were mostly isolated in about 80% yield. Disappointingly, the reaction with 2,6-dimethyl aniline gave lower yields (54%), due to the enhanced steric bulk at the nitrogen atom.

Recycling of catalysts is amongst the main goals in organometallic chemistry, and is one of the main principles of green chemistry.[10] However, generally it is very difficult to recover and reuse a homogenous catalyst because of the difficult separation of the catalyst from the reaction mixture. After carefully analyzing our catalytic system, we proposed that the real catalyst in the hydroamination reaction was $[Pd(NHC)]^{2+}[(OTf)_2]^{2-}$, which was generated *in situ* from the reaction of the precatalyst **2** with AgOTf. As we know, normally ionic compounds have poor solubility in diethyl ether, however, the more organic compounds are very soluble in ether. We assumed that the product imine would be separated from the reaction mixture by adding diethyl ether to the reaction mixture. To our delight, the catalyst did precipitate out from the reaction solution when 3 mL of diethyl ether was added to the cooled resulting mixture after the hydroamination. The catalyst was recovered by carefully removing the organic layer, and washing with ether (3 × 3 mL). The recyclability of the catalyst was investigated in the reaction of phenyl acetylene with aniline. Subsequently, the isolated yield of *N*-(1-phenylethyl)benzenamine was checked in repeated cycles 1–5 (81%, 80%, 80%, 67%, 65%) and the results are shown in Table 5. The results indicated that there is not a significant loss of activity of the catalyst after recycling 3 times.

Experimental section

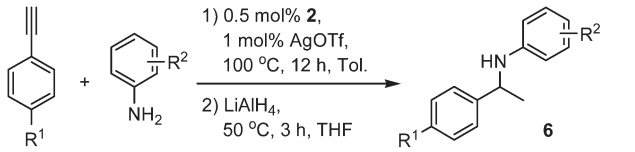
General considerations

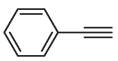
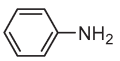
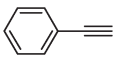
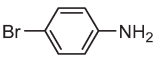
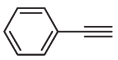
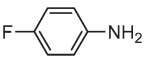
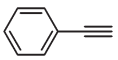
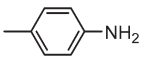
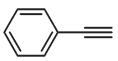
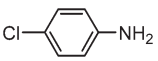
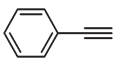
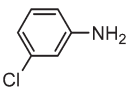
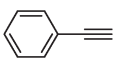
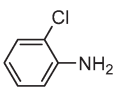
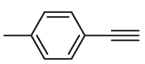
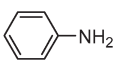
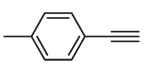
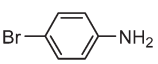
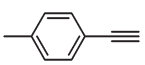
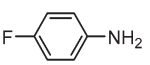
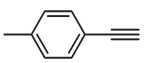
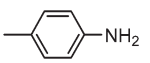
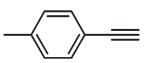
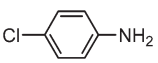
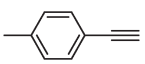
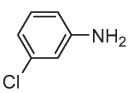
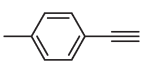
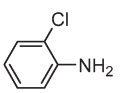
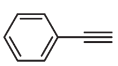
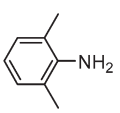
All reagents were commercially available and were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer at room temperature and referenced to the residual signals of the solvent. Elemental analyses were performed on a EuroVektor Euro EA-300 elemental analyzer. GC-MS was performed on an Agilent 6890-5973N system with electron ionization (EI) mass spectrometry.

X-ray crystallographic studies

Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode by using Mo-Kα radiation (λ = 0.71075 Å). The diffracted intensities were corrected for Lorentz polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given by full-matrix least-squares procedures based on F^2.

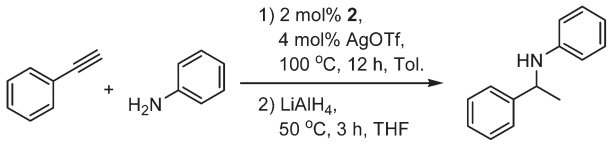
Table 4 Hydroamination of aniline with phenylacetylene



Entry[a]	Aryl halide	Amine	Product	Yield(%)[b]
1			**6a**	81
2			**6b**	80
3			**6c**	76
4			**6d**	74
5			**6e**	72
6			**6f**	83
7			**6g**	89
8			**6h**	81
9			**6i**	74
10			**6j**	81
11			**6k**	77
12			**6l**	83
13			**6m**	81
14			**6n**	80
15			**6o**	54

[a] Reaction conditions: (1) phenylacetylene (2.2 mmol), aniline (2 mmol), **2** (0.5 mol%) and AfOTf (1 mol%) in toluene (2 mL) at 100 °C for 12 h; (2) $LiAlH_4$ (3 mmol), THF (5 mL) at 50 °C for 3 h.
[b] Isolated yield from an average of two runs.

Table 5 Recycling study of the precatalyst **2** for hydroamination of phenylacetylene with aniline



Number of cycles	1[a]	2	3	4	5
Yield[b]	81%	80%	80%	67%	65%

[a] Reaction conditions: (1) phenylacetylene (2.2 mmol), aniline (2 mmol), **2** (2 mol%) and AgOTf (4 mol%) in toluene (2 mL) at 100 °C for 12 h; (2) $LiAlH_4$ (3 mmol), THF (5 mL) at 50 °C for 3 h. [b] Isolated yield from an average of two runs.

All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically (C–H bond lengths fixed at 0.95 Å), assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of the full-matrix least-squares refinement. The structure was solved by directed methods using the SHELXS-97 program and absorption correction was performed by SADABS program. CCDC-909117 and CCDC-909118 contain the supplementary crystallographic data for this paper.

General procedures for hydroamination

A vial was charged with AgOTf (0.02 mmol, 5.1 mg), and palladium catalyst (0.01 mmol, 4.8 mg) under argon. Phenylacetylene (2.2 mmol, 146 μl), aniline (2 mmol, 182 μl) and toluene (2 mL) were syringed into the vial. The mixture was heated at 100 °C for 12 h and then filtered through Celite. The filtrate was collected and dissolved in THF (5 mL). $LiAlH_4$ (3 mmol, 113.8 mg) was added to THF solution in small portions at 0 °C, and then the mixture was heated at 50 °C for 3 h. The remaining $LiAlH_4$ was quenched by NaOH aqueous solution (2 M) in an ice bath until the solid disappeared. The organic layer was separated and the aqueous layer was extracted by DCM (3 × 10 mL). The combined organic phase was dried over $MgSO_4$ and concentrated. The pure compound was isolated by column chromatography (petroleum ether/diethyl ether = 100 : 1).

General procedures for the recycling of the catalyst

The reaction conditions for hydroamination and reduction of imine to amine were the same as those mentioned above. After the hydroamination, diethyl ether (3 mL) was added to the cooled reaction solution. The mixture was stirred at room temperature for 10 min, and then was settled to enable the separation of solid (catalyst) and liquid (product) phases. The catalyst was recovered by removing the liquid, and washing with ether (3 × 3 mL). The used catalyst was added to the new substrates directly for the next run. The combined organic phase, including the imine product of hydroamination, was collected carefully and reduced by $LiAlH_4$ in THF.

Syntheses of complexes

[1,2-Ethanediylbis(1-butyl-1*H*-1,2,4-triazol-4(5*H*)-yl-5-ylidene)]dibromopalladium (1). 1,1′-Di-*n*-butyl-4,4′-(1,2-ethanediyl)-bistriazolium dibromide (1 mmol, 0.44 g) was dissolved in DMSO (10 mL) and $Pd(OAc)_2$ (0.96 mmol, 0.22 g) was added in small portions. The reaction mixture was heated at 90 °C overnight with stirring. The volatile component was removed under vacuum after the mixture was filtered over Celite. The resulting yellow solid was rinsed with DCM 3 times and gave the product as a white solid (0.33 g, 63%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.77 (s, 2H, NC*H*N), 5.21 (m, 2H, NCH_2), 4.73 (m, 2H, NCH_2), 4.55 (m, 2H, 1-CH_2 of Bu), 4.32 (m, 2H, 1′-CH_2 of Bu), 1.85 (m, 4H, 2-CH_2 of Bu), 1.31 (m, 4H, 3-CH_2 of Bu), 0.90 (t, J = 7.6 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.8, 143.9, 51.8, 44.7, 30.6, 19.2, 13.5. Anal. calc. for $C_{14}H_{24}Br_2N_6Pd$ (542.61 g mol^{-1}): C, 30.99; H, 4.46; N, 15.49. Found: C, 30.72; H, 4.34; N, 15.61%.

[1,2-Propanediylbis(1-butyl-1*H*-1,2,4-triazol-4(5*H*)-yl-5-ylidene)]dibromopalladium (2). 1,1′-Di-*n*-butyl-4,4′-(1,2-propanediyl)bistriazolium dibromide (1 mmol, 0.45 g) was dissolved in DMSO (10 mL) and $Pd(OAc)_2$ (0.96 mmol, 0.22 g) was added in small portions. The reaction mixture was heated at 90 °C overnight with stirring. The volatile component was removed under vacuum after the mixture was filtered over Celite. The resulting yellow solid was rinsed with DCM 3 times and gave the product as a white solid (0.45 g, 85%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.72 (s, 2H, NC*H*N), 4.79 (m, 2H, NCH_2), 4.61 (m, 4H, NCH_2), 4.30 (m, 2H, NCH_2), 2.41 (m, 1H, NCH_2CH_2), 1.94 (m, 3H, NCH_2CH_2), 1.77 (m, 2H, CH_2), 1.41 (m, 4H, CH_2CH_3), 0.90 (t, J = 7.6 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.1, 144.8, 52.2, 44.7, 31.0, 19.1, 13.4. Anal. calc. for $C_{15}H_{26}Br_2N_6Pd$ (556.64 g mol^{-1}): C, 32.37; H, 4.71; N, 15.10. Found: C, 32.18; H, 4.63; N, 15.25%.

[1,2-Butanediylbis(1-butyl-1*H*-1,2,4-triazol-4(5*H*)-yl-5-ylidene)]dibromopalladium (3). 1,1′-Di-*n*-butyl-4,4′-(1,2-butanediyl)bistriazolium dibromide (1 mmol, 0.46 g) was dissolved in DMSO (10 mL) and $Pd(OAc)_2$ (0.96 mmol, 0.22 g) was added in small portions. The reaction mixture was heated at 90 °C overnight with stirring. The volatile component was removed under vacuum after the mixture was filtered over Celite. The resulting yellow solid was rinsed with DCM 3 times and gave the product as a light yellow solid (0.20 g, 36%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.80 (s, 2H, NC*H*N), 4.97 (m, 2H, NCH_2), 4.56 (m, 2H, NCH_2), 4.31 (m, 4H, NCH_2), 2.30 (s, 1H, NCH_2CH_2), 2.07–1.81 (m, 7H, NCH_2CH_2), 1.39 (m, 4H, CH_2CH_3), 0.93 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.2, 145.0, 51.6, 48.8, 30.5, 19.2, 13.5. Anal. calc. for $C_{16}H_{28}Br_2N_6Pd$ (570.66 g mol^{-1}): C, 33.68; H, 4.95; N, 14.73. Found: C, 33.91; H, 4.86; N, 14.64%.

[1,2-Ethanediylbis(1-butyl-1*H*-1,2,4-triazol-4(5*H*)-yl-5-ylidene)]dichloropalladium (4). 1,1′-Di-*n*-butyl-4,4′-(1,2-ethanediyl)-bistriazolium dichloride (1 mmol, 0.35 g) was dissolved in DMSO (10 mL) and $Pd(OAc)_2$ (0.96 mmol, 0.22 g) was added in small portions. The reaction mixture was heated at 90 °C overnight with stirring. The volatile component was removed under vacuum after the mixture was filtered over Celite. The resulting yellow solid was rinsed with DCM 3 times and gave the product as a white solid (0.28 g, 63%). ^{1}H NMR (400 MHz,

DMSO-d_6): δ = 8.76 (s, 2H, NC*H*N), 5.21 (m, 2H, NCH_2), 4.73 (m, 2H, NCH_2), 4.60 (m, 2H, NCH_2), 4.32 (m, 2H, NCH_2), 1.85 (m, 4H, NCH$_2$CH_2), 1.31 (m, 4H, CH_2CH$_3$), 0.90 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.7, 144.7, 51.8, 44.9, 31.3, 19.1, 13.4. Anal. Calc. for $C_{14}H_{24}Cl_2N_6Pd$ (453.71 g mol^{-1}): C, 37.06; H, 5.33; N, 18.52. Found: C, 36.89; H, 5.44; N, 18.68%.

[1,2-Propanediylbis(1-butyl-1*H*-1,2,4-triazol-4(5*H*)-yl-5-ylidene)]dichloropalladium (5). 1,1′-Di-*n*-butyl-4,4′-(1,2-propanediyl)bistriazolium dichloride (1 mmol, 0.36 g) was dissolved in DMSO (10 mL) and Pd(OAc)$_2$ (0.96 mmol, 0.22 g) was added in small portions. The reaction mixture was heated at 90 °C overnight with stirring. The volatile component was removed under vacuum after the mixture was filtered over Celite. The resulting yellow solid was rinsed with DCM 3 times and gave the product as a white solid (0.35 g, 77%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.70 (s, 2H, NC*H*N), 4.79 (m, 2H, NCH_2), 4.61 (m, 4H, NCH_2), 4.33 (m, 2H, NCH_2), 2.50 (m, 2H, NCH$_2$CH_2), 1.94 (m, 2H, NCH$_2$CH_2), 1.77 (m, 2H, CH_2), 1.41 (m, 4H, CH_2CH$_3$), 0.92 (t, J = 7.2 Hz, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.0, 145.0, 51.6, 48.8, 30.8, 19.2, 13.5. Anal. calc. for $C_{15}H_{26}Cl_2N_6Pd$ (467.73 g mol^{-1}): C, 38.52; H, 5.60; N, 17.97. Found: C, 38.73; H, 5.44; N, 17.82%.

Characterization data for hydroamination products

***N*-(1-Phenylethyl)benzenamine (6a).** Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.35 (d, 2H, Ar–*H*), 7.33–7.29 (t, 2H, Ar–*H*), 7.24–7.20 (m, 1H, Ar–*H*), 7.08 (t, J = 7.6 Hz, 2H, Ar–*H*), 6.64 (t, J = 7.2 Hz, 1H, Ar–*H*), 6.51 (d, 2H, Ar–*H*), 4.47 (q, 1H, C*H*), 4.02 (s, 1H, N*H*), 1.52 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 147.3, 145.2, 129.0, 128.6, 126.8, 125.8, 117.2, 113.3, 53.4, 25.0.

4-Bromo-*N*-(1-phenylethyl)benzenamine (6b). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.31 (d, 4H, Ar–*H*), 7.28 (m, 1H, Ar–*H*), 7.15 (d, 2H, Ar–*H*), 6.37 (d, 2H, Ar–*H*), 4.43 (q, 1H, *CH*), 4.06 (s, 1H, N*H*), 1.52 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 146.1, 144.5, 131.7, 128.7, 127.0, 125.7, 114.8, 108.8, 53.4, 24.9.

4-Fluoro-*N*-(1-phenylethyl)benzenamine (6c). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.35–7.29 (m, 4H, Ar–*H*), 7.24–7.20 (m, 1H, Ar–*H*), 6.78 (m, 2H, Ar–*H*), 6.41 (m, 2H, Ar–*H*), 4.41 (q, 1H, *CH*), 3.91 (s, 1H, N*H*), 1.52 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 156.8, 154.4, 145.0, 143.6, 128.6, 126.9, 125.8, 115.6, 115.3, 114.1, 114.0, 54.0, 25.1.

4-Methyl-*N*-(1-phenylethyl)benzenamine (6d). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.37–7.29 (m, 4H, Ar–*H*), 7.24–7.21 (m, 1H, Ar–*H*), 6.89 (m, 2H, Ar–*H*), 6.43 (m, 2H, Ar–*H*), 4.44 (q, 1H, *CH*), 3.92 (s, 1H, N*H*), 2.17 (m, 3H, CH_3), 1.52 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 145.4, 145.0, 129.6, 128.6, 126.8, 126.3, 125.8, 113.4, 53.7, 25.0, 20.3.

4-Chloro-*N*-(1-phenylethyl)benzenamine (6e). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.33 (m, 4H, Ar–*H*), 7.24 (m, 1H, Ar–*H*), 7.03 (d, 2H, Ar–*H*), 6.42 (d, 2H, Ar–*H*), 4.44 (q, 1H, *CH*), 4.04 (s, 1H, N*H*), 1.51 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 145.7, 144.6, 128.9, 128.7, 127.0, 125.7, 121.7, 114.3, 53.5, 25.0.

3-Chloro-*N*-(1-phenylethyl)benzenamine (6f). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.34 (m, 4H, Ar–*H*), 7.25 (m, 1H, Ar–*H*), 6.98 (t, J = 8.0 Hz, 1H, Ar–*H*), 6.60 (d, 1H, Ar–*H*), 6.49 (s, 1H, Ar–*H*), 6.37 (d, 1H, Ar–*H*), 4.46 (q, 1H, *CH*), 4.11 (s, 1H, N*H*), 1.52 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 148.3, 144.5, 134.7, 130.0, 128.7, 127.1, 125.7, 117.1, 113.0, 111.4, 53.3, 24.8.

2-Chloro-*N*-(1-phenylethyl)benzenamine (6g). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.34–7.28 (m, 4H, Ar–*H*), 7.23–7.19 (m, 2H, Ar–*H*), 6.93 (t, J = 7.6 Hz, 1H, Ar–*H*), 6.54 (t, J = 7.6 Hz, 1H, Ar–*H*), 6.39 (d, 1H, Ar–*H*), 4.68 (s, 1H, N*H*), 4.49 (q, 1H, *CH*), 1.56 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 144.5, 142.9, 128.9, 128.7, 127.6, 127.0, 125.6, 118.8, 117.1, 112.4, 53.3, 25.1.

***N*-(1-*p*-Tolylethyl)benzenamine (6h).** Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.25 (d, 2H, Ar–*H*), 7.12–7.06 (m, 4H, Ar–*H*), 6.63 (t, J = 7.2 Hz, 1H, Ar–*H*), 6.51 (d, 2H, Ar–*H*), 4.44 (q, 1H, C*H*), 3.99 (s, 1H, N*H*), 2.31(s, 3H, CH_3), 1.49 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 147.3, 142.1, 136.3, 129.3, 129.0, 125.7, 117.1, 113.2, 53.1, 25.0, 21.0.

4-Bromo-*N*-(1-*p*-tolylethyl)benzenamine (6i). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.20 (m, 2H, Ar–*H*), 7.13 (m, 4H, Ar–*H*), 6.37 (d, 2H, Ar–*H*), 4.40 (q, 1H, *CH*), 4.05 (s, 1H, N*H*), 2.31 (s, 3H, CH_3), 1.49 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 146.2, 141.5, 136.6, 131.7, 129.3, 125.6, 114.8, 108.7, 53.1, 24.9, 21.0.

4-Fluoro-*N*-(1-*p*-tolylethyl)benzenamine (6j). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.24 (d, 2H, Ar–*H*), 7.13 (m, 2H, Ar–*H*), 6.78 (t, J = 8.8 Hz, 2H, Ar–*H*), 6.42 (m, 2H, Ar–*H*), 4.38 (q, 1H, C*H*), 3.91 (s, 1H, N*H*), 2.31 (s, 3H, CH_3), 1.49 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 156.7, 154.4, 143.62, 143.61, 142.0, 136.5, 129.3, 125.7, 115.5, 115.3, 114.0, 113.9, 53.7, 25.1, 21.0.

4-Methyl-*N*-(1-*p*-tolylethyl)benzenamine (6k). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.23 (m, 2H, Ar–*H*), 7.12 (d, 2H, Ar–*H*), 6.90 (d, 2H, Ar–*H*), 6.44 (d, 2H, Ar–*H*),4.42 (q, 1H, C*H*), 3.88 (s, 1H, N*H*), 2.31 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 1.48 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 145.0, 142.3, 136.2, 129.5, 129.2, 126.2, 125.7, 113.3, 53.3, 25.0, 21.02, 21.03.

4-Chloro-*N*-(1-*p*-tolylethyl)benzenamine (6l). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.22 (m, 2H, Ar–*H*), 7.13 (d, 2H, Ar–*H*), 7.02 (d, 2H, Ar–*H*), 6.42 (d, 2H, Ar–*H*), 4.41 (q, 1H, C*H*), 4.03 (s, 1H, N*H*), 2.31 (s, 3H, CH_3), 1.49 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 145.8, 141.6, 136.5, 129.3, 128.8, 125.6, 121.6, 114.3, 53.2, 25.0, 21.0.

3-Chloro-*N*-(1-*p*-tolylethyl)benzenamine (6m). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.23 (d, 2H, Ar–*H*), 7.13 (d, 2H, Ar–*H*), 6.97 (t, J = 8 Hz, 1H, Ar–*H*), 6.59 (d, 1H, Ar–*H*), 6.49 (d, 1H, Ar–*H*), 6.37 (d, 1H, Ar–*H*), 4.44 (q, 1H, C*H*), 4.09 (s, 1H, N*H*), 2.32 (s, 3H, CH_3), 1.49 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 148.4, 141.6, 136.6, 134.7, 130.0, 129.4, 125.6, 117.0, 112.9, 111.4, 53.0, 24.8, 21.0.

2-Chloro-*N*-(1-*p*-tolylethyl)benzenamine (6n). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.24 (d, 3H, Ar–*H*), 7.13 (d, 2H, Ar–*H*), 6.95 (t, J = 7.6 Hz, 1H, Ar–*H*), 6.55 (t, J = 7.6 Hz, 1H, Ar–*H*), 6.41 (d, 1H, Ar–*H*), 4.48 (q, 1H, C*H*), 4.67 (s, 1H, N*H*), 2.31 (s, 3H, CH_3), 1.56 (d, 3H, CH_3). ^{13}C NMR (CDCl$_3$, 100 MHz): 143.0, 141.5, 136.5, 129.3, 128.9, 127.6, 125.6, 118.8, 117.0, 112.4, 53.0, 25.1, 21.1.

2,6-Dimethyl-*N*-(1-phenylethyl)benzenamine (6o). Light yellow oil. ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.35 (d, 2H, Ar–*H*),

7.33–7.29 (t, 2H, Ar–*H*), 7.24–7.20 (m, 1H, Ar–*H*), 7.08 (t, J = 7.6 Hz, 2H, Ar–*H*), 6.64 (t, J = 7.2 Hz, 1H, Ar–*H*), 4.48 (q, 1H, C*H*), 4.02 (s, 1H, N*H*), 2.20 (s, 6H, C*H*), 1.51 (d, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): 147.2, 145.2, 129.0, 128.6, 126.8, 125.8, 117.2, 113.3, 53.4, 25.0, 16.6.

Conclusions

A series of triazole-based di-NHC–palladium complexes with different lengths of bridge were synthesized. Two of these complexes were characterized by X-ray crystallography and the structures showed a chelating coordination of the di-NHC ligand. The activity of the palladium complexes in the hydroamination was tested and the best catalytic performance was observed with the propylene-bridged Pd–NHC bromide complex **2**. The hydroamination catalyzed by **2** yielded imines with the exclusive formation of Markovnikov addition product in good yield. In addition, catalyst **2** can be re-used three times without significant loss in activity.

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