



Hydrative syntheses of amides from alkynes catalyzed by an Au(I) complex containing pyridyl-functionalized NHC ligand

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ABSTRACT

An Au(I)–NHC complex [L^1AuBr] (**1**) with appended pyridyl group on the ligand scaffold is synthesized and its catalytic efficacy for the direct synthesis of the amide from alkyne and sodium azide in acidic water is evaluated. Catalyst **1** readily converts a wide range of internal and terminal alkynes to the corresponding amides with low catalyst loading in TFA/DCE (2 mL, 1:1 v/v) at room temperature in short reaction time (2 h) and without the use of Ag(I) additive. A related catalyst that is devoid of the pyridyl fragment displays significantly lower activity illustrating the role of the promoter ligand for water activation. Mechanistic studies reveal an initial alkyne hydration to ketone followed by the Schmidt reaction to afford the amide.

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1. Introduction

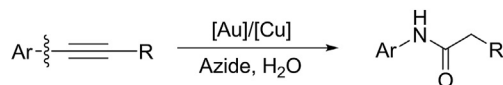
Amides have ubiquitous presence in chemical synthesis, natural products, and biology [1]. Traditional amide syntheses rely heavily on the reactions of activated carboxylic acid derivatives with amines [2]. Alternative methodologies are available but many of these methods suffer from poor atom economy and demand harsh reaction conditions [3]. Metal-catalyzed hydrative amide synthesis utilizing alkyne, azide and water is an attractive option that allows facile C–C bond functionalization through a nitrogenation process (Scheme 1) [4]. Nitrile hydration provides a direct, convenient and atom-economic route to amides [5]. Cadeirno and co-workers have developed several ruthenium/rhodium catalysts under homogeneous conditions which utilize a pendant Brønsted basic unit on the ligand scaffold to accelerate hydration activity [6].

We recently reported a Ni^{II} complex containing pyridyl-functionalized N-heterocyclic carbene (NHC) ligands for selective nitrile hydration to amide under base-free conditions. The hemilabile pyridyl unit is shown to promote nucleophilic water attack to a metal-bound nitrile through hydrogen-bonding interaction (Scheme 2a) [7]. Exploiting the combined effects of metal and ligand in bifunctional catalysts, hydration reactions of alkynes are

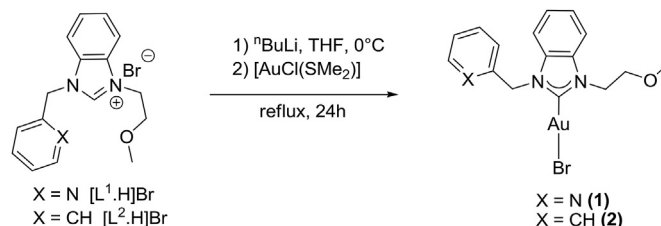
realized [8]. Grotjahn demonstrated that imidazole or pyridyl containing phosphine ligand on a CpRu fragment dramatically accelerates the rate and selectivity of anti-Markovnikov alkyne hydration (Scheme 2b) [9]. Recently, Iwasawa has reported an Au(I)-functionalized cavitand featuring phosphite and oxidized phosphite units for the catalytic hydration of alkynes. Synergic activation of alkyne and water at Au and P=O fragment respectively is proposed (Scheme 2c) [10]. As part of ongoing efforts to utilize a pyridyl-type fragment suitably placed on a metal catalyst for water reactions, we have reported nitrile hydration [11], olefin oxygenation [12] and oxidation of alcohol to acid [13]. Hydration activity of Au–NHC compounds for both terminal and internal alkynes is well recognized [14]. We sought to incorporate a basic group on the ligand scaffold and examine its role in promoting alkyne hydration and related chemistry [15]. Such complexes with basic groups have been investigated with both NHC and phosphane ligands [16]. Herein we report an Au(I)–NHC complex featuring a pendant pyridyl on the ligand architecture and study its catalytic utility for the hydrative syntheses of the amides from alkynes and sodium azide in acidic water. A related catalyst lacking the pyridyl group affords only 37% conversion for the phenylacetylene in comparison to >90% for the same precursor by the pyridyl-bearing catalyst, illustrating the role of the promoter ligand for water reactions.

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Scheme 1. Hydrative synthesis of amide.

Scheme 3. Syntheses of **1** and **2**.

2. Result and discussion

2.1. Syntheses and structure

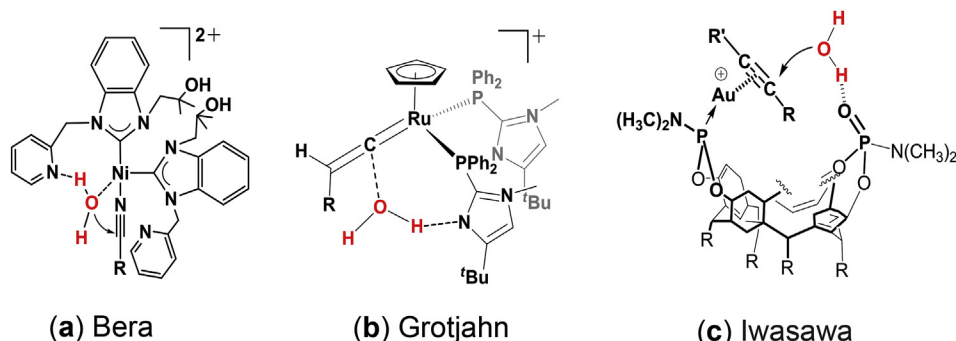
Syntheses of pyridyl- and benzyl-functionalized NHC ligand precursors $[L^1.H]Br$ and $[L^2.H]Br$ were earlier reported from our group [7]. The reaction of a THF solution of $[L^1.H]Br$ with $nBuLi$ (1.6 equivalent), followed by addition of $(SMe_2)AuCl$ in 1:1 ratio with respect to the ligand afforded $[L^1AuBr]$ (**1**) as a yellow solid in 82% yield. Following a similar procedure using $[L^2.H]Br$ afforded $[L^2AuBr]$ (**2**) in 77% yield (Scheme 3). Both compounds are characterized spectroscopically and by X-ray crystallography as well. ^1H NMR spectra of the products show the disappearance of imidazolium proton indicating metalation. The carbene carbon signals appear at $\delta = 191.77$ and 181.98 ppm for **1** and **2**, respectively. Molecular structures are determined by single crystal X-ray crystallography (Fig. 1). For both complexes, the Au center reveals linear coordination bound to NHC and Br. The Au1–C1 distance is $1.989(7)$ (Å) and the Au1–Br1 distance is $2.3954(8)$ (Å). The corresponding distances in **2** are $1.986(5)$ and $2.3950(6)$ (Å), respectively. The C1–Au1–Br1 angles $179.34(19)^\circ$ and $177.75(13)^\circ$, respectively for **1** and **2**, reflect the linear geometry around the metal. For **1**, a long Au1...N3 separation (5.048 Å) and the disposition of the pyridyl ring with respect to NHC (ϕ N1–C8–C9–N3 = $164.1(5)^\circ$) demonstrates the absence of any interaction between the pyridyl nitrogen and the metal. The ESI–MS signal at $m/z = 544.0359$ ($z = 1$) for **1** is assigned for $[M+H]^+$ (Fig. S1). Interestingly, the ESI–MS of **2** revealed a prominent signal at $m/z = 729.2546$ ($z = 1$) which is assigned for $[Au(L^2)_2]^+$. (Fig. S2).

2.2. Catalytic studies

The catalytic utility of **1** was investigated for the syntheses of secondary amides from alkynes. Phenylacetylene (1 equiv.), catalyst **1** (2 mol%), NaN_3 (2 equiv.) and H_2O (2 equiv.) were reacted in 2 mL trifluoroacetic acid (TFA)/1,2-dichloroethane (DCE) (1:1 v/v) to obtain *N*-phenylacetamide in 91% isolated yield after 2 h at room temperature ($25^\circ C$) (Scheme 4). The optimized condition was derived after a series of experiments (Table S2). Initially, 10 mol% catalyst loading gave 96% amide conversion (Table S2 entry 1). While decreasing the catalyst loading to 2 mol%, a similar yield of 91% was obtained. When catalyst loading was further reduced to

1 mol%, the formation of amide was drastically reduced to 52%. In absence of the catalyst, trace amount of amide and 15% acetophenone was observed. Employing 2 mol% $(SMe_2)AuCl$ as the catalyst afforded 25% conversion of the desired amide. Different solvent combinations were screened, among which TFA/DCE (1:1 v/v) gave the best result. When the reaction was performed in absence of TFA, the desired amide was not observed. The use of acetic acid instead of TFA failed to afford the product. The conversion was very similar when $TMSN_3$ was used as nitrogen source. We pursued the reaction with cheaper, accessible and easy-to-handle NaN_3 [17]. Two equivalents of NaN_3 were necessary to obtain the maximum conversion. A mixture of acetophenone and acetamide was observed when one equivalent of azide was employed. In the absence of the azide, acetophenone was observed exclusively in 94% yield.

The substrate scope was investigated using a variety of terminal and internal alkynes. Catalyst **1** exhibited greater proficiency for terminal alkynes compared to internal alkynes affording the corresponding secondary amides. Phenylacetylene and its electron-rich derivatives gave excellent yields (90–95%) (Table 1, entries 1–4). Yields are reduced for electron-deficient alkynes 4-bromophenylacetylene and 4-fluorophenylacetylene (85% and 68% respectively) (entries 5, 6). Bulkier substrate 2-ethynyl-naphthalene was successfully converted to *N*-(naphthalen-2-yl)acetamide albeit in a lower yield (71%) (entry 7). Heterocyclic alkynes such as 2-ethynylpyridine and 2-ethynylthiophene gave analogous amides with moderate yields 72% and 75% respectively (entries 8, 9). The substrate scope was further extended to long chain aliphatic alkynes where conversions were relatively lower and starting materials were found at the end of the reactions. Aliphatic alkynes 1-Hexyne, 1-heptyne and 1-octyne led to the formation of corresponding amides in yields 75%, 70% and 70% respectively (entries 10–12). *N*-cyclohexylacetamide was prepared from related alkynes with moderate yield (entry 13). A lower yield of 31% was observed for *N*-cyclopropylacetamide (entry 14). Ethynyltrimethylsilane did not afford the amide presumably due to decomposition under the reaction conditions as indicated by GC (entry 15).



Scheme 2. Strategies for water activation.

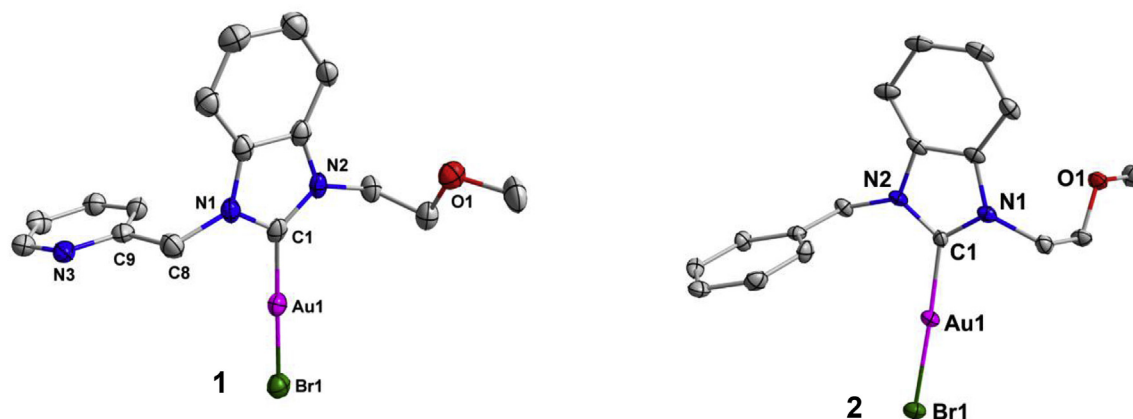
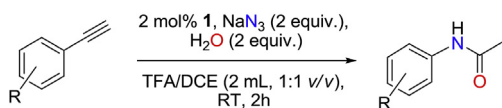


Fig. 1. X-ray structure (40% probability thermal ellipsoids) of **1** (left) and **2** (right) with important atoms labelled. Hydrogen atoms are omitted for the sake of clarity. Selected bond lengths (Å) and angles (°): For **1**, Au1–C1 1.989(7), Au1–Br1 2.3954(8), N3–Au1 5.048; C1–Au1–Br1 179.34(19); for **2**, Au1–C1 1.986(5), Au1–Br1 2.3950(6); C1–Au1–Br1 177.75(13).



Scheme 4. Synthesis of amide from alkyne catalyzed by **1**.

Further, internal alkynes were tested under optimized conditions (Table 2). The yields were in general lower than terminal alkynes. The nitrogenation occurs preferably at electron-rich side of the alkynes. Diphenylacetylene gave *N*,2-diphenylacetamide in 62% yield. Regioselectivity was observed when asymmetric alkynes were chosen for the synthesis of secondary amides. Alkynes 1,2-dimethyl-4-(phenylethynyl)benzene, 1,3-dimethyl-5-(phenylethynyl)benzene, 1,2-dimethoxy-4-(phenylethynyl)benzene and 1-ethoxy-4-(phenylethynyl)benzene were converted to their respective amides in the range of yields 61–68% (entries 2–5). For 1-fluoro-4-(phenylethynyl)benzene,

2-(4-fluorophenyl)-*N*-m-tolylacetamide was formed preferably in 47% yield illustrating the regioselectivity of the reaction (entry 6). For 1,3,5-trimethyl-2-(phenylethynyl)benzene, only *N*-mesityl-2-phenylacetamide was obtained with 55% yield (entry 7). The electronic factor appears to dominate over the steric consideration.

Catalyst **1** thus readily affords the amides from alkynes and sodium azide in acidic water with low catalyst loading and in short duration without needing Ag(I) salt as an additive.

3. Mechanistic investigation

3.1. Control experiments

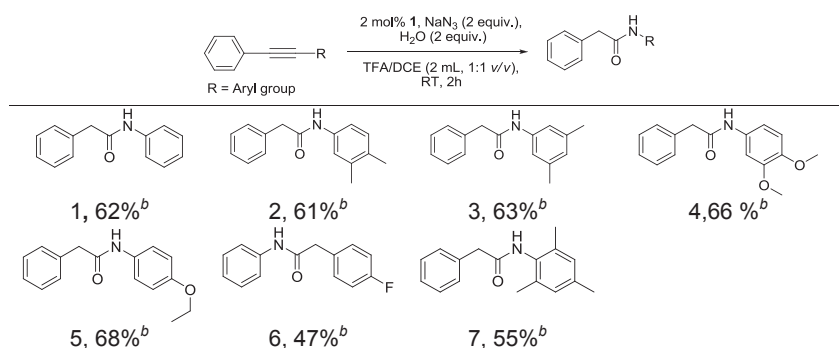
To gain insight into the reaction mechanism, several control experiments were carried out. At first, catalyst **2** that is devoid of the appended pyridyl functionality was evaluated for the same reaction. Under optimization conditions, catalyst **2** gave 37%

Table 1
Syntheses of secondary amides from terminal alkynes catalyzed by **1**.^a

2 mol% **1**, NaN₃ (2 equiv.),
H₂O (2 equiv.)
TFA/DCE (2 mL, 1:1 v/v),
RT, 2h

 1 , 91% ^b 4 , 90% ^b	 2 , 95% ^b 5 , 85% ^b	 3 , 94% ^b 6 , 68% ^b
 7 , 71% ^b	 8 , 72% ^b	 9 , 75% ^b
 10 , 75% ^b	 11 , 70% ^b	 12 , 70% ^b
 13 , 62% ^b	 14 , 31% ^c	 15 , 0% ^c

Table 2
Syntheses of amides from internal alkynes catalyzed by **1**.^a



^a Reaction conditions: 0.5 mmol alkyne, 1 mmol NaN₃, 1 mmol H₂O, 2 mol% **1**, 2 mL TFA/DCE (1:1 v/v), room temperature, 2 h ^bIsolated yields.

conversion of *N*-phenyl acetamide that is much lower than the 91% yield offered by **1** (Scheme 5a). This result clearly demonstrates the role of the basic unit to promote the amide synthesis. In the absence of water under the optimized reaction conditions, both catalysts failed to afford the amide product. When the reaction was performed in the absence of NaN₃ under the standard conditions, catalyst **1** afforded 94% conversion to acetophenone (Scheme 5b), suggesting that amide formation likely proceeds through the intermediacy of the hydration product ketone. When acetophenone was used as starting precursor under identical conditions, *N*-phenyl acetamide was obtained in 93% and 76% yields for catalysts **1** and **2** respectively. (Scheme 5c). However, without the catalyst, only trace amount of amide was observed (Scheme 5d).

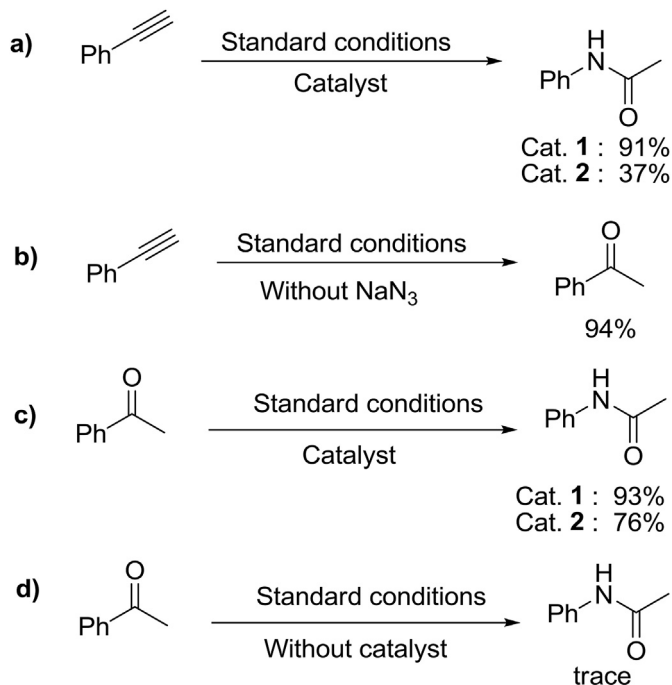
3.2. NMR experiment

The progress of the reaction was monitored by ¹H NMR spectroscopy. Phenylacetylene, sodium azide, catalyst **1** and D₂O were

taken with TFA/CD₂Cl₂ inside a NMR tube (Fig. 2). Within a minute, new signals at δ 5.24, 5.66 ppm and at δ 2.75 ppm appear. These signals grow in intensity up to 5 min after which the signals at δ 5.24, 5.66 ppm decrease and the signal at δ 2.75 ppm increases. We assume at this stage that these protons correspond to the alkyne hydration products. Two sets of protons at higher frequencies are attributed to olefinic protons of the enol **X**, which is in equilibrium with ketone **Y** that exhibits methyl protons at δ 2.75 ppm. Although ketone is the stable product, acid catalyzed enolization is evident here [18]. As the reaction progresses, the equilibrium is shifted towards ketone. The alkyne (δ 3.12 ppm) is gradually consumed with the advancement of the reaction. The amide product, identified by the methyl signal at δ = 2.26 ppm, starts appearing after 5 min and progressively grows in intensity. After 2 h, only product signals are observed with the trace amount of alkyne and no ketone.

3.3. Plausible mechanism

Two possible pathways could be proposed [19] for the amide formation from alkyne - (i) alkyne hydration [14] to ketone and subsequent Schmidt reaction [20], referred as 'hydrative' pathway, and (ii) hydroazidation of alkyne followed by acid catalyzed rearrangement [4]. The pyridyl group in catalyst **1** accelerates the amide formation and such effect is absent for catalyst **2** that lacks the promoter unit. Further, acetophenone is readily converted to the amide under the catalytic reaction conditions. These results led us to argue in favor of a water attack to alkyne over the azide reaction. NMR experiments do show the formation of ketone at the initial stage of the reaction which is subsequently consumed to the amide. Consistent with these observations, a hydrative mechanism (Scheme 6) is thus proposed. Initially, alkyne is coordinated to the metal (**A**) via removal of the bromide that is assisted by the *trans* NHC ligand [21]. It is followed by water attack to the metal-coordinated alkyne in accordance with Markovnikov's rule [22]. The pyridyl unit enhances the nucleophilicity of the catalytically relevant water molecule by hydrogen-bond interaction as shown in **B** [7]. It results in the formation of ketone via enol intermediate [17]. Nucleophilic attack of azide to carbonyl carbon, facilitated by the protons present in the reaction medium, affords **D**. A well-established Schmidt reaction is likely to operate in the final step. The aryl group preferably migrates to the nitrogen atom with the simultaneous liberation of N₂ leading to the release of **E**, which readily tautomerizes to the amide product. The alkyne coordination to the metal completes the catalytic cycle.



Scheme 5. Control experiments.

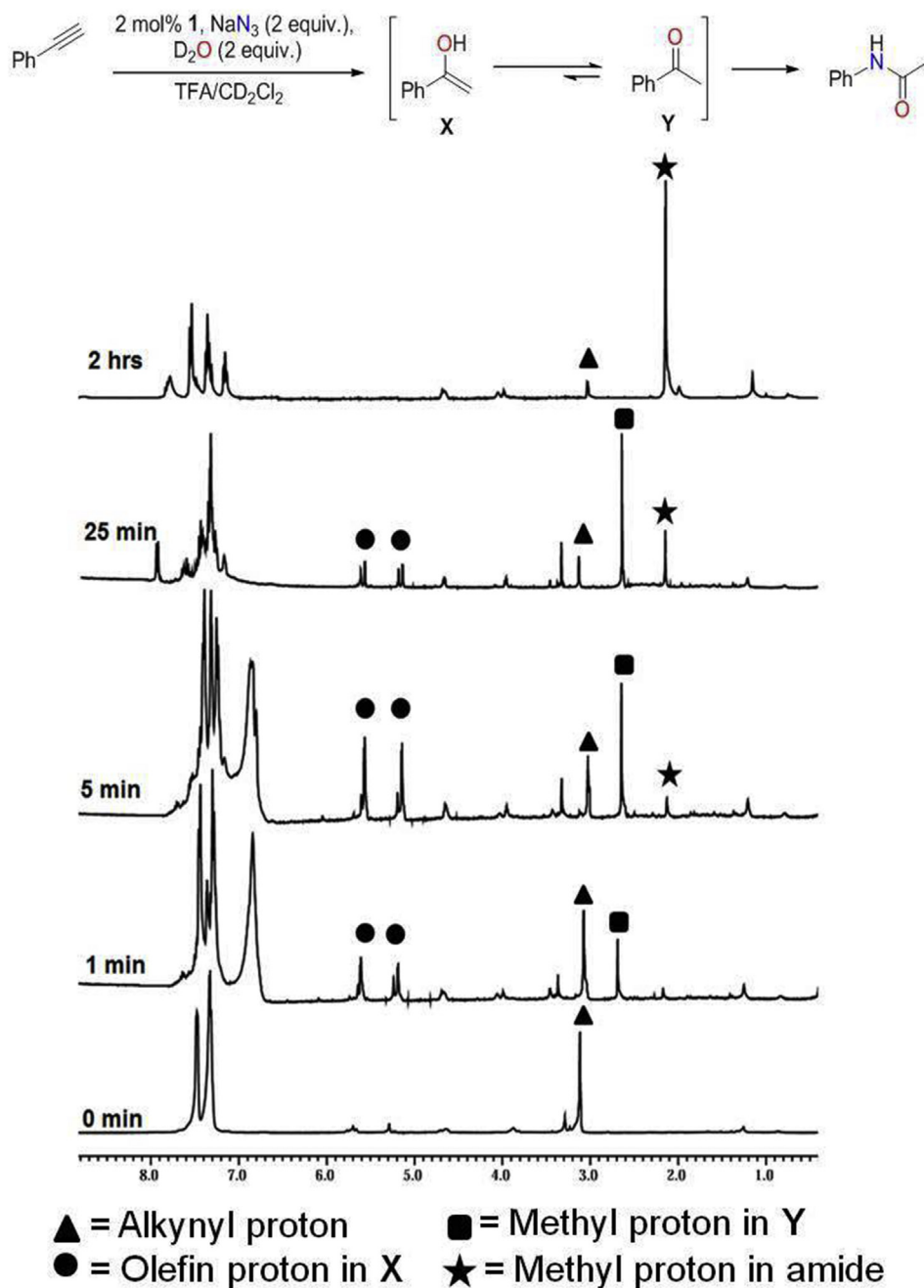


Fig. 2. Monitoring the progress of reaction by ^1H NMR spectroscopy. Reaction conditions: phenylacetylene (0.25 mmol), NaN_3 (0.50 mmol), **1** (2 mol%), D_2O (0.5 mmol) and CD_2Cl_2 (0.4 mL) were taken in NMR tube and TFA (200 μL) was added.

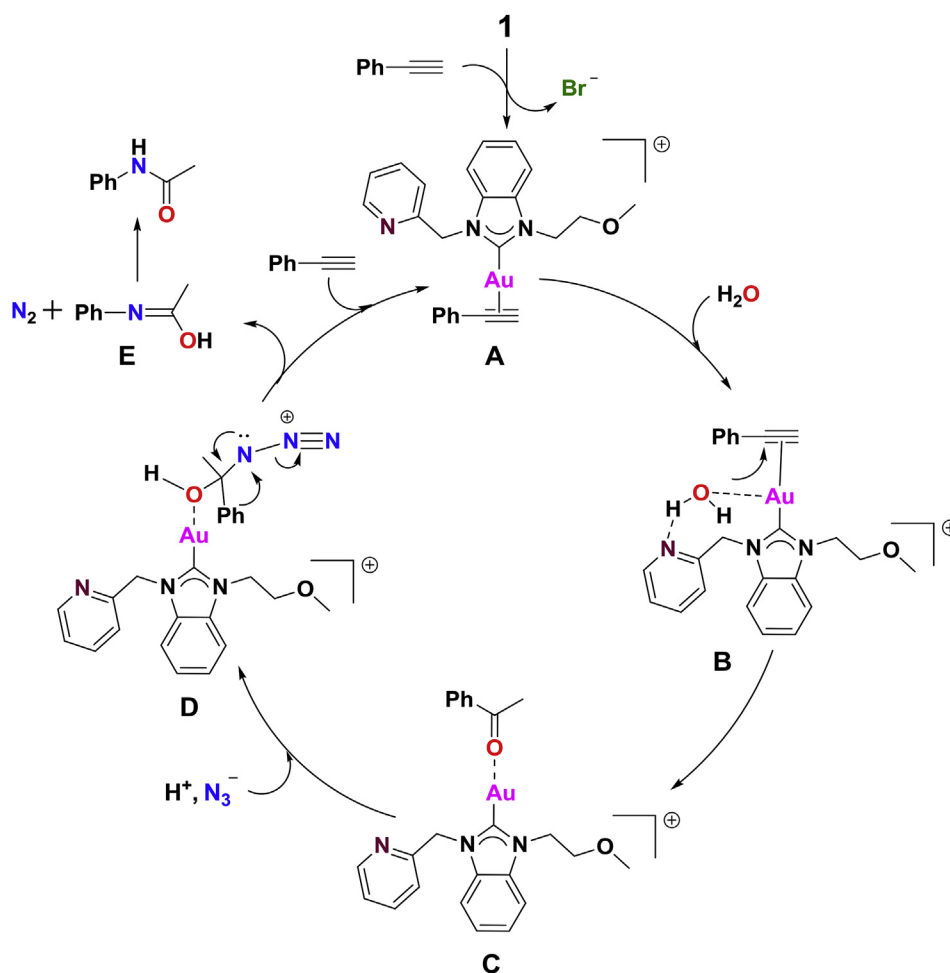
4. Concluding remarks

An Au(I) complex bearing pyridyl-functionalized NHC ligand is synthesized. It catalyses the amide synthesis from alkyne, azide and acidic water in excellent yield. This silver-free protocol is advantageous in terms of low catalyst loading, short reaction time, and works well for both terminal and internal alkynes. A related catalyst that lacks pyridyl fragment performs much inferior. The role of the pyridyl fragment to accelerate the amide synthesis is established. Control experiments and NMR data suggest a hydrative pathway. This work endorses the use of pyridyl functionality appended on the catalyst to promote water reactions.

5. Experimental section

5.1. General procedures

All reactions with metal complexes were carried out under an atmosphere of purified nitrogen using standard Schlenk–vessel and vacuum line techniques. NMR spectra were obtained on JEOL JNM–LA 400 MHz and 500 MHz spectrometer. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. Elemental analyses were performed on a Thermoquest EA1110 CHNS/O analyzer. The crystallized compounds were powdered, washed several times with dry diethyl



Scheme 6. Proposed hydrative mechanism for the synthesis of amide.

ether, and dried in vacuum for at least 48 h prior to elemental analyses. ESI–MS were recorded on a Waters Micromass Quattro Micro triple–quadrupole mass spectrometer. The GC–MS experiments were performed by using an Agilent 7890A GC and 5975C MS. Conversions were determined (uncorrected GC areas) with respect to the internal standard.

6. Materials

Solvents were dried by conventional methods, distilled under nitrogen and deoxygenated prior to use. Gold powder was purchased from Arora Matthey, India. ⁿBuLi was bought from Acros Organics. All other chemicals were purchased from Sigma–Aldrich. Chloro(dimethylsulfide)gold(I) [23], internal alkynes [24] and ligands [7] were synthesized following reported procedures.

Caution: Under the reaction conditions, NaN₃ may be hydrolyzed to form toxic and explosive HN₃. Protective measures are essential during experiment.

X-Ray Data Collection and Refinements: Single-crystal X-ray studies were performed on a CCD Bruker SMART APEX diffractometer equipped with an Oxford Instruments low–temperature attachment. All the data were collected at 100(2) K using graphite–monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages [25], and the data were corrected for absorption using the SADABS program [26]. The structures were

solved and refined with the SHELX suite of programs [27]. All hydrogen atoms were included in the final stages of the refinement and were refined with a typical riding model. Pertinent crystallographic data for compounds **1**, **2** are summarized in (Table S1.) The crystallographic figures used in this manuscript have been generated using Diamond 3.1e software [28]. CCDC numbers 1877275, 1877276 contain the supplementary crystallographic data for compounds **1** and **2**. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6.1. Synthesis of **1**

A flame dried Schlenk flask was charged with [L¹.H]Br (150 mg, 0.43 mmol). It was then dissolved in 15 mL THF and kept for cooling to 0 °C in ice bath. Dropwise ⁿBuLi (0.69 mmol, 1.6 M in hexanes, 1.6 equivalents) was added to the reaction mixture followed by addition of (SMe₂)AuCl (127 mg, 0.43 mmol, 1 equivalents). The reaction was heated to reflux for 24 h. After completion of the reaction, the mixture was allowed to cool and solvent was evaporated under reduced pressure. The resulted crude solid was further redissolved in 15 mL dichloromethane and the mixture was filtered through a small pad of celite. To induce precipitation, 15 mL diethyl ether was added after concentrating the reaction mixture under reduced pressure. Discarding the supernatant solution through cannula filtration, the precipitate was again washed with ether (3 × 10 mL).

Finally, a yellow solid was obtained after drying the precipitate under vacuum. Suitable crystals were grown for X-ray diffraction inside an 8 mm o.d. vacuum-sealed glass tube after layering diethyl ether over a concentrated dichloromethane solution. Yield: 192 mg (82%). Anal. Calcd. for $\text{Au}_1\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_1\text{Br}_1$: C, 35.36; H, 3.16; N, 7.74. Found: C, 35.02; H, 3.06; N, 7.31. ESI-MS, m/z : 544.0359 ($z = 1$), $[\text{M}+\text{H}]^+$. ^1H NMR (400 MHz, CDCl_3) δ = 8.55 (d, J = 4.56 Hz, 1H, Py), 7.66–7.54 (m, 4H, BzIm), 7.43–7.31 (m, 3H, Py), 5.80 (s, 2H, CH_2Py), 4.65 (t, J = 5.04 Hz, 2H, CH_2), 3.89 (t, J = 5.04 Hz, 2H, CH_2), 3.30 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 191.77, 154.85, 149.59, 137.53, 134.14, 133.52, 124.97, 124.74, 123.48, 122.32, 112.56, 112.24, 77.54, 59.23, 54.17, 49.50.

6.2. Synthesis of 2

Compound **2** was synthesized following a similar procedure as for **1** using $[\text{L}^2\text{-H}]\text{Br}$ (150 mg, 0.43 mmol), $^n\text{BuLi}$ (0.69 mmol, 1.6 M in hexanes) and $(\text{SMe}_2)\text{AuCl}$ (127 mg, 0.43 mmol). Yield: 180 mg (77%). Anal. Calcd. for $\text{Au}_1\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_1\text{Br}_1$: C, 37.64; H, 3.35; N, 5.17. Found: C, 37.11; H, 3.12; N, 5.03. ESI-MS, m/z : 729.2546 ($z = 1$), $[\text{2} + \text{L}^2\text{-Br}]^+$. ^1H NMR (400 MHz, CDCl_3) δ = 7.59 (d, J = 6.44 Hz, 1H, BzIm), 7.37–7.30 (m, 8H, all aromatic), 5.71 (s, 2H, CH_2Ben), 4.66 (t, J = 5.48 Hz, 2H, CH_2), 3.90 (t, J = 5.48 Hz, 2H, CH_2), 3.31 (s, 3H, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ = 181.98, 134.57, 134.43, 132.76, 129.13, 128.62, 127.46, 124.65, 112.63, 111.94, 72.00, 59.25, 52.91, 48.86.

6.3. General procedure for catalysis

Alkynes (0.5 mmol), NaN_3 (1 mmol), H_2O (1 mmol), catalyst **1** (2 mol%) and TFA/DCE (2 mL, 1:1 v/v) were taken in a Schlenk tube inside a fume hood. The reaction mixture was allowed to stir for 2 h at room temperature. Then 25 mL water was added to it and the organics were extracted with ethyl acetate (3×10 mL). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the desired amide product. Yields were calculated based on isolated products. GC yields were reported in presence of internal standard dodecane.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jorganchem.2019.02.011>.

References

- [1] a) A. Greenberg, C.M. Breneman, J.F. Liebman (Eds.), *The Amide Linkage: Selected Structural Aspects in Chemistry, Biochemistry, and Materials Science*, Wiley-Interscience, New York, 2000; b) T. Wieland, M. Bodanszky, *The World of Peptides: A Brief History of Peptide Chemistry*, Springer, 1991; c) N. Sewald, H.-D. Jakubke, *Peptides: Chemistry and Biology*, Wiley-VCH, Weinheim, Germany, 2002; d) V.R. Pattabiraman, J.W. Bode, *Nature* 480 (2011) 471; e) J.M. Humphrey, A.R. Chamberlin, *Chem. Rev.* 97 (1997) 2243; f) B. Saha, G. Sengupta, A. Sarbajna, I. Dutta, J.K. Bera, *J. Organomet. Chem.* 771 (2014) 124.
- [2] a) R.C. Larock, *Comprehensive Organic Transformations*, Wiley-VCH, New York, 1999; b) M.B. Smith, in: *Compendium of Organic Synthetic Methods*, vol. 9, Wiley, New York, 2001; c) J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, 2001; d) J. March, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, third ed., Wiley, New York, 1985; e) E. Valeur, M. Bradley, *Chem. Soc. Rev.* 38 (2009) 606; f) P.D. Bailey, I.D. Collier, K.M. Morgan, in: A.R. Katritzky, O. Meth-Cohn, C.W. Rees (Eds.), *Comprehensive Organic Functional Group Transformations*, vol. 5, Pergamon, Cambridge, 1995 (Chapter 6).
- [3] a) B.L. Bray, *Nat. Rev.* 2 (2003) 587; b) F. Albericio, *Curr. Opin. Chem. Biol.* 8 (2004) 211; c) P.A.S. Smith, *Org. React.* 3 (1946); d) R.E. Gawley, *Org. React.* 35 (1988); e) J.H. Boyer, J. Hamer, *J. Am. Chem. Soc.* 77 (1955) 951; f) N.A. Owston, A.J. Parker, J.M.J. Williams, *Org. Lett.* 9 (2007) 3599; g) S. Murahashi, T. Naota, E. Saito, *J. Am. Chem. Soc.* 108 (1986) 7846; h) J.M. Lee, D.-S. Ahn, D.Y. Jung, J. Lee, Y. Do, S.K. Kim, S. Chang, *J. Am. Chem. Soc.* 128 (2006) 12954; i) W.-J. Yoo, C.-J. Li, *J. Am. Chem. Soc.* 128 (2006) 13064; j) W.-K. Chan, C.-M. Ho, M.-K. Wong, C.-M. Che, *J. Am. Chem. Soc.* 128 (2006) 14796; k) C. Zhang, N. Jiao, *J. Am. Chem. Soc.* 132 (2010) 28; l) N.D. Schley, G.E. Dobereiner, R.H. Crabtree, *Organometallics* 30 (2011) 4174; m) H. Jiang, B. Liu, Y. Li, A. Wang, H. Huang, *Org. Lett.* 13 (2011) 1028; n) J.Y. Kim, S.H. Park, J. Ryu, S.H. Cho, S.H. Kim, S. Chang, *J. Am. Chem. Soc.* 134 (2012) 9110; o) R. Cadoni, A. Porcheddu, G. Giacomelli, L.D. Luca, *Org. Lett.* 14 (2012) 5014; p) S.C. Ghosh, J.S.Y. Ngiam, A.M. Seayad, D.T. Tuan, C.L.L. Chai, A. Chen, *J. Org. Chem.* 77 (2012) 8007; q) C. Zhang, X. Zong, L. Zhang, N. Jiao, *Org. Lett.* 14 (2012) 3280; r) B. Zhou, Y. Yang, J. Shi, H. Feng, Y. Li, *Chem. Eur. J.* 19 (2013) 10511; s) I. Kim, C. Lee, *Angew. Chem. Int. Ed.* 52 (2013) 10023.
- [4] a) S.H. Cho, E.J. Yoo, I. Bae, S. Chang, *J. Am. Chem. Soc.* 127 (2005) 16046; b) S.H. Cho, S. Chang, *Angew. Chem. Int. Ed.* 46 (2007) 1897; c) C. Qin, P. Feng, Y. Ou, T. Shen, T. Wang, N. Jiao, *Angew. Chem. Int. Ed.* 52 (2013) 7850; d) Q. Nie, F. Yi, B. Huang, M. Cai, *Adv. Synth. Catal.* 359 (2017) 3968.
- [5] a) J. Zabicky (Ed.), *The Chemistry of Amides*, Wiley-Interscience, New York, 1970; b) A. Greenberg, C.M. Breneman, J.F. Liebman (Eds.), *The Amide Linkage: Structural Significance in Chemistry, Biochemistry and Materials Science*, John Wiley & Sons, New York, 2000; c) T.J. Ahmed, S.M.M. Knapp, D.R. Tyler, *Coord. Chem. Rev.* 255 (2011) 949; d) *The Chemistry of Functional Groups*, in: Z. Pappoport, S. Patai (Eds.), *The Chemistry of Cyano Group*, Wiley, London, 1970; e) V.R. Pattabiraman, J.W. Bode, *Nature* 480 (2011) 471; f) X. Xing, C. Xu, B. Chen, C. Li, S. C. Virgil, R. H. Grubbs, *J. Am. Chem. Soc.* DOI: 10.1021/jacs.8b11667; g) I.G. Molnár, P. Calleja, M. Ernst, A.S.K. Hashmi, T. Schaub, *ChemCatChem* 9 (2017) 4175.
- [6] a) R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, *Organometallics* 29 (2010) 3955; b) R. García-Álvarez, M. Zablocka, P. Crochet, C. Duhayon, J.-P. Majoral, V. Cadierno, *Green Chem.* 15 (2013) 2447; c) V. Cadierno, J. Francos, J. Gimeno, *Chem. Eur. J.* 14 (2008) 6601; d) V. Cadierno, J. Díez, J. Francos, J. Gimeno, *Chem. Eur. J.* 16 (2010) 9808; e) R. García-Álvarez, J. Francos, P. Crochet, V. Cadierno, *Tetrahedron Lett.* 52 (2011) 4218; f) R. García-Álvarez, J. Díez, P. Crochet, V. Cadierno, *Organometallics* 30 (2011) 5442; g) R. García-Álvarez, A.E. Díaz-Álvarez, P. Crochet, V. Cadierno, *RSC Adv.* 3 (2013) 5889; h) E. Tomás-Mendivil, F.L. Suárez, J. Díez, V. Cadierno, *Chem. Commun.* 50 (2014) 9661; i) E. Tomás-Mendivil, R. García-Álvarez, C. Vidal, P. Crochet, V. Cadierno, *ACS Catal.* 4 (2014) 1901; j) R. González-Fernández, P. Crochet, V. Cadierno, *Chem. Select* 3 (2018) 4324; k) R. González-Fernández, P. Crochet, V. Cadierno, M.I. Menéndez, R. López, *Chem. Eur. J.* 23 (2017) 15210.
- [7] K. Singh, A. Sarbajna, I. Dutta, P. Pandey, J.K. Bera, *Chem. Eur. J.* 23 (2017) 7761.
- [8] a) F. Boeck, T. Kribber, L. Xiao, L. Hintermann, *J. Am. Chem. Soc.* 133 (2011) 8138; b) D.B. Grotjahn, *Chem. Eur. J.* 11 (2005) 7153; c) A. Labonne, T. Kribber, L. Hintermann, *Org. Lett.* 8 (2006) 5854; d) D.B. Grotjahn, E.J. Kragulj, C.D. Zeinalipour-Yazdi, V. Miranda-Soto, D.A. Lev, A.L. Cooksy, *J. Am. Chem. Soc.* 130 (2008) 10860.
- [9] a) D.B. Grotjahn, C.D. Incarvito, A.L. Rheingold, *Angew. Chem. Int. Ed.* 40 (2001) 3884; b) D.B. Grotjahn, D.A. Lev, *J. Am. Chem. Soc.* 126 (2004) 12232.
- [10] M. Inoue, K. Ugawa, T. Maruyama, T. Iwasawa, *Eur. J. Org. Chem.* (2018) 5304.
- [11] P. Daw, A. Sinha, S.M.W. Rahaman, S. Dinda, J.K. Bera, *Organometallics* 31 (2012) 3790.
- [12] T. Ghatak, M. Sarkar, S. Dinda, I. Dutta, S.M.W. Rahaman, J.K. Bera, *J. Am. Chem. Soc.* 137 (2015) 6168.
- [13] A. Sarbajna, I. Dutta, P. Daw, S. Dinda, S.M.W. Rahaman, A. Sarkar, J.K. Bera,

- ACS Catal. 7 (2017) 2786.
- [14] a) S. Díez-González, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612;
b) F. Li, N. Wang, L. Lu, G. Zhu, J. Org. Chem. 80 (2015) 3538;
c) R. Dorel, A.M. Echavarren, Chem. Rev. 115 (2015) 9028;
d) A.S.K. Hashmi, Chem. Rev. 107 (2007) 3180;
e) R. Casado, M. Contel, M. Laguna, P. Romero, S. Sanz, J. Am. Chem. Soc. 125 (2003) 11925;
f) A. Leyva, A. Corma, J. Org. Chem. 74 (2009) 2067;
g) E. Mizushima, K. Sato, T. Hayashi, M. Tanaka, Angew. Chem. Int. Ed. 41 (2002) 4563;
h) D. Pflästerer, A.S.K. Hashmi, Chem. Soc. Rev. 45 (2016) 1331;
i) A.M. Asiri, A.S.K. Hashmi, Chem. Soc. Rev. 45 (2016) 4471.
- [15] a) C.M. Krauter, A.S.K. Hashmi, M. Pernpointner, ChemCatChem 2 (2010) 1226;
b) M. Lein, M. Rudolph, A.S.K. Hashmi, P. Schwerdtfeger, Organometallics 29 (2010) 2206;
c) M.C.B. Jaimes, F. Rominger, M.M. Pereira, R.M.B. Carrilho, S.A.C. Carabineiro, A.S.K. Hashmi, Chem. Commun. 50 (2014) 4937;
d) M.C.B. Jaimes, C.R.N. Böhlring, J.M. Serrano-Becerra, A.S.K. Hashmi, Angew. Chem. Int. Ed. 52 (2013) 7963.
- [16] a) M. Pažický, A. Loos, M.J. Ferreira, D. Serra, N. Vinokurov, F. Rominger, C. Jäkel, A.S.K. Hashmi, M. Limbach, Organometallics 29 (2010) 4448;
b) L. Huang, F. Rominger, M. Rudolph, A.S.K. Hashmi, Chem. Commun. 52 (2016) 6435;
c) L. Huang, M. Rudolph, F. Rominger, A.S.K. Hashmi, Angew. Chem. Int. Ed. 55 (2016) 4808;
d) C. Khin, A.S.K. Hashmi, F. Rominger, Eur. J. Inorg. Chem. (2010) 1063.
- [17] a) W. Zhua, D. Ma, Chem. Commun. (2004) 888;
b) H. Sharghi, R. Khalifeh, M.M. Doroodmand, Adv. Synth. Catal. 351 (2009) 207;
c) H.R. Sahoo, J.G. Kralj, K.F. Jensen, Angew. Chem. Int. Ed. 46 (2007) 5704;
d) M. Nasrollahzadeh, Y. Bayat, D. Habibi, S. Moshaei, Tetrahedron Lett. 41 (2000) 4193.
- [18] a) G.E. Lienhard, T.-C. Wang, J. Am. Chem. Soc. 91 (1969) 1146;
b) Y. Chiang, f A.J. Kresge, s,t J.A. Santaballa/1, J. Wirz, J. Am. Chem. Soc. 110 (1988) 5506;
c) J.A. Keith, P.M. Henry, Angew. Chem. Int. Ed. 48 (2009) 9038.
- [19] A.S.K. Hashmi, Angew. Chem. Int. Ed. 49 (2010) 5232.
- [20] a) K.F.Z. Schmidt, Angew. Chem. 36 (1923) 511;
b) S. Lang, J.A. Murphy, Chem. Soc. Rev. 35 (2006) 146.
- [21] H. Ibrahim, P. d. Frémont, P. Braunstein, V. Théry, L. Nauton, F. Cisnetti, A. Gautier, Adv. Synth. Catal. 357 (2015) 3893.
- [22] a) W. Markownikoff, Eur. J. Org. Chem. (1870) 228;
b) F. Li, N. Wang, L. Lu, G. Zhu, J. Org. Chem. 80 (2015) 3538;
c) A.K. Das, S. Park, S. Muthaiah, S.H. Hong, Synlett 26 (2015) 2517.
- [23] M.-C. Brandys, M.C. Jennings, R.J. Puddephatt, J. Chem. Soc., Dalton Trans. (2000) 4601.
- [24] a) K. Sonogashira, Y. Tohda, N. Hagihara, Tetrahedron Lett. 16 (1975) 4467;
b) J.-C. Hierso, A. Fihri, R. Amardeil, P. Meunier, Org. Lett. 6 (2004) 3473;
c) G. Adjabeng, T. Brenstrum, C.S. Frampton, A.J. Roberson, J. Hillhouse, J. McNulty, A. Capretta, J. Org. Chem. 69 (2004) 5082.
- [25] SAINT+ Software for CCD Diffractometers, Bruker AXS, Madison, WI, 2000.
- [26] G.M. Sheldrick, SADABS 2.0, 2000.
- [27] G.M. Sheldrick, SHELXL-2014: Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 2014.
- [28] K. Bradenburg, Diamond, version 3.1e, Crystal Impact GbR, Bonn, Germany, 2005.