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Research paper

Cyanosilylation of aldehydes catalyzed by mixed ligand copper(II) complexes

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The new mixed ligand copper(II) complexes $[Cu(HL)(H_2O)(A)]\cdot 2H_2O$ (**1**, NaH_2L = sodium (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzenesulfonate, A = dimethylsulfoxide, $[Cu(HL)(H_2O)(B)]$ (**2**, B = 1,3,4-thiadiazol-2-amine), $[Cu(HL)(H_2O)(Y)]\cdot 1/2CH_3OH$ (**3**, C = hexamethylenetetramine) and $[Cu(HR)_2(H_2O)_2](H_2L)_2$ (**4**, HR = methyl picolinimidate derived from 2-cyanopyridine) were synthesized and characterized by IR and ESI-MS spectroscopies, elemental and X-ray crystal structural analyses. These compounds act as homogenous catalysts for the cyanosilylation reaction of a variety of both aromatic and aliphatic aldehydes with trimethylsilyl cyanide affording the corresponding cyanohydrin trimethylsilyl ethers in high yields (up to 85–99 %) in methanol and at room temperature.

1. Introduction

Catalytic hydrocyanation and cyanosilylation of aldehydes or ketones are among the most important strategies for synthesis of cyanohydrin trimethylsilyl ethers in synthetic chemistry (Scheme 1) [1]. The cyanohydrin trimethylsilyl ethers are industrially valuable and important intermediates for the synthesis of many valuable molecules such as α-hydroxy aldehydes, α-hydroxy acids and β-amino alcohols and other biologically active compounds [1]. Hence, a number of catalysts such as Lewis acids [2–4], Lewis bases [5–7], *N*-heterocyclic carbenes [8,9], aminothiourea [10,11], organic–inorganic salts [12–16], nonionic bases [17,18], oxazaborolidinium ion [19,20], V-, Mn-, Al-, and Ti-salen complexes [21–24], chiral Ti-α,α,α,α-1,3-dioxolane-tetraaryl-4,5-dimethanols [25,26], Ti,Al-phosphine oxide bifunctional catalysts with carbohydrate or binaphthol scaffolds [27–29], Ti,Al-*N*-oxide bifunctional catalysts with proline, pyrrolidine and 1,2-diamino ligands [30–32], metal organic frameworks [33–36], Cu(II) and Co (II/III) hydrazone complexes [37–40], etc. have been utilized. Based on the existing methods, it is clear that most of these protocols have many disadvantages, such as low yield, long reaction time, harmful solvents, etc. Therefore, the development of a new homogeneous catalytic system, which is inexpensive, commonly available, easy to handle and time resolved, is highly desirable.

On the other hand, the design and synthesis of mixed ligand complexes have received considerable attention due to their structural diversity as well as their potential applications as functional materials in various fields such as catalysis, pharmacology, molecular recognition, molecular switches, etc. [41–44]. Up to now, a great number of mixed ligand copper(II) complexes with interesting structures and properties have been obtained by selecting the appropriate hydrazone (main) and auxiliary ligands [45]. However, the controllable synthesis of mixed ligand copper(II) complexes with desired catalytic properties is still a great challenge because there are many chemical and physical factors playing important roles in the synthetic operation, such as the molecular structures of the main ligands, acid-base properties of auxiliary ligands, reaction condition, etc.

Therefore, the two main objectives of the current work are as follows: i) to synthesize of mixed ligand copper(II) complexes by using known sodium (*Z*)-2-(2-(1,3-dioxo-1-(phenylamino)butan-2-ylidene)hydrazinyl)benzenesulfonate (NaH_2L) [46] and axulliary components such as dimethylsulfoxide, 1,3,4-thiadiazol-2-amine, hexamethylenetetramine and 2-cyanopyridine; ii) to apply the derived mixed ligand copper(II) complexes as the homogeneous

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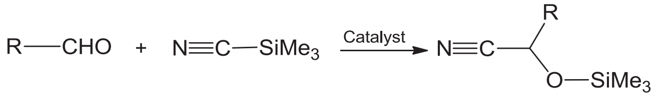

Scheme 1. Cyanosilylation of aldehydes.

catalysts for the cyanosilylation reaction of aldehydes with trimethylsilyl cyanide.

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. The NaH_2L was synthesized according to the reported procedure [46]. Infrared spectra (4000–400 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets. Carbon, hydrogen, and nitrogen elemental analyses were done using a “2400 CHN Elemental Analyzer” (Perkin Elmer). The ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance II + 300 (UltraShield^{TM} Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as the internal reference. Electrospray mass spectra (ESI-MS) were run with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray ion source. For electrospray ionization, the drying gas and flow rate were optimized according to the particular sample with 35 p.s.i. nebulizer pressure. Scanning was performed from *m*/*z* 0 to 1100 in methanol solution. The compounds were observed in the positive mode (capillary voltage = 80–105 V).

2.2. Synthesis

2.2.1. Synthesis of **1**

0.1 mmol (37 mg) of NaH_2L were dissolved in 25 mL of methanol, then 0.1 mmol (23 mg) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.1 mL of dimethylsulfoxide were added and the system was stirred for 10 min. After *ca.* 3 d at room temperature, greenish crystals precipitated which were then filtered off and dried in air.

1: Yield, 53 % (based on Cu). Calcd. for $C_{18}H_{25}CuN_3O_9S_2$ (*Mr* = 555.08): C 38.95, H 4.54, N 7.57; found C 38.82, H 4.38, N 7.49. MS (ESI, positive ion mode), *m*/*z*: 520.06 $[Mr - 2H_2O{+}H]^+$. IR (KBr): 3480 (s, br) *ν*(OH), 3005 *ν*(NH), 1610 (s) *ν*(C = O), 1594 *ν* (C = N) cm^{-1}.

2.2.2. Synthesis of **2**

0.1 mmol (37 mg) of NaH_2L were dissolved in 25 mL of methanol, then 0.1 mmol (23 mg) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.1 mmol (10 mg) of 1,3,4-thiadiazol-2-amine were added and the system was stirred for 10 min. After *ca.* 2 d at room temperature, greenish crystals precipitated which were then filtered off and dried in air.

2: Yield, 53 % (based on Cu). Calcd. for $C_{18}H_{18}CuN_6O_6S_2$ (*Mr* = 542.05): C 39.88, H 3.35, N 15.50; found C 39.47, H 3.43, N 15.23. MS (ESI, positive ion mode), *m*/*z*: 543.01 $[Mr + H]^+$. IR (KBr): 3333 (s, br) *ν*(OH), 3078 *ν*(NH), 1600 (s) *ν*(C = O), 1556 *ν* (C = N) cm^{-1}.

2.2.3. Synthesis of **3**

0.1 mmol (37 mg) of NaH_2L were dissolved in 25 mL of methanol, then 0.1 mmol (23 mg) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.1 mmol (14 mg) of hexamethylenetetramine were added and the system was stirred for 10 min. After *ca.* 3 d at room temperature, greenish crystals precipitated which were then filtered off and dried in air.

3: Yield, 53 % (based on Cu). Calcd. for $C_{45}H_{58}Cu_2N_{14}O_{13}S_2$ (*Mr* = 1194.25): C 45.26, H 4.90, N 16.42; found C 45.15, H 4.76, N 16.37. MS (ESI, positive ion mode), *m*/*z*: 582.1 $[C_{22}H_{27}CuN_7O_6S + H]^+$. IR (KBr): 3410 (s, br) *ν*(OH), 3134 *ν*(NH), 1665 (s) *ν*(C = O), 1600 *ν* (C = N) cm^{-1}.

2.2.4. Synthesis of **4**

0.1 mmol (37 mg) of NaH_2L were dissolved in 25 mL of methanol, then 0.05 mmol (12 mg) of $Cu(NO_3)_2{\cdot}2.5H_2O$ and 0.1 mmol (10 mg) of 2-cyanopyridine were added and the system was stirred for 10 min. After *ca.* 3 d at room temperature, greenish crystals precipitated which were then filtered off and dried in air.

4: Yield, 53 % (based on Cu). Calcd. for $C_{46}H_{48}CuN_{10}O_{14}S_2$ (*Mr* = 1092.61): C 50.57, H 4.43, N 12.82; found C 50.49, H 4.25, N 12.69. MS (ESI, positive ion mode), *m*/*z*: 185.8 $[C_{14}H_{20}CuN_4O_4]^{2+}$ and 362.4 $[C_{16}H_{14}N_3O_5S + 2H]^+$. IR (KBr): 3427 (s, br) *ν*(OH), 3158 and 2986 *ν*(NH), 1633(s) *ν*(C = O), 1587 *ν*(C = N) cm^{-1}.

Table 1
Crystallographic data and structure refinement details for **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{18}H_{25}CuN_3O_9S_2$	$C_{18}H_{18}CuN_6O_6S_2$	$C_{45}H_{58}Cu_2N_{14}O_{13}S_2$	$C_{46}H_{48}CuN_{10}O_{14}S_2$
fw	555.07	542.04	1194.25	1092.60
Temperature (K)	293(2)	296(2)	293(2)	293(2)
Cryst. Syst.	triclinic	monoclinic	triclinic	triclinic
Space group	*P*-1	*P*21/*c*	*P*-1	*P*-1
a (Å)	8.5077(9)	9.5281(4)	11.633(3)	8.2542(4)
b (Å)	11.4878(12)	9.2619(4)	14.183(3)	10.7845(5)
c (Å)	13.0362(13)	25.1485(9)	15.958(4)	14.1552(6)
α, °	71.172(4)	90	87.861(9)	78. 288(2)
β, °	82.268(4)	94.0610(10)	82.562(9)	81.389(2)
γ, °	76.584(4)	90	89.164(9)	77.816(2)
V ($Å^3$)	1170.5(2)	2213.74(16)	2608.8(11)	1198.49(10)
Z	2	4	2	1
ρ_{calc} (g cm^{-3})	1.575	1.626	1.520	1.514
μ(Mo Kα) (mm^{-1})	1.165	1.224	0.972	0.622
F (0 0 0)	574	1108	1240	567
R1[a] ($I \geq 2\sigma$)	0.0289	0.0430	0.0310	0.0317
wR2[b] ($I \geq 2\sigma$)	0.0729	0.1142	0.0753	0.0808
GOOF	1.025	1.052	1.032	1.009

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\ \Sigma[w(F_o^2)^2]]^{1/2}$.