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ARTICLE TYPE

Synthesis, structure and catalytic activities of new Cu(I) thiocarboxylate complexes†

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Thiobenzoate complexes of Cu(I), $[Cu(SCOPh)]_n$(**1**), $[Cu(bpy)(\mu\text{-}SCOPh)]_2$ (**2**), [Cu(dppf)(SCOPh)] (**3**), [where bpy = 2,2'-bipyridyl; dppf = [1,1'-Bis(diphenylphosphino)ferrocene] were synthesized and characterized structurally by X-ray crystallography. NBO calculations were performed to understand the nature of Cu-Cu (2.706 Å) interaction in **2**. All the complexes were found to catalyze azide-alkyne cycloaddition for the regioselective synthesis of glycoconjugate triazoles under click reaction.

Introduction

The sulfur chemistry of transition metals represents a challenging and exciting research topic.[1] Sulfur species possessing high polarizability, large negative charge, and coordination versatility represent themselves as excellent ligands and exhibit highly adaptable behaviour in chemical, redox and electronic properties.[2] A number of transition metal sulfur based compounds exhibit interesting properties like luminescence, photoconductivity, chemical sensing, catalysis, magnetic resonance imaging, energy storage technology etc.[3]

Among such sulfur-based ligands thiocarboxylates represent themselves as a very interesting class of ligands as they possess both soft (S) and hard (O) donor sites. Accordingly they bind to respective hard or soft metal centers, and also show chelating and bridging (through S atom) coordination modes. Further, the replacement of oxygen from carboxylates by sulfur atom in thiocarboxylates initiates many structural changes in the respective complexes. Metal thiocarboxylates undergo facile thiocarboxylic anhydride elimination [4] hence they can be used as single molecular precursors for metal sulfide materials.[5] Quite a few metal sulphides (both binary and ternary) have already been prepared using the corresponding metal thiocarboxylate complexes.[6]

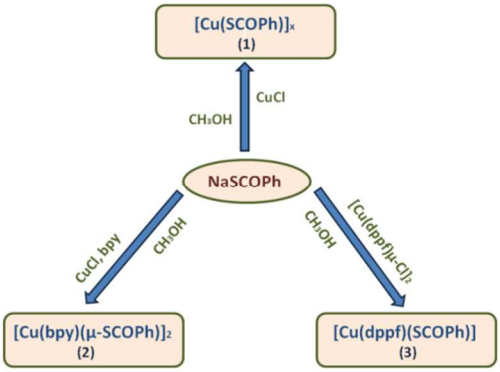
The chemistry of copper is extremely rich because it can easily access Cu^0, Cu^I, Cu^{II}, and Cu^{III} oxidation states. Copper is known to catalyse a variety of reactions such as coupling reactions (C-C, [7] C-N,[8] C-O,[9] C-S[10]). In biological systems copper is an important constituent in systems such as cytochrome *c* oxidase, [11] nitrous oxide reductase,[12] and the proposed catalytic copper center in particulate methane monooxygenase.[13] Copper plays important role in the click chemistry,[14] the concept first introduced by Kolb, Finn and Sharpless. Meldal [15]and Sharpless [16] independently discovered Cu(I)-catalysed azide-alkyne cycloaddition, which was then studied intensively and many areas of research have been benefited by its application.[17,18] In this context we here present the synthesis of three Cu(I) thiobenzoate complexes, their structural study and their catalytic activity in azide-alkyne cycloaddtion reaction for the regioselective synthesis of glycoconjugate triazoles under click reaction.

Experimental

Materials and methods

Standard methods were used for the purification of solvents. Thiobenzoic acid, bis(diphenylphosphino)ferrocene, cuprous chloride, triphenylphosphine (Sigma-Aldrich), 2,2'-bipyridine (s. d. fine chemicals) were used as such without further purification. The precursor $[Cu(dppf)\mu\text{-}Cl]_2$was synthesized using a method given in the literature.[19] Thin layer chromatography (TLC) was performed using silica gel 60 F-254 plates with I_2 vapors as detecting agents followed by spraying with methanolic-H_2SO_4 solution and *Draggendorff* reagent.

IR spectra were recorded using Perkin-Elmer RX-1, FTIR and Varian-3100 FTIR instruments, ^1H and ^{13}C NMR spectra were obtained using a JEOL AL300 FT NMR spectrometer. Electronic spectra were recorded on a Shimazdu UV-1700 PharmaSpec spectrophotometer using freshly prepared solutions of compounds in chloroform or DMSO. Single crystal X-ray data were collected on an Xcalibur Oxford EOS diffractometer using graphite monochromated Mo *K*α radiation (λ = 0.7107Å). Data collections were carried out at room temperature (293 K). The structures were solved and refined by SHELX set of software[20] using WINGX (ver. 1.80.05)[21] platform. Non-hydrogen atoms were refined anisotropically while the hydrogen atoms were placed at the calculated positions using SHELX default parameters. Disordered atoms were modelled by refining them at two different sites (without fixing sof). Restraints like DFIX and DELU were used wherever essential. NBO calculations[22] were performed using the atomic coordinates obtained from X-ray crystallographic results. A summary of crystallographic data and structure refinements are given in table 1. The calculations were performed at B3LYP[23] level using 6-31G** as basis set for all the atoms. All the calculations were carried out using GAUSSIAN 09 program package.[24]



Scheme 1. Synthesis of complexes **1**-**3**.

Synthesis of $[CuSCOPh]_x$ (1)

Sodium metal (0.023 g, 1 mmol) was added to methanol (10 mL) followed by a methanolic solution (10 mL) of thiobenzoic acid (117 µL, 1 mmol). The reaction mixture was cooled by keeping in an ice bath and CuCl (0.099 g, 1 mmol) was added in small portions. An orange precipitate started to appear immediately. The reaction mixture stirred for 10 min. The precipitate was filtered, washed with methanol, re-dissolved in hot acetonitrile and kept for crystallisation. After two days bright orange fine crystals were obtained. Yield: 0.132 g (66%). M.P. 195 ^{o}C (dec). Anal. Calc. for $C_7H_5Cu_1O_1S_1$: C 41.89; H 2.51. Found : C 42.07; H 2.48 %. IR(KBr pellet) 1583, 1557 ν(C=O), 1206 ν(Ph-C), 906 ν(C-S), 686 δ(SCO). ^{13}C NMR (75 MHz, DMSO-d_6, δ ppm): 127.83-158.64 (Ph ring), 185.45 (COS).

Synthesis of $[Cu(bpy)(\mu\text{-}SCOPh)]_2$ (2)

To a solution of NaOMe (0.054 g, 1.0 mmol in 10 mL methanol) was added solid CuCl (0.098 g, 1.0 mmol) followed by a solution of 2,2'-bipyridine (0.156 g, 1 mmol) in 10 mL methanol. The solution turned reddish-brown immediately. After stirring the reaction mixture for 10 min. in an ice bath added a methanolic solution of thiobenzoic acid (117 µL, 1.0 mmol). After stirring further for 5 min. brick red precipitate formed was filtered, washed with 10 mL of methanol and vacuum dried. Reddish-brown crystals were obtained by slow evaporation of a dichloromethane solution by keeping it in a small vial inside an empty desiccator. Yield: 0.278 g (78%). M.P. 155 ^{o}C (dec). Anal. Calc. for $C_{34}H_{26}Cu_2N_4O_2S_2$: C 57.21 ; H 3.67 ; N 7.85 %. Found : C 57.07 ; H 3.84 ; N 7.92 %. IR(KBr pellet) 1598,1563 ν(C=O), 1195 ν(Ph-C), 910 ν(C-S), 696 δ(SCO). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 125.95-143.03 (Ph, bpy rings), 187.56 (COS).

Synthesis of [Cu(dppf)(SCOPh)] (3)

In 10 mL methanol solution was added Na metal (0.023 g, 1.0 mmol) and thiobenzoic acid (117 µL) while keeping in an ice bath. The yellow solution was stirred for a few minutes followed by the addition of $[Cu(dppf)(\mu\text{-}Cl)]_2$ (0.653 g, 0.5 mmol). The reaction mixture was stirred for 1 h, the deep yellow precipitate formed was filtered, washed with methanol (10 mL) and dried in vacuum. Recrystallized from dichloromethane/diethyl ether. Yield: 0.521g (69%). M.P. 195 ^{o}C (dec). Anal. Calc. for $C_{41}H_{33}Cu_1Fe_1O_1P_2S_1$: C 65.21 ; H 4.40. Found : C 65.07 ; H 4.44 %. IR(KBr pellet) 1613 ν(C=O), 1196 ν(Ph-C), 912 ν(C-S), 693 δ(SCO). ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): 7.25-8.15 (Ph rings), 4.33, 4.22 (Cp rings). ^{13}C NMR (75 MHz, $CDCl_3$, δ ppm): 71.75-73.97 (Cp rings), 127.40-142.62 (Ph rings).

Synthesis of 4-Propyl-1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1H-1,2,3-triazole (6a)

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl azide **5a** was treated with (0.1 g, 0.26 mmol) and 1-pentyne **4a** (0.031 ml, 0.33 mmol) in dichloromethane in presence of DIPEA (0.045 ml, 0.26 mmol) and complex **1** as catalyst afforded **6a** (0.082 g, 70%) as yellowish liquid. (Completion of reaction was detected by TLC.) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (s, 1 H, triazole-H), 5.84 (d, J = 9.3 Hz, 1 H, H-1), 5.50 (m, 2 H, H-2, H-4), 5.30-5.25 (m, 1 H, H-3), 4.25-4.17 (m, 3 H, H-5, H_a-6, H_b-6), 2.22-1.88 (m, 16 H, 3×CH_3 of OAc, aliphatic-4 H), 0.97 (t, J = 7.2Hz, 3 H). ^{13}C NMR (70 MHz, $CDCl_3$): δ 170.3, 169.9, 169.7, 169.1, 169.0, 151.9, 119.0, 86.1, 73.9, 70.6, 68.1, 66.9, 61.1, 30.0, 20.5, 20.4, 20.1, 9.3 ppm.

Synthesis of 4-Butyl-1-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1H-1,2,3-triazole (6b)

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl azide **5a** (0.1 g, 0.2mmol) was treated with 1-Hexyne **1b** (0.036 ml, 0.32mmol) in dichloromethane in presence of DIPEA (0.045 ml, 0.2 mmol) and complex **1** as catalyst (6 mg) afforded **6b** (0.85 g, 70%) as yellowish viscous liquid. (Completion of reaction was detected by TLC). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (s, 1H, triazole-H), 5.77 (d, J = 9.3 Hz, 1 H, H-1), 5.51-5.48 (m, 2 H, H-2, H-4), 5.21-5.17 (m, 1 H, H-3,), 4.18-4.07 (m, 3 H, H-5, H_a-6, H_b-6), 2.65 (t, J = 7.2 Hz, 2 H), 2.15, 1.97, 1.93, 1,80 (s, 12 H, 4×CH_3 of OAc), 1.59, (t, J = 7.2 Hz, 2 H), 1.34-1.29 (m, 2 H), 0.86 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.2, 169.8, 169.6, 168.6, 148.9, 118.7, 85.9, 73.8, 70.6, 67.6, 66.7, 61.1, 31.1, 25.1, 22.0, 20.5, 20.3, 20.0, 13.6 ppm.

Synthesis of 4-Phenyl-1-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-1H-1,2,3-triazole (3c)

2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl azide **5b** (0.1 g, 0.2 mmol) and phenylacetylene **4c** (0.029 mL, 0.2 mmol) were dissolved in dichloromethane. DIPEA (0.046 ml, 0.2 mmol) and complex **1** as catalyst (4 mg) were added in solution. The reaction mixture was stirred vigorously under argon atmosphere for 12 h. After completion of reaction (monitored by TLC), the reaction mixture was *in vacuo* concentrated followed by silica gel column chromatography to afford **6c** (0.108 g, 85%) as white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (s, 1 H, triazole-H), 7.84-7.82 (m, 2 H, Ar-H), 7.45-7.35 (m, 3 H, Ar-H), 5.94 (d, J = 9.0 Hz, 1 H, H-1), 5.56-5.41 (m, 2 H, H-2, H-4), 5.27 (t, J = 9.6 Hz, 1 H, H-3), 4.36-4.30 (m, 1 H, H-5), 4.18-4.02 (m, 2 H, H_a-6, H_b-6), 2.08, 2.04 (m, 9 H, CH_3 of OAc), 1.88 (s, 3 H, CH_3 of OAc); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 169.8, 169.3, 168.9, 148.4, 129.8, 128.8, 128.5, 125.8, 117.7, 85.8, 75.1, 72.6, 70.1, 67.6, 61.5, 20.6, 20.5, 20.4, 20.2 ppm.

Synthesis of 1-(Methyl-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranose-5-yl)-4-phenyl-1H-1,2,3-triazole (6d)

Methyl-6-azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranose **5c** (0.05 g, 0.10 mmol) was treated with **4c** (0.013 ml, 0.12 mmol) in dichloromethane in presence of DIPEA (0.017

ml, 0.10 mmol) and complex **1** as catalyst (5 mg) afforded **6d** (0.057 g, 95%) as white solid. (Completion of reaction was detected by TLC). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.82-7.79 (m, 3 H, triazole-H, Ar-H), 7.41-7.31 (m, 18 H, Ar-H), 5.00-4.56 (m, 9 H, benzylic-6 H, Sugar-3 H), 4.01 (t, J = 8.4 Hz, 1 H, Sugar-H), 3.43-3.18 (m, 5 H, Sugar-H, OCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.6, 138.4, 137.9, 130.6, 128.7, 128.4, 128.2, 128.0, 127.8, 127.6, 125.6, 121.0, 98.0, 81.8, 79.9, 77.9, 75.7, 75.0, 73.4, 69.1, 55.3, 50.6 ppm.

Synthesis of 4-(1,2:3,4-Di-*O*-isopropylidene-α-D-glucofuranos)-1-(methyl-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranosyl)-1H-1,2,3-triazole (6e)

Methyl-6-azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranose **5c** (0.082 g, 0.16 mmol) was treated with 1,2:3,4-di-*O*-isopropylidene-3-*O*-propargyl-α-D-glucofuranose **4d** (0.05 g, 0.16 mmol) in dichloromethane in presence of DIPEA and complex **1** as catalyst (5 mg) afforded **6e** (0.116 g, 88%) as yellowish viscous liquid. (Completion of reaction was detected by TLC). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (s, 1 H, triazolyl-H), 7.33-7.31 (m, 15 H, Ar-H), 5.85 (d, J = 1.8 Hz, 1 H, H-1), 5.84-4.46 (m, 12 H, Sugar-H), 2.89 (d, J = 6.3 Hz, 1 H, Sugar-H), 4.12-3.96 (m, 6 H, Sugar-H), 3.42 (d, J = 9.1 Hz, 1 H, Sugar-H), 3.17-3.13 (m, 4 H, Sugar-H), 1.48, 1.41, 1.32, 1.29 (each s, 4×CH_3, >$(CH_3)_2$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.6, 138.2, 137.8, 137.8, 128.4, 128.1, 127.9, 127.6, 123.8, 111.7, 108.9, 105.0, 98.0, 82.6, 81.7, 81.0, 79.8, 77.8, 75.7, 74.8, 73.3, 72.3, 69.1, 67.2, 64.0, 55.1, 50.6, 26.7, 26.1, 25.4 ppm.

Similar procedures were adopted two representative reactions for the synthesis of **6c** and **6e** using complexes **2**, **3** as catalysts. Control experiments using CuCl (as catalyst) and blank experiments (without any catalyst) were also carried out by repeating all these reactions while maintaining the other conditions same. The results are summarized in Table 3.

Results and discussion

Synthesis of complexes

All the Cu(I) complexes were synthesized using CuCl or $[Cu(dppf)Cl]_2$ as precursor. Synthetic routes for all the three complexes are shown in scheme 1. Complex **1** and **2** were synthesized using methanol as solvent where as complex **3** was prepared in dichloromethane. The attempt to synthesize $Cu^{II}(SCOPh)_2$ by using $CuCl_2$ and two equivalents of thiobenzoate ligand failed and the only product obtained was complex **1**. It may be noted that thiolate ions are known to get oxidized by transition metal ions to corresponding disulfides[25] and cuprous thiobenzoate has been reported[26] to decompose on prolonged heating giving dibenzoyldisulfide. We have also observed oxidation of thiobenzoate ions catalyzed by Ag(I) ion.[4b] Evidently, Cu(II) ion in the present case oxidized one equivalent of the ligand leading to the formation of a stable Cu(I) with the remaining thiobenzoate ligand.

Complex **1** was sparingly soluble in DMSO and MeCN where as complexes **2** and **3** were highly soluble in DCM. The compounds **1** and **3** are quite stable both in solid state and also in solution. Solution of compound **2**, however, was found to change its color under ambient conditions on standing for several days. In the IR spectra of these complexes strong bands due to C=O, Ph-C, C-S stretching vibrations were observed which are characteristic for thiobenzoate ligands. These IR bands are important signals for analysing the bonding modes of the thiobenzoate ligands.[27]

Structural description of complexes

All the complexes synthesized were characterized by single crystal X-ray diffraction technique. Summary of crystallographic data and refinement parameters are given in table 1 whereas selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic data and refinement parameters for **1-3**.

	1	**2**	**3**
Empirical formula	$C_7H_5Cu_1O_1S_1$	$C_{68}H_{51}Cu_4N_8O_4S_4$	$C_{41}H_{33}Cu_1Fe_1O_1P_2S_1$
Formula weight	200.73	1426.65	755.08
Temperature(K)	293	293	293
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pbca*	*Cc*	*P21/c*
A (Å)	5.7290(11)	20.7022(19)	11.211(5)
b(Å)	7.0037(10)	18.1635(12)	8.560(5)
c(Å)	31.751(5)	17.000(17)	36.116(5)
β (°)		105.635(8)	98.857(6)
V (Å^3)	1274.0(4)	6152.6(9)	3425(3)
Z	8	4	4
F (000)	800	2908	1552
Datas/Restraints/Parameters			
GOF on F^2	1.012	0.804	0.728
Final R indices [I>2σI]	R_1=0.0548	R_1=0.0997	R_1=0.0472
	wR_2=0.0948	wR_2=0.2576	wR_2=0.0731
Largest difference peak and hole(eÅ^{-3})	0.611 & -0.923	02.175 & -0.656	0.490 & -0.472

Table 2. Selected bond lengths and angles for **1-3**.

Complex	Bond length (Å)		Bond angle (°)	
1	Cu1-S1$_{04}$	2.277(14)	S1$_{04}$-Cu1-O1	102.45 (10)
	Cu1-O1	2.130(3)	O1-Cu1-S1	105.92(10)
	Cu1-S1$_{03}$	2.494(15)	S1-Cu1-S1$_{03}$	113.48(4)
	Cu1-S1	2.304(13)	S1-Cu1-S1$_{04}$	133.75(4)
2	Cu1-Cu2	2.706(3)	S1-Cu1-N2	127.5(6)
	Cu1-S1	2.221(6)	N2-Cu1-N1	85.7(7)
	Cu1-S2	2.413(4)	N1-Cu1-S2	105.4(5)
	Cu2-S1	2.629(6)	S2-Cu1-S1	106.6(2)
	Cu2-S2	2.195(4)	S1-Cu2-N4	117.3(4)
	Cu1-N1	2.03(2)	N4-Cu2-N3	79.6(6)
	Cu1-N2	1.86(2)	N3-Cu2-S2	132.6(5)
	Cu2-N3	2.04(2)	S2-Cu2-S1	109.4(32)
	Cu2-N4	2.09 (2)		
3	Cu1-S1	2.210(12)	P1-Cu1-S1	121.41(4)
	Cu1-P2	2.260(11)	S1-Cu1-P2	125.99(5)
	Cu1-P1	2.248(13)	P2-Cu1-P1	112.23(4)

Compound **1** is a two dimensional coordination polymer crystallised in orthorhombic system with *Pbca* space group. Fig 1 shows the asymmetric unit of complex **1** where as Fig 2 represents its polymeric structure.

Copper is at the center of a distorted tetrahedron constituted by

three sulfur and one oxygen atoms of four different thiobenzoate moieties. Each sulfur atom is coordinated to three different copper atoms while each oxygen binds to one Cu atom only. The Cu-S and Cu-O bond lengths are comparable to the respective covalent bonds observed in other cases.[28] Two adjacent Cu atoms are held together by a bidentate (S, O) thiobenzoate ligand from one side and a sulfur atom of another thiobenzoate group from the other side forming a five membered ring. Each Cu is placed at the center of four six-membered fused rings which are in boat (or twisted boat) conformation (Fig 3).

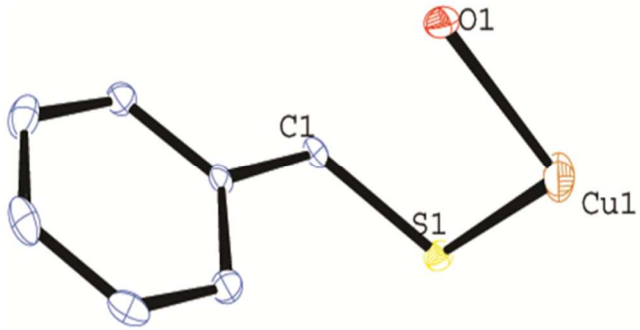


Fig. 1. Thermal ellipsoid (at 30% probability level) of complex **1**. For clarity hydrogen atoms are omitted.

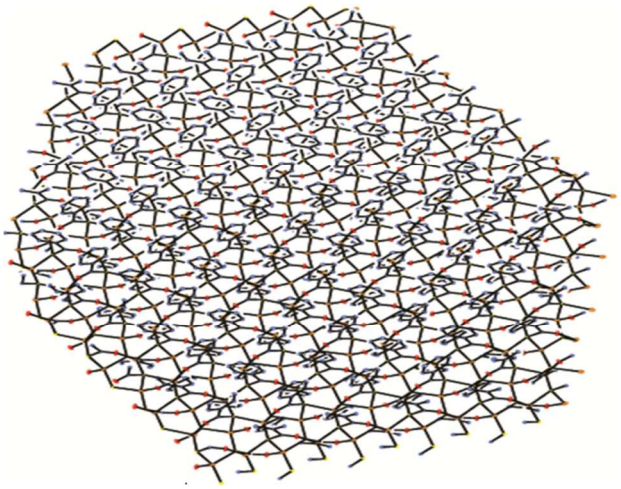


Fig. 2. Polymeric structure of complex **1**.

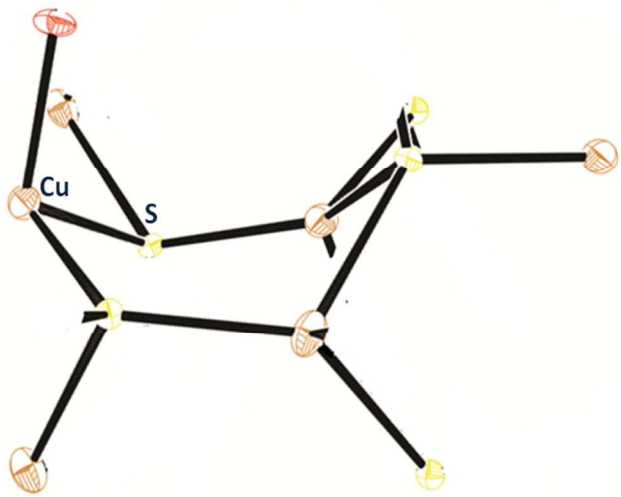


Fig. 3. Twisted boat shaped six membered ring for complex **1**.

The Cu-Cu distance is 3.173 Å which is quite longer than the sum of their van der Waals radii. It may be noted that Cu(I) carboxylates are structurally quite different from **1.** Structure of Cu(OAc) complex has been described as distorted square planar around the Cu(I) atom.[29] The oxygen atoms are present at three coordination sites while the fourth site is occupied by the neighbouring Cu atom at a distance of 2.54 Å. Each oxygen atom binds with two Cu centres forming a ribbon like structure. $Cu(O_2CPh)$ on the other hand, is tetrameric[30]**.** Four Cu(I) atoms are bridged by benzoate groups forming a parallelogram. The O-Cu-O bond angles range between 167 and 178° imparting a nearly linear coordination geometry around the metal.

Complex **2** crystallized in monoclinic system with the space group *Cc*. Fig. 4 shows the molecular structure of the complex. The molecule is dimeric with the two sulfur atoms from two different thiobenzoate moieties acting as bridging atoms. Both the copper atoms possess distorted tetrahedral geometry formed by the coordination of two nitrogens of bipyridyl ligand and the two bridging sulfurs of thiobenzoate groups. The observed distortion in the structure arises possibly due to the small bite angle (~79.1°) of the bipyridyl ligand. Complex **2** may be compared with a thiobenzoate complex $[(PPh_3)Cu(\mu\text{-}SCOPh)_2Cu(PPh_3)_2]$ reported earlier.[31] In the latter complex the bonding mode of thiobenzoate ligands are similar to that in **2,** however, one of the copper is in four coordinate environment while the other one (undergoes a triphenylphosphine elimination) acquires trigonal geometry. The Cu_2S_2 core in **2** is essentially non planar in sharp contrast to the planar core in $[(PPh_3)Cu(\mu\text{-}SCOPh)_2Cu(PPh_3)_2]$. The benzoyl groups on the two S atoms have *syn* stereochemistry in the case of **2** unlike the *anti* arrangement observed in the reported complex. The Cu-Cu distance in **2** (2.706 Å) is slightly longer than the corresponding distance in the above mentioned phosphine complex. It may be noted that the ideal Cu-Cu covalent bond distance is 2.64 Å while the corresponding van der Waals' bond distance is 2.80 Å. Though the N-Cu-N, N-Cu-S and S-Cu-S angles in **2** do not suggest a five coordinate geometry around Cu, yet the Cu-Cu distance indicates some interaction between the two centres. We have carried out some DFT calculations to understand the nature of interaction which has been described later.

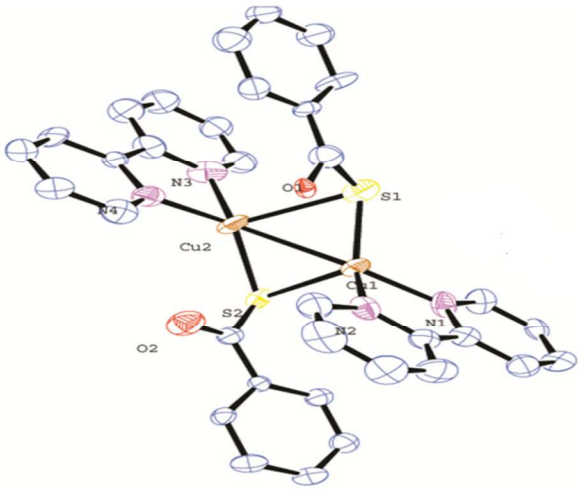


Fig. 4. Thermal ellipsoid (at 30% probability level) of complex **2**. For clarity hydrogen atoms are omitted.

Complex **3** crystallized in monoclinic system with $P2_1/c$ space group. Molecular structure for complex **3** is depicted in Fig 5. The geometry around copper atom is essentially trigonal planar. Two phosphorus atoms of the dppf ligand occupy two coordination sites while the third one is engaged by the sulfur atom of the thiocarboxylate ligand. The Cu-O distance (3.314 Å) is too long to have any bonding interaction between the two centers. It may be mentioned here that the corresponding carboxylate complex $[Cu_2(\mu\text{-}OCOCH_3)_2(dppf)_2]$[32] is a dimer in which both the acetates act as bridging ligands. As a result, each of the copper atoms possesses a four coordinate geometry. The monomeric nature of complex **3** can be attributed to poor tendency of thiocarboxylate group to bind bidentately.

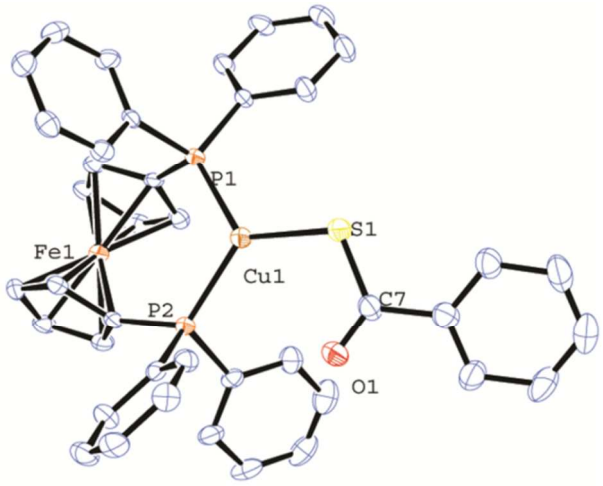


Fig. 5. Thermal ellipsoid (at 30% probability level) of complex **3**. For clarity hydrogen atoms are omitted.

Electronic absorption spectra

The electronic absorption spectrum of compound **1** was recorded in DMSO while those of **2** and **3** were recorded in chloroform. Complex **1** gives a broad band in the UV region centered at 315 nm. Complex **2** gives 3 bands in the UV region; a sharp band at 244 nm and two broad bands at 297 and 355 nm. Complex **3** absorbs in the visible region giving a broad band at around 450 nm. All the absorption peaks (except the one at 450 nm in the case of **3**) may be assigned as intra/interligand and LMCT transitions while the band at 450 nm for **3** can be assigned as an $e_{2g} \rightarrow e_{1g}$ transition in the ferrocenyl moiety[33].

Density functional calculations

DFT calculations were carried out for the complex **2.** As mentioned already the distance between the two copper atoms in this bimetallic complex is 2.706 Å which although slightly longer than the corresponding covalent bond length (2.64 Å)[34] but much smaller than the sum of their van der Waals radii. To understand the nature of Cu-Cu interaction, (if any) NBO calculations were carried out. Notably, cuprophilic interactions were reported in several Cu(I) complexes.[34] Close Cu-Cu contacts in some cases are stabilized by bridging ligands or by electrostatic interactions. In other cases, such as in a ligand unsupported Cu(I) dimer, Cu....Cu σ bond was held responsible for such interactions[35]**.** NBO study in the present case actually revealed the nature of this interaction. The Wiberg bond index was found to be 0.12. NBO calculations revealed *d* orbital (of Cu atoms) participation in bonding. The natural electronic configuration of Cu(I) is $4s^{0.35}3d^{9.48}4p^{0.67}$ instead of $4s^03d^{10}$. The hybrid orbital of Cu1, for example, which formed Cu-S covalent bond is the resultant of mixing of 27.42% 4*s*, 4.14% 3*d* and 68.41% 4*p* orbitals. The details of orbital occupancies of Cu(I) are listed in table S-1 (ESI†).

The Cu(1) $d_{x^2-y^2}$ orbital's occupancy is 1.81 as a result it can overlap (to the limited extent only) with analogous orbital of Cu(2) as shown in fig 6.

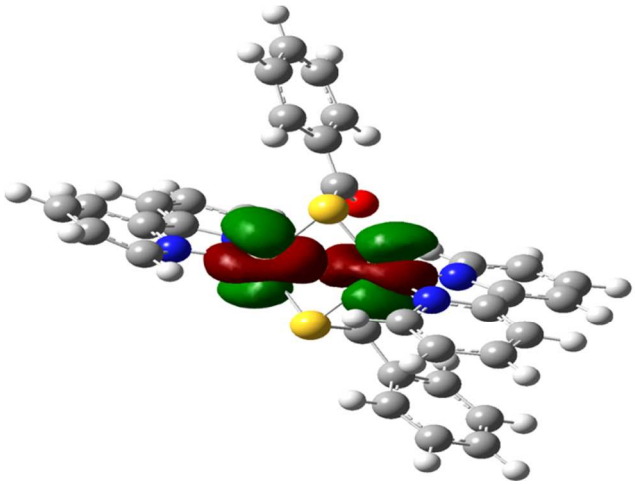
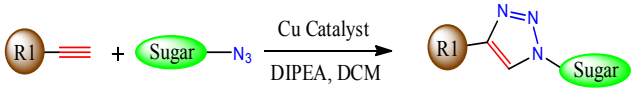


Fig. 6. $dx^2\text{-}y^2 - dx^2\text{-}y^2$ orbital overlap between two copper atoms in complex **2**.

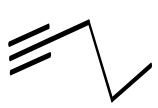
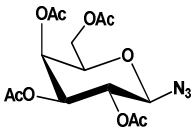
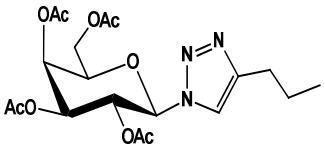
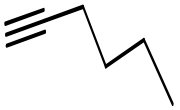
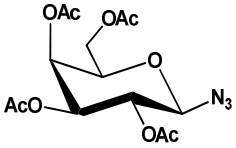
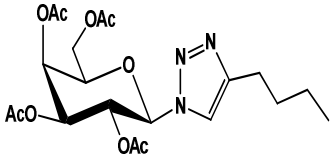
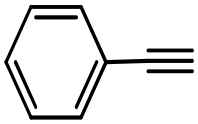
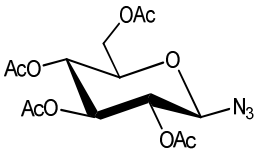
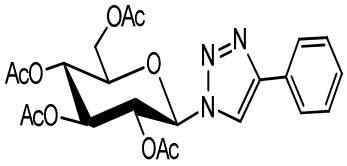
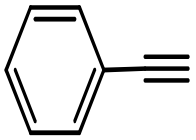
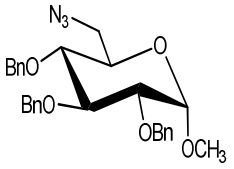
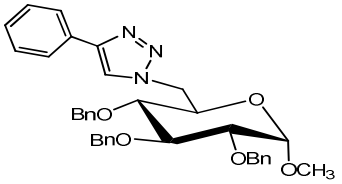
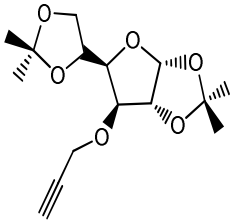
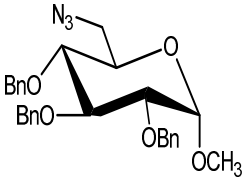
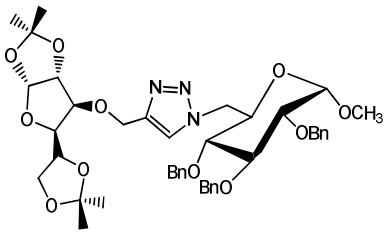
Catalytic Activity of Developed Cu-complexes in Click Chemistry: Synthesis of 1,2,3-Triazolyl Glycoconjugates

To investigate the catalytic activity these complexes were employed as catalysts independently in azide-alkyne cycloaddtion reactions[36] of different alkynes and sugar azides to achieve the regioselective 1,4-disubstituted triazolyl glycoconjugates. A group of experiments were designed for cycloaddition reaction between simple alkynes (**4a**, **4b, 4c**) with 2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl azide (**5a**)/(**5b**) or methyl-6-azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranose (**5c**) for the synthesis of triazolyl monosaccharides. Similarly a reaction of 1,2,3,4-di-*O*-isopropylidene-3-*O*-propargyl-α-D-glucofuranose (**4d**) and methyl-6-azido-2,3,4-tri-*O*-benzyl-6-deoxy-α-D-glucopyranose (**5c**) for the synthesis of triazolyl disaccharide was also carried out. In our reactions, we have used DIPEA (as a base) and dry dichloromethane as a solvent. Reaction without DIPEA does not proceed well. The complex **1** was screened as a catalyst for azide-alkyne click reactions. Two representative reactions were also carried out by using 2 or 3 as catalyst. (For a proper comparison each reaction has been attempted using CuCl as a catalyst and also without using any catalyst). The details of results are summarized in scheme 2 and table 3.



Scheme 2. Synthesis of triazolyl saccharides *via* CuAAC.

Table 3. Optimization of copper complexes for Azide-Alkyne cycloaddition reaction.

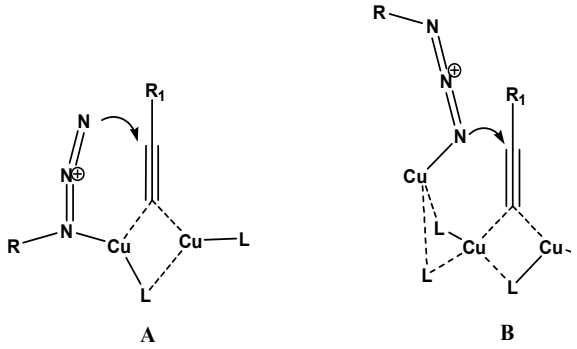
Alkyne (R)	Azido sugar	Product	Time (h)	Catalyst, yield* (%)
 **4a**	 **5a**	 **6a**	12h	**1**, 70 CuCl, 40
 **4b**	 **5b**	 **6b**	12h	**1**, 70 CuCl, 50
 **4c**	 **5c**	 **6c**	12h	**1**, 85 **2**, 82 **3**, 40 CuCl, 50
 **4c**	 **5c**	 **6d**	12h	**1**, 95 CuCl, 35
 **4d**	 **5c**	 **6e**	12h	**1**, 20 **2**, 88 **3**, 45 CuCl, 65

*Without using a catalyst [CuCl or complexes (**1**-**3**)] the yields of the products were not detectable .

From the table 3 it is evident that **1** acts as a very good catalyst in the cyclization process except during the formation of **6e** in which the yield is only 20%. Interestingly, **2** showed excellent catalytic activity during the same reaction.

The role of ligands in the catalytic effect of Cu(I) in triazole formation is primarily to protect the Cu(I) from oxidation in the presence of adventurous oxygen. Furthermore, the number and nature of ligands may affect the mechanism of the catalytic process in several ways[18]. Non-labile ligands occupying all the four coordination sites of Cu(I) would reduce its catalytic activity.[37] Thiobenzoate ligands in the complexes **1**-**3** are expected to serve both the purpose; at one hand they will not allow oxidation of the metal ion and on the other hand their labile nature is expected to provide free coordination site at Cu(I) for the bonding of alkyne. In view of the accepted structures of the intermediates **A** or **B** (Scheme 3)[18] a better catalytic activity of **2** is expected. Though bipyridine ligands are known to affect the kinetics adversely in these reactions[37] yet, the good performance of **2** in the synthesis of **6c** and **6e** makes it clear that longer reaction times allow the reactions to get completed and the overall yield is not affected. Other factors which depend on the nature of ligands as well as the substrates also play significant role on the kinetics and mechanism of these reactions.

Due to the complexity of ligand interaction with Cu(I) and the nature of alkyne complexation it is not possible, with the present state of knowledge to unambiguously explain the structural aspects of the transition state responsible for the selectivity and rate enhancement in the Cu(I) catalyzed cycloaddition reactions[18]



Scheme 3. The reported structures of intermediates formed during cycloaddition.[18]

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Conclusions

Three Cu(I) thiobenzoato complexes $[Cu(SCOPh)]_n$ (**1**), $[Cu(bpy)(\mu\text{-}SCOPh)]_2$ (**2**) and [Cu(dppf)(SCOPh)] (**3**) were synthesized. Complex **1** was polymeric adopting a distorted tetrahedral geometry. Complex **2** was dinuclear in which both the copper atoms were in distorted tetrahedral geometry. NBO studies on **2** revealed the existence of orbital overlap between the two Cu centers which is responsible for the short adjacent Cu-Cu distances. Geometry around copper atom in **3** was found to be trigonal planar. The complexes were found to catalyze azide-alkyne cycloaddition for the regioselective synthesis of glycoconjugate triazoles under click reaction.

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†Table S-1, ^{1}H NMR and ^{13}C NMR data for compounds **6a- 6e** are provided as supplementary material. CCDC 984648 (**1**), 984646 (**2**), 984647 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Notes and reference

1 (a) Y. Niu, H. Zheng, H. Hou and X. Xin, *Coord. Chem*., *Rev*. 2004, **248**, 169; (b) C. G. Young, *J. Inorg. Biochem*., 2007, **101**, 1562; (c) C. S. Clarke, D. A. Haynes and J. M. Rawson, *Annu. Rep. Prog. Chem*., *Sect. A: Inorg. Chem*., 2008, **104**, 124; (d) J. R. Dilworth, P. Arnold, D. Morales, Y. L. Wong and Y. Zheng, *Modern Coordination Chemistry*, *Royal Society of Chemistry*: G. J. Leigh and N Winterton, Eds., Cambridge, UK, 2002, 217; (e) Handbook of Chalcogen Chemistry: New perspective of Sulfur, Selenium and Tellurium, F. Devillanaova, *Royal Society Chemistry*: London, England, 2006.

2 W. Kaim, F. M. Hornung, R. Schafer, J. Fiedler, M. Krejcik and S. Zalis, High Technology, *Transition Metal Sulfides* : NATO ASI Series 3, Kluwer Academic , Varna, Bulgaria, 1998, **60**, 37.

3 (a) Q. Wang, Z. Xu, H, Yin and Q. Nie, *Mater. chem.*. *Phys.*, 2005, **90**, 73; (b) Y. Wang, *Acc. chem. Res.*, 1991, **24**, 133; (c) H. Chander, *Proc. ASID*, 2006, 11; (d) I. Dance, *Chem. Aust.*, 1997, 38; (e) M. A. Sriram and P. N. Kumta, *J. mater. Chem.*, 1998, **8**, 2441; (f) E. I. Stiefel, K. D. Karlin, Ed., Dithiolene Chemistry: Synthesis, Properties and Applications, *Progress in Inorganic Chemistry*, Wiley-Interscience, New York, 2004, Vol. **52**; (g) J. A. McCleverty and T. J. Meyer, Eds., *Comprehensive Coordination Chemistry II (Technological Application of Coordination Chemistry)*, Pergamon Press−Elsevier, The Netherlands, 2004, Vol. **9**.

4 (a) P. Singh, S. Bhattacharya, V. D. Gupta, H. Nöth, *Chem. Ber* 1996, **129**, 1093; (b) S. Singh, J. Chaturvedi, S. Bhattacharya, H. Nöth, *Polyhedron*, 2011, **30**, 93.

5 M. D. Nyman, M. J. Hampden-Smith, E. N. Duesler, *Inorg. Chem.*, 1997, **36**, 2218.

6 J. J. Vittal, M. T. Ng, *Acc. Chem. Res.*, 2006, **39**, 869 and references therein.

7 I. Cepanec, M. Litvić, J. Udiković, I. Pogorelić and M. Lovrić, *Tetrahedron*, 2007, **63**, 5614.

8 C.-Z. Tao, J. Li, Y. Fu, L. Liu and Q.-X. Guo, *Tetrahedron Letters*, 2008, **49**, 70.

9 A. Ouali, J. -F. Spindler, H. J. Cristau, M. Taillefer, *Adv. Synth. Catal.*, 2006, **348**, 499.

10 M. Gholinejad, *Eur. J. Org. Chem.*, 2013, 257.

11 H. Beinert, *Eur. J. Biochem.*, 1997, **245**, 521.

12 P. Chen, S. I. Gorelsky, S. Ghosh, E. I. Solomon, *Angew. Chem., Int. Ed.*, 2004, **43**, 4132.

13 (a) R. Balasubramanian, A. C. Rosenzweig, *Acc. Chem. Res.*, 2007, **40**, 573; (b) S. I. Chan, S. S. F. Yu, *Acc. Chem.*, *Res.*, 2008, **41**, 969; (c) A. S. Hakemian, A. C. Rosenzweig, *Annu. Rev. Biochem.*, 2007, **76**, 223.

14 H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004.

15 C. W. Tornøe, C. Christensen, M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057.

16 V. V. Rostovtsev, L. G. Green, V. V. Fokin, K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596.

17 (a) H. C. Kolb, K. B. Sharpless, *Drug Discovery Today*, 2003, **8**, 1128; (b) S. G. Agalave, S. R. Maujan, V. S. Pore, *Chem.-Asian J.*, 2011, **6**, 2696; (c) C. J. Hawker, K. L. Wooley, *Science*, 2005, **309**, 1200; (d) J. E. Moses, A. D. Moorhouse, *Chem. Soc. Rev.*, 2007, **36**, 1249; (e) E. Lallana, R. Riguera, E. Fernandez-Megia, *Angew. Chem., Int. Ed.*, 2011, **50**, 8794.

18 M. Meldal, C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952.

19 X. Liu, S. Zhang, Y. Ding, *J. Mol. St.*, 2012, **1018**, 185.

20 G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

21 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

22 A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, 1988, **88**, 899.

23 (a) C. T. Lee, W. T. Yang, R.G. Parr, *Phys. Rev. B: Condens.Matter Mater. Phys.*, 1988, **37**, 785; (b) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

24 M. J. Frisch, et al., *Gaussian 09*, revision A.01, Gaussian, Inc., Wallingford, CT, 2009.

25 (a) R. Hekmatshoar, S. Sajadi, M.M. Heravi, F.F. Bamoharram, *Molecules*, 2007, **12**, 2223; (b) A. Supale, G. Gokavi, *React. Kinet. Catal. Lett*., 2008, **93**, 141.

26 A. Ferretti, *Can. J. Chem*., 1972, **50**, 4056.

27 S. Bhattacharya, Spectrochim. Acta, 2005, **A 61**, 3145.

28 T. C. Deivaraj, G. X. Lai and J. J. Vittal, *Inorg. Chem*., 2000, **39**, 1028.

29 M. G. B. Drew, *J. Chem. Soc.*, *Chem. Comm.*, 1973, 124.

30 M. G. B. Drew, D. A. Edwards and R. Richards, *J. Chem. Soc., Dalton Trans*., 1977, 299.

31 G.Speier, *Transtion Met. Chem.*, 1991, **16**, 576; T. C. Deivaraj, G. X. Lai and J. J. Vittal, *Inorg. Chem.*, 2000, **39**,1028.

32 S. P. Neo, Z.-Y. Zhou, T. C. W. Mak and T. S. A. Hor, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 3451.
33 B. Corain, B. Longato, G. Favero, D. AjÒ, G. Pilloni, U. Russo and F. R. Kriessl, *Inorg. Chim. Acta*, 1989, **157**, 260.
34 S. Sculfort and P. Braunstein, *Chem. Soc. Rev*., 2011, **40**, 2741-2760.
35 S. –L. Zheng, M. Messerschmidt and P. Coppens, *Angew. Chem. Int. Ed*., 2005, **44**, 4614-4617.
36 (a) D. Kushwaha, P. Dwivedu, S. K. Kuawar and V. K. Tiwari, *Curr. Org. Syn.*, 2013, **9***,* 89; (b) D. Kushwaha and V. K. Tiwari, *J. Org. Chem*., 2013, **78**, 8184; (c) K. B. Mishra and V. K. Tiwari, *J. Org. Chem*., 2014, **79** 5752.
37 P. L. Golas, N. V. Tsarevsky, B. S. Sumerlin, and K. Matyjaszewski, Macromolecules 2006, **39**, 6451.