

Substrate Selectivity in the Alkyne Hydration Mediated by NHC-Au(I) controlled by Encapsulation of the Catalyst within a Hydrogen Bonded Hexameric Host

Alessandra Cavarzan,^[a] Joost N.H. Reek,^[b] Francesco Trentin,^[a] Alessandro Scarso,^{[a],*} Giorgio Strukul^{[a],*}

a) Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari di Venezia, Calle Larga S. Marta 2137, 30123, Venezia (ITALY). Fax: +39-041-2340517; Tel:+39-041-2348569;

b) Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Postbus 94720, 1090 GE Amsterdam, The Netherlands.

alesca@unive.it; strukul@unive.it

Reagents and Materials.

General

¹H NMR were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 MHz. δ values in ppm are relative to SiMe₄. GC analysis were performed on HP SERIES II 5890 equipped with a HP5 column (30 m, I. D. 0.25 mm, film 0.25 μ m) using He as gas carrier and FID. GC-MS analyses were performed on a GC Trace GC 2000 equipped with a HP5-MS column (30 m, I.D. 0.25 mm, film 0.25 μ m) using He gas carrier and coupled with a quadrupole MS Thermo Finnigan Trace MS with *Full Scan* method.

Solvents and reactants were used as received; otherwise they were purified as reported in the literature.¹ TLC analysis were performed on TLC Polygram[®] Sil G/UV254 of 0.25 mm thickness and flash-chromatography separations were performed on silica gel Merk 60, 230-400 mesh.²

Substrates and catalyst

Ethynyl-cyclohexane, 1-octyne, 1-dodecyne, phenylacetylene, *p*-methyl-phenylacetylene and *p*-(*t*-butyl)-phenylacetylene are all commercially available products (Aldrich) and were used as received without any further purification. Resorcin[4]arene³ and catalyst **1**⁴ were prepared as reported in the literature. All the hydration products were identified by GC-MS and ¹H-NMR analysis.

Catalytic Studies

Competitive catalytic hydration studies of alkynes

Water saturated solvent was prepared by shaking benzene-d₆ with bidistilled water at room temperature in a separation funnel. Catalyst **1** (3.3 mM, 5% mol) was placed in a screw-capped vial equipped with silicone septum and dissolved in the water saturated benzene-d₆ (0.6 mL). Resorcin[4]arene **2** (10 equivalents, 33 mM) was then added to the solution. After stirring for 2h at room temperature, three competitive alkynes (ethynyl-cyclohexane, 1-octyne, 1-dodecyne, or phenylacetylene, *p*-methyl-phenylacetylene and *p*-(*t*-butyl)-phenylacetylene, each one 65 mM) and bidistilled water (2 μ L, 4 mmol) were added. The reaction was then thermostatted at the desired temperature (40°C

for aliphatic alkynes and 80°C for aromatic alkynes). Reaction progress was monitored by ¹H-NMR and GC analysis by periodically sampling directly from the reaction mixtures. Conversion, product assignment and distribution were determined by direct GC analysis of the reaction mixture as the average of three experiments.

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