

## Research Article

# Alkyne-Azide Cycloaddition Catalyzed by Silver Chloride and “Abnormal” Silver *N*-Heterocyclic Carbene Complex

Aldo I. Ortega-Arizmendi,<sup>1</sup> Eugenia Aldeco-Pérez,<sup>2</sup> and Erick Cuevas-Yañez<sup>1</sup>

<sup>1</sup> Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Atlacomulco Km. 14.5, 50200 Toluca, MEX, Mexico

<sup>2</sup> Facultad de Química, Universidad Autónoma de Querétaro, Centro Universitario Cerro de las Campanas s/n, 76010 Querétaro, QRO, Mexico

Correspondence should be addressed to Eugenia Aldeco-Pérez; josefina.aldeco@uaq.edu.mx and Erick Cuevas-Yañez; ecuevasy@uaemex.mx

Received 12 August 2013; Accepted 11 September 2013

Academic Editors: A. Brandi, A. Marra, O. Navarro, D. Savoia, and G. C. Vougioukalakis

Copyright © 2013 Aldo I. Ortega-Arizmendi et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A library of 1,2,3-triazoles was synthesized from diverse alkynes and azides using catalytic amounts of silver chloride instead of copper compounds. In addition, a novel “abnormal” silver *N*-heterocyclic carbene complex was tested as catalyst in this process. The results suggest that the reaction requires only 0.5% of silver complex, affording 1,2,3-triazoles in good yields.

## 1. Introduction

The study about the comprehension and applications of the classical (3 + 2) dipolar cycloaddition, the Huisgen Reaction, was revolutionized with the introduction of copper catalysts to this process, which increases selectivity and efficiency to the reaction, allowing diverse applications in several solvents and conditions for an important number of purposes. These characteristics make the copper catalyzed alkyne azide cycloaddition (CuAAC) in the most important “Click” reaction [1].

An essential component in this reaction is the catalyst, based mainly on a copper (I) salt. In this regard, a wide variety of copper compounds and conditions have been proposed and developed in order to optimize this process [2, 3]. In addition, some research groups have explored other metals as alternative catalyst sources, such as ruthenium [4–6], magnesium (through Grignard reagents) [7], and zinc compounds [8]. In spite of these examples, the number of reports about alkyne azide cycloadditions catalyzed by different metals is still limited.

Recently, McNulty and coworkers demonstrated that P,O type silver complexes can catalyze AAC without other copper

additives [9, 10]. These promising reports carried us to report our recent results in this area.

## 2. Experimental Section

The starting materials were purchased from Aldrich Chemical Co. and were used without further purification. Solvents were distilled before use. Silica plates of 0.20 mm thickness were used for thin layer chromatography. Melting points were determined with a Fisher-Johns melting point apparatus, and they are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Varian 500; the chemical shifts ( $\delta$ ) are given in ppm relative to TMS as internal standard (0.00). For analytical purposes, the mass spectra were recorded on a Shimadzu GCMS-QP2010 Plus in the EI mode, 70 eV, 200°C via direct inlet probe. Only the molecular and parent ions (*m/z*) are reported. IR spectra were recorded on a Bruker Tensor 27 equipment.

1,3-Bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium chloride (**13**) was synthesized according to a previous report [11].

For the RX diffraction studies, crystals of compound **14** were obtained by slow evaporation of a dilute EtOH

solution, and the reflections were acquired with a Bruker diffractometer. Three standard reflections every 97 reflections were used to monitor the crystal stability. The structure was solved by direct methods; missing atoms were found by difference-Fourier synthesis and refined on F2 by a full-matrix least-squares procedure using anisotropic displacement parameters using SHELX-97. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 900045). Copies of available materials can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (facsimile: (44) 01223 336033); e-mail: deposit@ccdc.ac.uk.

**2.1. Synthesis of Silver Complex of 1,3-Bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium Chloride.** 1,3-Bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium chloride (1g, 1.6 mmol) were dissolved in dry THF (20 mL) and cooled down to  $-70^{\circ}\text{C}$ . After 15 min, a 1 M solution of NaHMDS in THF (4 mL) was added, and the resulting mixture was stirred 1 hour at room temperature. After precipitation of all solids contained in the reaction mixture, the solution was filtered, and a suspension of silver chloride (229 mg, 1.6 mmol) in THF (30 mL) was added and the reaction mixture was stirred 12 hours at room temperature. After evaporation of the solvent under vacuum, purification was done by adding 30 mL of dichloromethane, filtering from a black precipitate, and pumping down the solvent under reduced pressure. 586 mg (54% yield) of a gray powder were obtained.  $^1\text{H}$  NMR: (300 MHz,  $\text{CDCl}_3$  +  $\text{DMSO}-d_6$ )  $\delta$  0.81 (d,  $J = 6.9$  Hz, 3H), 0.82 (d,  $J = 6.9$  Hz, 3H), 0.95 (d,  $J = 6.9$  Hz, 3H), 1.38 (d,  $J = 6.6$  Hz, 3H), 2.57 (sept,  $J = 6.9$  Hz, 1H), 2.65 (sept.,  $J = 6.9$  Hz, 1H), 6.88–6.85 (m, 2H), 7.09–7.04 (m, 2H), 7.33–7.18 (m, 8H), and 7.48–7.38 (m, 4H).  $^{13}\text{C}$  NMR: (75 MHz,  $\text{CDCl}_3$  +  $\text{DMSO}-d_6$ )  $\delta$  22.4, 23.2, 25.5, 25.6, 28.4, 28.5, 124.6, 125.1, 128.0, 128.1, 128.9, 129.2, 130.2, 130.4, 131.1, 135.8, 141.9, 142.0, 144.4, 144.6, and 161.4 (dd,  $J_{\text{C-107Ag}} = 247$  Hz,  $J_{\text{C-109Ag}} = 265$  Hz, C-Ag). Crystal and structure parameters of silver complex  $\text{C}_{40}\text{H}_{46}\text{AgCl}_3\text{N}_2$ : volume = 1863.51(11)  $\text{\AA}^3$ , triclinic, space group  $P-1$ ,  $a = 9.8904(3)$   $\text{\AA}$ ,  $b = 11.3602(4)$   $\text{\AA}$ ,  $c = 17.9355(6)$   $\text{\AA}$ ,  $\alpha = 95.1220(10)^{\circ}$ ,  $\beta = 92.6030(10)^{\circ}$ ,  $\gamma = 111.2940(10)^{\circ}$ ,  $\rho_{\text{calcd}} = 1.370$   $\text{g/cm}^3$ , Mo-radiation ( $\lambda = 0.71073$   $\text{\AA}$ ),  $T = 100(2)$  K, reflections collected = 19486, independent reflections = 6602 (Rint. = 0.0316), absorption coefficient  $\mu = 0.786$   $\text{mm}^{-1}$ , 433 variables converged at  $R1 = 2.96\%$ ,  $wR2 = 7.70\%$  for all data, with intensity  $I > 2\sigma(I)$ , the final difference map was 0.513 and  $-0.437$   $\text{e}\text{\AA}^{-3}$ .

### 2.2. Synthesis of 1,2,3-Triazoles Performed under AgCl Catalysis

**General Procedure.** AgCl (0.005 g, 0.035 mmol) was added to a stirred solution containing the corresponding alkyne (1.0 mmol) and the appropriate azide (1.1 mmol) in  $\text{H}_2\text{O}$  (3 mL) and acetone (1 mL). The resulting reaction mixture was stirred at room temperature for 24 h. The acetone was removed *in vacuo*, and  $\text{CH}_2\text{Cl}_2$  (20 mL) was added. The organic layer was separated, and the aqueous phase

was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The organic phases were joined, dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed under reduced pressure and the final product was purified by crystallization.

### 2.3. Synthesis of 1,2,3-Triazoles Performed under Silver Complex Catalysis

**General Procedure.** The silver complex **14** (0.0005 mmol) was added to a stirred solution containing the corresponding alkyne (1.0 mmol) and the appropriate azide (1.05 mmol) in THF (4 mL). The resulting reaction mixture was stirred at room temperature for 24 h. The acetone was removed *in vacuo*, and  $\text{CH}_2\text{Cl}_2$  (20 mL) was added. The organic layer was separated, and the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 10$  mL). The organic phases were joined, dried over  $\text{Na}_2\text{SO}_4$ , and filtered. The solvent was removed under reduced pressure, and the final product was purified by crystallization.

**2.4. 1-Benzyl-4-phenyl-1,2,3-triazole (3).** Phenylacetylene and benzyl azide afforded 1-benzyl-4-phenyl-1,2,3-triazole as white solid. Yields: 150.8 mg (64%, under AgCl catalysis) and 181.1 mg (77%, under silver complex catalysis). m.p.  $132^{\circ}\text{C}$  (lit.  $130$ – $130.9^{\circ}\text{C}$ ) [12]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3250, 2850, 1650, and 1600.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 5.59 (s, 2H), 7.33–7.39 (m, 1H), 7.41–7.41 (m, 4H), 7.68–7.82 (m, 2H), and 7.68 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 54.2 ( $\text{CH}_2$ ), 119.5 (CH), 125.6 ( $2 \times \text{CH}$ ), 127.9 ( $2 \times \text{CH}$ ), 128.1 (CH), 128.7 (CH), 128.8 ( $2 \times \text{CH}$ ), 129.1 ( $2 \times \text{CH}$ ), 130.5 (CH), 134.6 (C), and 148.2 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 235 [ $\text{M}^+$ ] (21), 206 [ $\text{M}-\text{HN}_2$ ] $^+$  (74), 116 [ $\text{M}-\text{C}_6\text{H}_5\text{N}_3$ ] $^+$  (100), and 91 [ $\text{C}_6\text{H}_5\text{CH}_2$ ] $^+$  (94).

**2.5. (1-Benzyl-1,2,3-triazol-4-yl)-methanol (4).** Propargyl alcohol and benzyl azide afforded (1-benzyl-1,2,3-triazol-4-yl)-methanol as white solid. Yields: 109.7 mg (58%, under AgCl catalysis) and 120.3 mg (63%, under silver complex catalysis). m.p.  $77.8^{\circ}\text{C}$  (lit.  $76$ – $77^{\circ}\text{C}$ ) [13]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3330, 2850, and 1600.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 3.36 (s, 1H), 4.51 (s, 2H), 5.57 (s, 2H), 7.30–7.37 (m, 5H), and 8.00 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 53.1 ( $\text{CH}_2$ ), 55.4 ( $\text{CH}_2$ ), 123.2 (CH), 128.3 ( $2 \times \text{CH}$ ), 128.5 (CH), 129.1 ( $2 \times \text{CH}$ ), 136.6 (C), and 148.7 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 189 [ $\text{M}^+$ ] (4), 91 [ $\text{C}_6\text{H}_5\text{CH}_2$ ] + (100).

**2.6. 4-(1-Benzyl-1,2,3-triazol-4-ylmethoxy)-benzoic Acid Methyl Ester (5).** 4-Prop-2-ynyloxy-benzoic acid methyl ester and benzyl azide afforded 4-(1-benzyl-1,2,3-triazol-4-ylmethoxy)-benzoic acid methyl ester as white solid. Yields: 231.6 mg (72%, under AgCl catalysis) and 174.3 mg (54%, under silver complex catalysis). m.p.  $145.7^{\circ}\text{C}$ . IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1753, 1650, 1600.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 3.87 (s, 3H), 5.22 (s, 2H), 5.53 (s, 2H), 6.96–6.99 (dd, 2H,  $J = 3$  Hz), 7.96–7.99 (dd, 2H,  $J = 3$  Hz), 7.26–7.28 (m, 2H), 7.35–7.39 (m, 3H), 7.53 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$ /ppm: 51.8 ( $\text{CH}_3$ ), 54.3 ( $\text{CH}_2$ ), 62.1 ( $\text{CH}_2$ ), 114.2 ( $2 \times \text{CH}$ ), 122.7 (C), 123.1 (CH), 127.6 ( $2 \times \text{CH}$ ), 128.8 (CH), 129.4 ( $2 \times \text{CH}$ ), 131.6 ( $2 \times \text{CH}$ ), 134.0 (C), 143.9 (C), 161.8 (C), 166.7 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 323 [ $\text{M}^+$ ] (15), 91 [ $\text{C}_6\text{H}_5\text{CH}_2$ ] $^+$  (100), 144

$[\text{C}_{10}\text{H}_{10}\text{N}]^+$  (95),  $172 [\text{C}_{10}\text{H}_{10}\text{N}_3]^+$  (45). HRMS (EI): calcd. for  $\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_3$ : 323.1270; found: 323.1274.

**2.7. 1-Benzyl-4-(4-methoxy-phenoxy-methyl)-1,2,3-triazole (6).** 1-Methoxy-4-prop-2-ynyloxy-benzene and benzyl azide afforded 1-benzyl-4-(4-methoxy-phenoxy-methyl)-1,2,3-triazole as white solid. Yields: 162.3 mg (55%, under AgCl catalysis) and 189.3 mg (64%, under silver complex catalysis). m.p.  $92.7^\circ\text{C}$  (lit.  $92\text{--}93^\circ\text{C}$ ) [14]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 2950, 1650, and 1600.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 3.76 (s, 3H), 5.13 (s, 2H), 5.52 (s, 2H), 6.80–6.82 (dd, 2H,  $J = 2$  Hz,  $J = 9$  Hz), 6.88–6.90 (dd, 2H,  $J = 2$  Hz,  $J = 9$  Hz), 7.26–7.27 (m, 2H), 7.36–7.38 (m, 3H), and 7.50 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 54.2 ( $\text{CH}_3$ ), 55.6 ( $\text{CH}_2$ ), 62.8 ( $\text{CH}_2$ ), 114.6 ( $2 \times \text{CH}$ ), 115.9 ( $2 \times \text{CH}$ ), 122.9 (CH), 128.1 ( $2 \times \text{CH}$ ), 128.8 (CH), 129.1 ( $2 \times \text{CH}$ ), 134.5 (C), 144.9 (C), 152.4 (C), and 154.3 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 295 [ $\text{M}]^+$  (40), 91 [ $\text{C}_6\text{H}_5\text{CH}_2$ ] $^+$  (100), 144 [ $\text{C}_{10}\text{H}_{10}\text{N}]^+$  (80), 124 [ $\text{C}_7\text{H}_8\text{O}_2$ ] $^+$  (68), and 172 [ $\text{C}_{10}\text{H}_{10}\text{N}_3$ ] $^+$  (5).

**2.8. 1-Benzyl-4-(4'-chlorophenoxy-methyl)-1,2,3-triazole (7).** 1-Chloro-4-prop-2-ynyloxy-benzene and benzyl azide afforded 1-benzyl-4-(4'-chlorophenoxy-methyl)-1,2,3-triazole as white solid. Yields: 201.6 mg (67%, under AgCl catalysis) and 216.4 mg (72%, under silver complex catalysis).  $102.3^\circ\text{C}$  (lit.  $102\text{--}103^\circ\text{C}$ ) [15]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1650, and 1600.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 5.16 (s, 2H), 5.54 (s, 2H), 6.89–6.92 (dd, 2H,  $J = 2$  Hz,  $J = 9$  Hz), 7.22–7.25 (dd, 2H,  $J = 3$  Hz,  $J = 9$  Hz), 7.27–7.30 (m, 2H), 7.38–7.40 (m, 3H), and 7.53 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 54.2 ( $\text{CH}_2$ ), 62.2 ( $\text{CH}_2$ ), 116.0 ( $2 \times \text{CH}$ ), 122.6 (CH), 126.1 (C), 128.0 ( $2 \times \text{CH}$ ), 128.8, 129.4 ( $2 \times \text{CH}$ ), 129.7 ( $2 \times \text{CH}$ ), 134.3 (C), 144.1 (C), and 156.7 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 299 [ $\text{M}]^+$  (15), 91 [ $\text{C}_6\text{H}_5\text{CH}_2$ ] $^+$  (100), 144 [ $\text{C}_{10}\text{H}_{10}\text{N}]^+$  (78), and 172 [ $\text{C}_{10}\text{H}_{10}\text{N}_3$ ] $^+$  (25).

**2.9. 4-(1-Benzyl-1,2,3-triazol-4-ylmethoxy)-benzaldehyde (8).** 4-Prop-2-ynyloxy-benzaldehyde and benzyl azide afforded 4-(1-benzyl-1,2,3-triazol-4-ylmethoxy)-benzaldehyde as white solid. Yields: 83.0 mg (28%, under AgCl catalysis) and 107.8 mg (37%, under silver complex catalysis). m.p.  $79.3^\circ\text{C}$  (lit.  $79\text{--}80^\circ\text{C}$ ) [16]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1660, 1600.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 5.26 (s, 2H), 5.54 (s, 2H), 7.07–7.09 (dd, 2H,  $J = 3$  Hz,  $J = 9$  Hz), 7.82–7.83 (dd, 2H,  $J = 3$  Hz,  $J = 9$  Hz), 7.26–7.29 (m, 2H), 7.36–7.38 (m, 3H), 7.54 (s, 1H), and 9.88 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 54.3 ( $\text{CH}_2$ ), 62.2 ( $\text{CH}_2$ ), 115.3 ( $2 \times \text{CH}$ ), 123.1 (CH), 128.2 ( $2 \times \text{CH}$ ), 128.9 (CH), 129.2 ( $2 \times \text{CH}$ ), 130.3 (C), 130.9 ( $2 \times \text{CH}$ ), 134.3 (C), 143.6 (C), 163.3 (C), and 190.7 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 293 [ $\text{M}]^+$  (5), 91 [ $\text{C}_6\text{H}_5\text{CH}_2$ ] $^+$  (100), 144 [ $\text{C}_{10}\text{H}_{10}\text{N}]^+$  (65), and 172 [ $\text{C}_{10}\text{H}_{10}\text{N}_3$ ] $^+$  (35).

**2.10. 1-(4-Nitrophenyl)-4-phenyl-1,2,3-triazole (9).** Phenylacetylene and 1-azido-4-nitro-benzene afforded 1-(4-Nitrophenyl)-4-phenyl-1,2,3-triazole as orange solid. Yields: 204.7 mg (77%, under AgCl catalysis) and 200.7 mg (75%, under silver complex catalysis). m.p.  $254^\circ\text{C}$  (dec.) [17]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3050, 1600, 1550, and 1350.  $^1\text{H}$  NMR (500 MHz,

$\text{DMSO-d}_6$ )  $\delta/\text{ppm}$ : 7.40 (t,  $J = 7.5$  Hz, 1H), 7.51 (t,  $J = 8.0$  Hz, 2H), 7.95 (m, 2H), 8.25 (m, 2H), 8.48 (m, 2H), 9.51 (s, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ )  $\delta/\text{ppm}$ : 120.4 (CH), 120.9 ( $2 \times \text{CH}$ ), 125.9 ( $2 \times \text{CH}$ ), 126.1 ( $2 \times \text{CH}$ ), 129.0 (CH), 129.5 ( $2 \times \text{CH}$ ), 130.2 (C), 141.3 (C), 147.1 (C), and 148.3 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 266 [ $\text{M}]^+$  (15), 138 (75), 88 (100), and 57 (90).

**2.11. 1-(2-Nitro-phenyl)-4-phenyl-1,2,3-triazole (10).** Phenylacetylene and 1-azido-2-nitro-benzene afforded 1-(2-nitrophenyl)-4-phenyl-1,2,3-triazole as orange solid. Yields: 190.8 mg (72%, under AgCl catalysis) and 186.0 mg (70%, under silver complex catalysis). m.p.  $142.7^\circ\text{C}$  (lit.  $144\text{--}145^\circ\text{C}$ ) [18]. IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3050, 1600, 1550, 1350.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ )  $\delta/\text{ppm}$ : 7.38 (m,  $J = 7.5$  Hz, 1H), 7.47–7.48 (m,  $J = 7.5$  Hz, 1H), 7.68–7.73 (m, 2H), 7.80–7.81 (m, 1H), 7.89–7.91 (d,  $J = 9$  Hz, 2H), and 8.06–8.11 (m, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-d}_6$ )  $\delta/\text{ppm}$ : 120.9 (CH), 125.6 (CH), 126.2 (CH), 127.8 ( $2 \times \text{CH}$ ), 128.8 (CH), 129.1 ( $2 \times \text{CH}$ ), 129.8 (C), 130.3 (C), 130.8 (CH), 133.8 (CH), 144.3 (C), and 148.4 (C). MS ( $\text{EI}^+$ )  $m/z$  (%): 266 [ $\text{M}]^+$  (5), and 88 (100).

**2.12. 4-Phenyl-1-{2-[2-(4-phenyl-1,2,3-triazol-1-yl)-ethoxy]-ethyl}-1,2,3-triazole.** Phenylacetylene and 1-azido-2-(2-azido-ethoxy)-ethane afforded 4-phenyl-1-{2-[2-(4-phenyl-1,2,3-triazol-1-yl)-ethoxy]-ethyl}-1,2,3-triazole as white solid. Yields: 178.8 mg (62%, under AgCl catalysis) and 202.2 mg (70%, under silver complex catalysis). m.p.  $177.5^\circ\text{C}$ . IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3150, 1600, 1350, 1260.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 3.31 (s, 4H), 3.93 (s, 4H), 4.60 (s, 4H), 7.82 (m, 8H), 7.77 (m, 2H), and 8.25 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 47.9 ( $2 \times \text{CH}_2$ ), 67.0 ( $2 \times \text{CH}_2$ ), 119.5 ( $2 \times \text{CH}$ ), 123.4 ( $4 \times \text{CH}$ ), 125.8 ( $2 \times \text{CH}$ ), 126.8 ( $4 \times \text{CH}$ ), 128.9 ( $2 \times \text{C}$ ), and 144.8 ( $2 \times \text{C}$ ). MS ( $\text{EI}^+$ )  $m/z$  (%): 418 (23), 324 (64), 288 (100), 290 (80), 254 (70), and 161 (54). HRMS (EI): calcd. for  $\text{C}_{20}\text{H}_{20}\text{N}_6\text{O}$  calcd. 360.1699, found 360.1701.

**2.13. 4-Chlorophenoxy-methyl-1-{2-[2-(4-chlorophenoxy-methyl-1,2,3-triazol-1-yl)-ethoxy]-ethyl}-1,2,3-triazole.** 1-Chloro-4-prop-2-ynyloxy-benzene and 1-azido-2-(2-azido-ethoxy)-ethane afforded 4-chlorophenoxy-methyl-1-{2-[2-(4-chlorophenoxy-methyl-1,2,3-triazol-1-yl)-ethoxy]-ethyl}-1,2,3-triazole as white solid. Yields: 357.2 mg (73%, under AgCl catalysis) and 355.9 mg (71%, under silver complex catalysis). m.p.  $185^\circ\text{C}$ . IR (ATR)  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3150, 1600, 1350, 1260.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 3.31 (s, 4H), 3.93 (s, 4H), 4.60 (s, 4H), 7.82 (m, 8H), 7.77 (m, 2H), and 8.25 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta/\text{ppm}$ : 49.6 ( $2 \times \text{CH}_2$ ), 61.3 ( $2 \times \text{CH}_2$ ), 68.6 ( $2 \times \text{CH}_2$ ), 120.9 ( $4 \times \text{CH}$ ), 123.6 ( $2 \times \text{CH}$ ), 124.3 ( $2 \times \text{C}$ ), 129.9 ( $4 \times \text{CH}$ ), 142.7 ( $2 \times \text{C}$ ), and 158.4 ( $2 \times \text{C}$ ). MS ( $\text{EI}^+$ )  $m/z$  (%): 488 (20), 266 (100). HRMS (EI): calcd. for  $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{N}_6\text{O}_3$  calcd. 488.1130, found 488.1132.

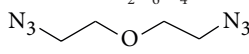
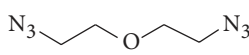
### 3. Results and Discussion

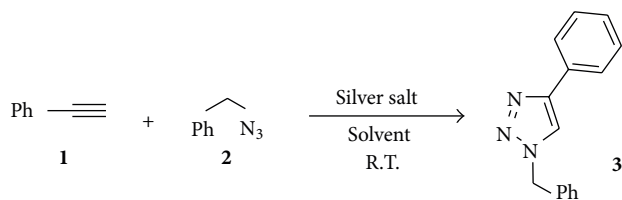
Our initial studies were carried out on phenylacetylene (1) and benzyl azide (2) using catalytic amounts of diverse silver salts (Scheme 1). According to McNulty and coworkers [9, 10], only starting materials were detected using silver nitrate

TABLE 1: Synthesis of triazole 3 catalyzed by silver salts.

Entry	Silver salt	Catalyst ratio (% mol)	Solvent	Reaction time (h)	% Yield
1	AgNO <sub>3</sub>	1	H <sub>2</sub> O	48	0
2	AgNO <sub>3</sub>	1	THF	48	8
3	Ag <sub>2</sub> SO <sub>4</sub>	1	H <sub>2</sub> O	48	0
4	Ag <sub>2</sub> SO <sub>4</sub>	1	THF	48	0
5	Ag <sub>2</sub> O	1	H <sub>2</sub> O	48	0
6	Ag <sub>2</sub> O	1	THF	48	0
7	AgCl	0.5	Acetone	24	35
8	AgCl	0.5	THF	24	27
9	AgCl	0.6	H <sub>2</sub> O	24	35
10	AgCl	0.6	Acetone	24	47
11	AgCl	0.6	H <sub>2</sub> O/acetone	24	55
12	AgCl	0.6	CH <sub>2</sub> Cl <sub>2</sub>	24	0
13	AgCl	0.6	CH <sub>3</sub> OH	24	31
14	AgCl	0.6	THF	24	25
15	AgCl	1	H <sub>2</sub> O/acetone	24	58
16	AgCl	3.5	H <sub>2</sub> O/acetone	24	64
17	AgCl	5	H <sub>2</sub> O/acetone	24	64

TABLE 2: Synthesis of triazoles catalyzed by silver chloride.

Compound	R <sup>1</sup>	R <sup>2</sup>	% Yield
3	Ph	PhCH <sub>2</sub>	64
4	CH <sub>2</sub> OH	PhCH <sub>2</sub>	58
5	CH <sub>2</sub> O(4-CO <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	72
6	CH <sub>2</sub> O(4-COCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	55
7	CH <sub>2</sub> O(4-Cl)C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	67
8	CH <sub>2</sub> O(4-CHO)C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	28
9	Ph	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	77
10	Ph	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	72
11	Ph		62
12	CH <sub>2</sub> O(4-Cl)C <sub>6</sub> H <sub>4</sub>		73



SCHEME 1: Cycloaddition between azide 2 and alkyne 1 using silver salts.

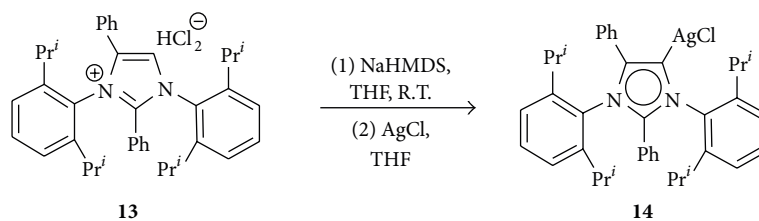
as catalyst, and a similar result was obtained with silver sulfate. However, in presence of catalytic amounts of silver chloride, alkyne 1 and azide 2 afforded 1-benzyl-4-phenyl-1,2,3-triazole (3) as only reaction product.

This last result motivated us to investigate the role of the solvent and catalyst ratio in this process. The results, summarized in Table 1, indicate that a mixture 3 : 1 acetone-H<sub>2</sub>O

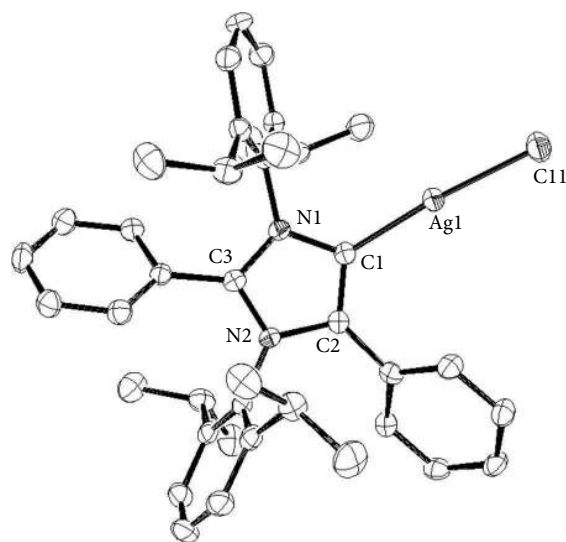
affords the best yields compared to other polar and unpolar solvents. In addition, we carried out reactions between alkyne 1 and azide 2 with different catalyst concentrations. Although silver chloride is effective as catalyst in 1% mol concentration, the best results were obtained using 3.5% mol catalyst, affording triazole 3 in highest yield (64%) and shortest time (24 h, Table 1).

In order to explore the reaction scope, diverse alkynes and azides were reacted in presence of catalytic silver chloride. In all cases, 1,2,3-triazoles were obtained in moderate to good yields (Table 2). As conventional CuAAC, this process does not require additional special conditions, such as inert atmospheres; moreover, the workup and purification of final products are similar to those described for copper catalyzed reactions.

Another highlight of this procedure is that it does not necessitate additional reagents such as bases or reducing agents which are essential for CuAAC in some cases [2].

SCHEME 2: Preparation of carbene complex **14** from imidazolium salt **13**.TABLE 3: Synthesis of triazole **3** catalyzed by silver complex **14**.

Entry	Catalyst ratio (% mol)	Solvent	Reaction time (h)	% Yield
1	0.6	CH <sub>2</sub> Cl <sub>2</sub>	24	58
2	0.5	CH <sub>3</sub> OH	24	45
3	0.5	H <sub>2</sub> O	24	0
4	0.5	H <sub>2</sub> O/acetone	15	65
5	2	THF	15	76
6	1	THF	15	75
7	0.5	THF	15	77
8	0.1	THF	15	68

FIGURE 1: ORTEP representations for silver carbene complex **14**.

Other oxidation products like bistriazoles which are observed in some CuAAC reactions [19] were not detected in this process (Figure 2).

On the other hand, *N*-heterocyclic carbene metal complexes have emerged in recent years as a useful source of catalysts with many applications in a wide variety of processes [20–25]. In this context, “abnormal” *N*-heterocyclic carbene (aNHC) metal complexes represent the newest study trend in this area [26–28]. In these metal complexes, the carbene carbon in imidazolylidene ring is located at C4/C5 which is coordinated to a transition metal. This bonding, together with the reduced heteroatom stabilization, the lack of delocalization through the heterocycle, and the high steric

hindrance, provides a unique electronic behaviour which develops aNHCs into interesting ligands for catalysis.

Inspired by these facts, we decided to design a novel catalyst for AAC from a novel kind of stable aNHCs that have been described previously by Aldeco-Perez et al. [11]. Thus, 1,3-bis-(2,6-diisopropylphenyl)-2,4-diphenylimidazolium chloride **13** was successively treated with two equivalents NaHMDS and AgCl at room temperature to afford the silver complex **14** as a light gray powder in 54% yield (Scheme 2).

The silver carbene complex **14** was characterized by the conventional spectroscopic techniques. In addition, complex **14** was a crystalline solid which was studied by X-ray crystallography, confirming the proposed structure for this compound (Figure 1). To the best of our knowledge, this is the first example about the synthesis and isolation of a silver aNHC complex.

X-ray data reveal that silver (I) complex is a two-coordinate compound, showing an environment nearly linear (Cl–Ag–Cl angle 172.9 (6) Å). Ag–Cl bond distance is 2.071 (2) Å, in agreement with other silver monocarbene complexes (derived from NHCs) reported (from 2.056 to 2.094 Å) [29]. As expected, silver-carbon bond is longer than the gold carbene bond, found for the analogous aNHC–AuCl (1.981 (2) Å) [11].

Ag–Cl distance is as well in the range of silver chloride complexes (2.3278 (6) Å), and no evident argentophilic interactions were detected.

Preliminary experiments demonstrated that complex **14** is an efficient catalyst for synthesis of triazole **3** from AAC in several solvents at room temperature, affording the best yields with THF (Table 3). A noteworthy feature is that complex **14** exhibits a remarkable catalytic activity in this process, requiring only 0.5% mol catalyst; the reaction also proceeds with 0.1% mol catalyst, but with a lower yield. Thus, the change of ligand increases the catalytic ability in the silver

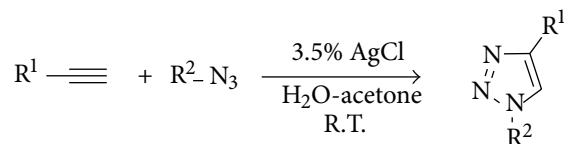


FIGURE 2

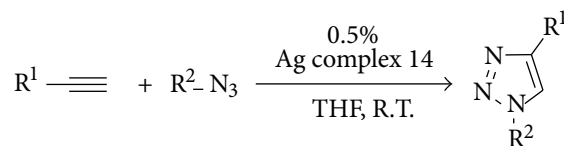


FIGURE 3

TABLE 4: Synthesis of triazoles catalyzed by silver complex 14.

Compound	R <sup>1</sup>	R <sup>2</sup>	% Yield
3	Ph	PhCH <sub>2</sub>	77
4	CH <sub>2</sub> OH	PhCH <sub>2</sub>	63
5	CH <sub>2</sub> O(4-CO <sub>2</sub> CH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	54
6	CH <sub>2</sub> O(4-COCH <sub>3</sub> )C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	64
7	CH <sub>2</sub> O(4-Cl)C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	72
8	CH <sub>2</sub> O(4-CHO)C <sub>6</sub> H <sub>4</sub>	PhCH <sub>2</sub>	37
9	Ph	4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	75
10	Ph	2-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	70
11	Ph	N <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —N <sub>3</sub>	70
12	CH <sub>2</sub> O(4-Cl)C <sub>6</sub> H <sub>4</sub>	N <sub>3</sub> —CH <sub>2</sub> —CH <sub>2</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —N <sub>3</sub>	71

complex, similar to some ligands based on *N*-heterocyclic carbenes [30–32], phosphines [33, 34], phosphoramidites [35], or phosphinites [36] which stabilize and improve the catalytic power in some copper complexes.

Furthermore, complex 14 displayed a broad functional group tolerance when various alkynes and azides were treated with catalytic complex 14 to give the corresponding 1,2,3-triazoles with moderate-good yields (Table 4). In consequence, complex 14 resulted in an effective catalyst for AAC (Figure 3).

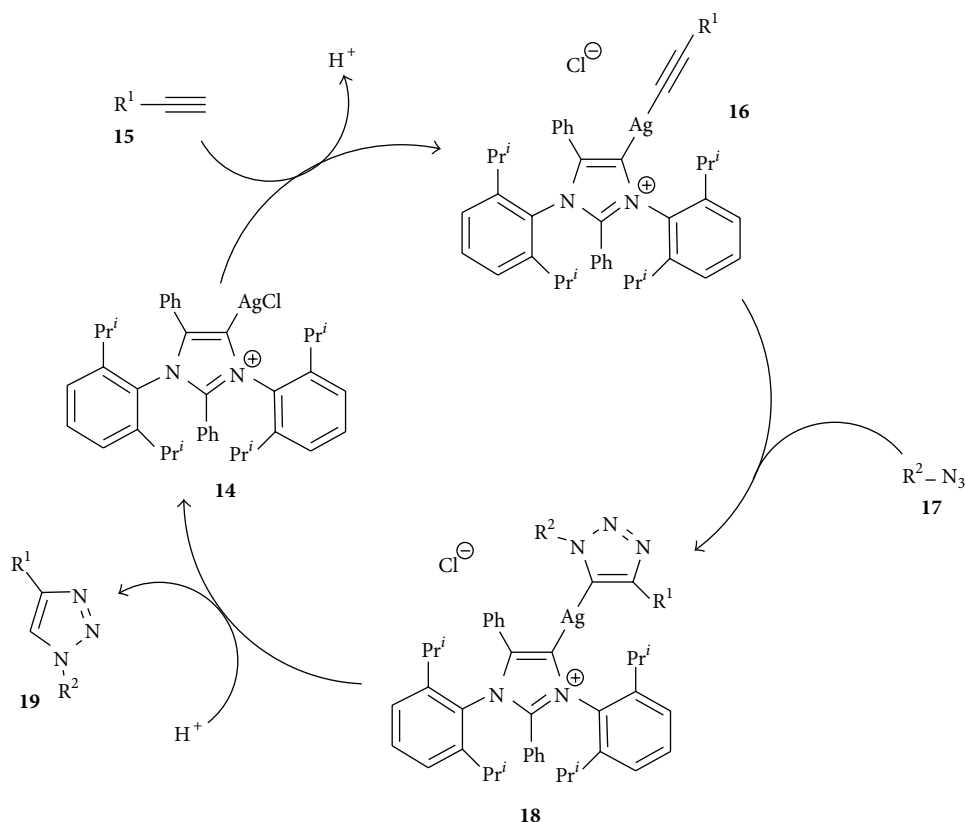
Although the mechanistic details are not clear, previous experiments by McNulty and coworkers [9, 10] showed that silver acetylide formation plays an important role in the catalytic cycle as well as other intermediates [37].

A rational explanation of the high catalytic activity of complex 14 in AAC should include the above mentioned elements together with the ability of the aNHC ligand to protect the silver (I) ion and stabilize some intermediates such as silver acetylides. Thus, the reaction mechanism probably occurs through the formation of an intermediate like the silver acetylide complex 16 derived from an alkyne 15 and silver complex 14, with the subsequent hydrogen

interchange from the alkyne carbon to the imidazolylidene ring (Scheme 3). In the next step, an azide 17 is incorporated to acetylide complex 16 to form a silver triazolide 18, similar to the formation of some copper triazolides [38]. Finally, a second hydrogen transfer might take place to afford the corresponding triazole 19 and regenerating the catalyst 14.

## 4. Conclusions

In conclusion, silver compounds represent a new source of potential catalysts for AAC. In this case, silver chloride by itself can easily catalyze the cycloaddition of diverse alkynes and azides in good yields. The catalytic activity in this kind of compounds is improved with the introduction of aNHC ligands avoiding side reactions and facilitating the purification of final products, such as many copper catalyzed cycloadditions. These last results display alternative synthesis methodologies to obtain diverse 1,2,3-triazoles, which complement and extend the results of McNulty and coworkers [9, 10]. The simplicity of the method suggests that this route to 1,2,3-triazoles will enjoy widespread application.



SCHEME 3: A plausible reaction mechanism of catalytic cycle.

## Acknowledgments

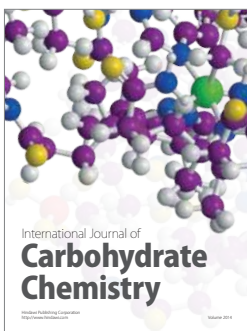
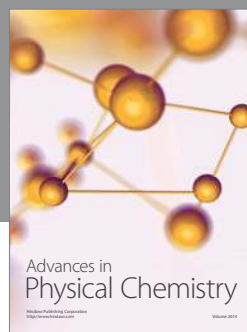
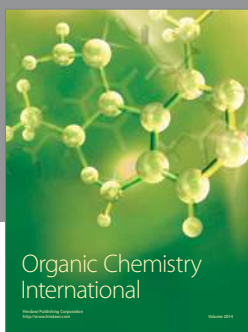
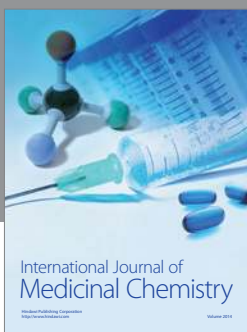
Financial support from CONACYT (Project no. 135053) is gratefully acknowledged. The authors would like to thank Signa S.A. de C. V., N. Zavala, A. Nuñez, and L. Triana for the technical support.

## References

- [1] H. C. Kolb and K. B. Sharpless, "The growing impact of click chemistry on drug discovery," *Drug Discovery Today*, vol. 8, no. 24, pp. 1128–1137, 2003.
- [2] M. Meldal and C. W. Tomøe, "Cu-catalyzed azide–alkyne cycloaddition," *Chemical Reviews*, vol. 108, no. 8, pp. 2952–3015, 2008.
- [3] P. Fabbrizzi, S. Cicchi, A. Brandi, L. Sperotto, and G. Van Koten, "An efficient (2-aminoarenethiolato)copper(I) complex for the copper-catalysed huisgen reaction (CuAAC)," *European Journal of Organic Chemistry*, no. 31, pp. 5423–5430, 2009.
- [4] B. C. Boren, S. Narayan, L. K. Rasmussen et al., "Ruthenium-catalyzed azide-alkyne cycloaddition: scope and mechanism," *Journal of the American Chemical Society*, vol. 130, no. 28, pp. 8923–8930, 2008.
- [5] L. K. Rasmussen, B. C. Boren, and V. V. Fokin, "Ruthenium-catalyzed cycloaddition of aryl azides and alkynes," *Organic Letters*, vol. 9, no. 26, pp. 5337–5339, 2007.
- [6] L. Zhang, X. Chen, P. Xue et al., "Ruthenium-catalyzed cycloaddition of alkynes and organic azides," *Journal of the American Chemical Society*, vol. 127, no. 46, pp. 15998–15999, 2005.
- [7] A. Krasinski, V. V. Fokin, and K. B. Sharpless, "Direct synthesis of 1,5-disubstituted-4-magnesio-1,2,3-triazoles, revisited," *Organic Letters*, vol. 6, no. 8, pp. 1237–1240, 2004.
- [8] X. Meng, X. Xu, T. Gao, and B. Chen, "Zn/C-catalyzed cycloaddition of azides and aryl alkynes," *European Journal of Organic Chemistry*, no. 28, pp. 5409–5414, 2010.
- [9] J. McNulty and K. Keskar, "Discovery of a robust and efficient homogeneous silver(I) catalyst for the cycloaddition of azides onto terminal alkynes," *European Journal of Organic Chemistry*, vol. 2012, no. 28, pp. 5462–5470, 2012.
- [10] J. McNulty, K. Keskar, and R. Vemula, "The first well-defined silver(I)-complex-catalyzed cycloaddition of azides onto terminal alkynes at room temperature," *Chemistry: A European Journal*, vol. 17, no. 52, pp. 14727–14730, 2011.
- [11] E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, and G. Bertrand, "Isolation of a C5-deprotonated Imidazolium, a crystalline "Abnormal" N-Heterocyclic Carbene," *Science*, vol. 326, no. 5952, pp. 556–559, 2009.
- [12] H. Gallardo, G. Conte, F. Bryk, M. C. S. Lourenço, M. S. Costac, and V. F. Ferreira, "Synthesis and evaluation of 1-alkyl-4-phenyl-[1,2,3]-triazole derivatives as antimycobacterial agent," *Journal of the Brazilian Chemical Society*, vol. 18, no. 6, pp. 1285–1291, 2007.
- [13] F. Moulin, "Recherches sur les benzyl-1-et phenyl-1-triazoles-1,2,3 substitués," *Helvetica Chimica Acta*, vol. 35, no. 1, pp. 167–180, 1952.
- [14] B. R. Buckley, S. E. Dann, D. P. Harris, H. Heaney, and E. C. Stubbs, "Alkynylcopper(i) polymers and their use in a

- mechanistic study of alkyne-azide click reactions,” *Chemical Communications*, vol. 46, no. 13, pp. 2274–2276, 2010.
- [15] Y. Jiang, X. Chen, L. Qu et al., “An efficient ultrasound-assisted method for the synthesis of 1,4-disubstituted triazoles,” *Zeitschrift für Naturforschung Section B*, vol. 66, no. 1, pp. 77–82, 2011.
- [16] M. A. García, Z. G. Ríos, J. González et al., “The use of glucose as alternative reducing agent in copper-catalyzed alkyne-azide cycloaddition,” *Letters in Organic Chemistry*, vol. 8, no. 10, pp. 701–706, 2011.
- [17] R. Huisgen, L. Moebius, and G. Szeimies, “1,3-Dipolare Cycloadditionen, XIV: Die Anlagerung organischer Azide an Enoläther: Orientierung und Triazolol-Zerfall,” *Chemische Berichte*, vol. 98, no. 4, pp. 1138–1152, 1965.
- [18] B. Saha, S. Sharma, D. Sawant, and B. Kundu, “Cu-FeCl<sub>3</sub>-mediated one-pot multicomponent reaction leading to N-aryl- and N-alkyltriazaoles in water,” *Synlett*, no. 10, pp. 1591–1594, 2007.
- [19] J. González, V. M. Pérez, D. O. Jiménez, G. Lopez-Valdez, D. Corona, and E. Cuevas-Yañez, “Effect of temperature on triazole and bistriazole formation through copper-catalyzed alkyne-azide cycloaddition,” *Tetrahedron Letters*, vol. 52, no. 27, pp. 3514–3517, 2011.
- [20] J. C. Garrison and W. J. Youngs, “Ag(I) *N*-Heterocyclic carbene complexes: synthesis, structure, and application,” *Chemical Reviews*, vol. 105, no. 11, pp. 3978–4008, 2005.
- [21] S. Díez-González, N. Marion, and S. P. Nolan, “*N*-Heterocyclic carbenes in late transition metal catalysis,” *Chemical Reviews*, vol. 109, no. 8, pp. 3612–3676, 2009.
- [22] M. Poyatos, J. A. Mata, and E. Peris, “Complexes with poly(*N*-Heterocyclic carbene) ligands: structural features and catalytic applications,” *Chemical Reviews*, vol. 109, no. 8, pp. 3677–3707, 2009.
- [23] C. Samojłowicz, M. Bieniek, and K. Grela, “Ruthenium-based olefin metathesis catalysts bearing *N*-Heterocyclic carbene ligands,” *Chemical Reviews*, vol. 109, no. 8, pp. 3708–3742, 2009.
- [24] G. C. Vougioukalakis and R. H. Grubbs, “Ruthenium-based heterocyclic carbene-coordinated olefin metathesis catalysts,” *Chemical Reviews*, vol. 110, no. 3, pp. 1746–1787, 2010.
- [25] X.-P. Fu, L. Liu, D. Wang, Y.-J. Chen, and C.-J. Li, ““On water”-promoted direct alkylation of isatins catalyzed by NHC-silver complexes for the efficient synthesis of 3-hydroxy-3-ethynylindolin-2-ones,” *Green Chemistry*, vol. 13, no. 3, pp. 549–553, 2011.
- [26] P. L. Arnold and S. Pearson, “Abnormal *N*-Heterocyclic carbenes,” *Coordination Chemistry Reviews*, vol. 251, no. 5-6, pp. 596–609, 2007.
- [27] O. Schuster, L. Yang, H. G. Raubenheimer, and M. Albrecht, “Beyond conventional *N*-Heterocyclic carbenes: abnormal, remote, and other classes of NHC ligands with reduced heteroatom stabilization,” *Chemical Reviews*, vol. 109, no. 8, pp. 3445–3478, 2009.
- [28] R. H. Crabtree, “Abnormal, mesoionic and remote *N*-Heterocyclic carbene complexes,” *Coordination Chemistry Reviews*, vol. 257, no. 3-4, pp. 755–766, 2013.
- [29] P. De Frémont, N. M. Scott, E. D. Stevens et al., “Synthesis of well-defined *N*-Heterocyclic carbene silver(I) complexes,” *Organometallics*, vol. 24, no. 26, pp. 6301–6309, 2005.
- [30] S. Díez-González and S. P. Nolan, “[NHC]<sub>2</sub>CuX complexes as efficient catalysts for azide-alkyne click chemistry at low catalyst loadings,” *Angewandte Chemie International Edition*, vol. 47, no. 46, pp. 8881–8884, 2008.
- [31] S. Díez-González, A. Correa, L. Cavallo, and S. P. Nolan, “(NHC)copper(I)-catalyzed [3 + 2] cycloaddition of azides and Mono- or disubstituted alkynes,” *Chemistry: A European Journal*, vol. 12, no. 29, pp. 7558–7564, 2006.
- [32] S. Díez-González, E. C. Escudero-Adán, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawin, and S. P. Nolan, “Complexes: synthesis, characterization and catalytic activities in reduction reactions and Click Chemistry. on the advantage of using well-defined catalytic systems,” *Dalton Transactions*, vol. 39, no. 32, pp. 7595–7606, 2010.
- [33] D. Wang, M. Zhao, X. Liu, Y. Chen, N. Li, and B. Chen, “Quick and highly efficient copper-catalyzed cycloaddition of organic azides with terminal alkynes,” *Organic and Biomolecular Chemistry*, vol. 10, no. 2, pp. 229–231, 2012.
- [34] S. Lal and S. Díez-González, “[CuBr(PPh<sub>3</sub>)<sub>3</sub>] for azide-alkyne cycloaddition reactions under strict click conditions,” *Journal of Organic Chemistry*, vol. 76, no. 7, pp. 2367–2373, 2011.
- [35] L. S. Campbell-Verduyn, L. Mirfeizi, R. A. Dierckx, P. H. Elsinga, and B. L. Feringa, “Phosphoramidate accelerated copper(i)-catalyzed [3 + 2] cycloadditions of azides and alkynes,” *Chemical Communications*, no. 16, pp. 2139–2141, 2009.
- [36] S. Lal, J. McNally, A. J. P. White, and S. Díez-González, “Novel phosphinite and phosphonite copper(I) complexes: efficient catalysts for click azide-alkyne cycloaddition reactions,” *Organometallics*, vol. 30, no. 22, pp. 6225–6232, 2011.
- [37] Y. Yamamoto, “Silver-catalyzed Csp-H and Csp-Si bond transformations and related processes,” *Chemical Reviews*, vol. 108, no. 8, pp. 3199–3222, 2008.
- [38] C. Nolte, P. Mayer, and B. F. Straub, “Isolation of a copper(I) triazolide: a “click” intermediate,” *Angewandte Chemie International Edition*, vol. 46, no. 12, pp. 2101–2103, 2007.





**Hindawi**

Submit your manuscripts at  
<http://www.hindawi.com>

