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Some aspects of copper and silver colloids in silane activation

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Abstract

Copper metallic particles are formed and get anchored in the siloxane oligomer obtained during the reaction of phenylsilane and ethyleneglycol with bis-pyridinium tetrachlorocopper(II). These supported metallic copper particles can catalyse the coupling reactions of silanes with alcohols. *cis*-Butenediol reacts with diphenylsilane or methylphenylsilane in the presence of bis-pyridinium tetrachlorocopper(II) and gives siloxane oligomers. The double bonds of the parent monomers are retained in these siloxanes. The bis-pyridinium tetrachlorocopper(II) catalysed reactions involve Cu(I)–Cu(II) couple and colloidal metallic particles. Triphenylsilylethyl ether is formed in the catalytic reaction of silver nitrate with triphenylsilane in ethanol. In this reaction silver particles gets attached to the silylether.

Keywords: Copper-colloid; Silver colloid; Hydrosilanes; Siloxane; Catalysis; Oligomerisation

1. Introduction

Transition metal complexes are widely used in dehydrogenative coupling reactions of silanes with alcohols to form Si–O bonds [1–5]. Many of such reactions involve oxidative addition and reductive elimination involving lower oxidation states of a metal [4–8]. First row transition metal complexes are less stable at lower oxidation without appropriate ligands [6]. However, coinage metals can be easily reduced to metallic particles by silanes and these metallic particles either in supported or unsupported form may participate in catalytic reactions [4–6,9,10]. In this article synthetic and mechanistic aspects of oligomerisation reactions of few polyhydrosilanes with polyhydric alcohols by bis-pyridinium tetrachlorocopper(II) as catalyst is described. The role of colloidal silver in the case of $AgNO_3$ catalysed Si–H bond activation is also discussed. This study has objective to understand the role of supported metallic particles in these reactions.

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2. Experimental

The silanes were obtained from Sigma Aldrich (USA) and used without further purification. Acetonitrile used in the experiments were HPLC grade and was distilled over P_2O_5 prior to use. Cleaning of glass plates for deposition of siloxanes was done by literature procedure [11]. The glass plates (15 mm × 15 mm × 1 mm) were immersed in piranha solution in a hot water bath prior to use. After cooling, the plates were washed with deionised water. The deionised water was used from a Millipore Elix-3 water purification system. The molecular weights were determine by a Water-600 HPLC-GPC system equipped with refractive index detector and ultrastyrgyl column® using poly methylmethacrylate as standard with THF as eluent. Bis-pyridinium tetrachlorocopper(II) was prepared by dissolving copper(II) chloride dihydrate (600 mg, 3.5 mmol) in methanol (15 ml) followed by addition of hydrochloric acid (11.6 N, 0.5 ml). To this solution pyridine (624 mg, 8 mmol) was added in dropwise fashion. Addition of excess diethylether (30 ml) to the solution precipitated the bis-pyridinium tetrachlorocopper(II). Yield (30%); IR (KBr) 3071(bs), 1599(s), 1524(s), 1482(s), 1444(s), 1327(s), 1183 (m), 1044(m), 745(s) cm^{-1}. Elemental. Anal. Cald. C, 32.83; H, 3.28; N, 7.66. Found: 32.86; H, 3.26; N, 7.26.

3. Procedure of deposition of copper and its further reaction

A clean glass sheet (15 mm × 15 mm × 1 mm) was placed inside a dry Schlenk tube. A solution of phenylsilane (300 mg, 2.4 mmol) and ethyleneglycol (409 mg, 6.6 mmol) in acetonitrile (4 ml) was added to this under an inert atmosphere. A solution of bis-pyridinium tetrachlorocopper(II) (40 mg, 0.11 mmol) in acetonitrile (1 ml) was added to this solution. The reaction mixture was left standing at room temperature for 6 h. The brown precipitate deposited on the glass plate was taken out under an inert atmosphere and characterized by recording the SEM and the X-ray powder diffraction.

For study of the catalytic activity of copper powder, the brown precipitate formed at the bottom of the Schlenk tube was collected by decantation of the supernatant liquid and washed with hexane. This precipitate was subjected to reaction with triphenylsilane (260 mg, 1 mmol) in ethanol (1 ml) at 60 °C. The silylether formation was confirmed by injecting the sample to GC (FID detector) and comparing with authentic sample of triphenylsilylethylether.

4. Procedure for dehydrogenative oligomerisation of dihydrosilanes with dihydroxyalcohols

In a typical experiment bis-pyridinium tetrachlorocopper(II) (40 mg, 0.11 mmol) was added to a solution of 1,3-propanediol (0.15 g, 2.0 mmol, in 3 ml acetonitrile) and diphenylsilane (0.2 ml, 1.1 mmol). The reaction mixture was stirred at 60 °C for 6 h. The solvent and excess alcohol was removed under reduced pressure and the desired oligomer was extracted with dichloromethane (10 ml). The dichloromethane was removed under reduced pressure to obtain the oligomer in 70% yield as a colorless viscous oil. ^{1}H NMR ($CDCl_3$) 7–7.9 (m, 10H), 3.6–3.8 (m, 4H), 1.6–1.9 (2H). ^{13}C NMR ($CDCl_3$) 134.7, 134.5, 130.0, 127.8, 60.9, 34.2 δ; IR(neat): 3440(bm), 3075(w), 2927(m), 2864(m), 1531(m), 1265(m), 1109(bm), 741(s) cm^{-1}. M_n (THF) 1663.

5. Procedure for synthesis for silylation of allylalcohol by triethylsilane

Bis-pyridinium tetrachlorocopper(II) (40 mg, 0.11 mmol) was dissolved in excess allyl alcohol (1 ml) and to this triethylsilane (120 mg, 1 mmol) was added and the reaction mixture was strirred at 60 °C for 2 h. After completion of the reaction hexane was added to the reaction mixture and filtered. From the filtrate hexane was removed and the crude silylated product was purified by chromatography by using silica gel. The product was confirmed by comparing its NMR spectra, IR and with authentic sample. Isolated yield 68%.