

Available online at www.sciencedirect.com



Tetrahedron

Tetrahedron 61 (2005) 12145-12152

Copper (I) 1,3-R₂-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R=mesityl, 2-propyl): synthesis, X-ray structures, immobilization and catalytic activity

Bhasker Bantu,^{a,b} Dongren Wang,^{a,b} Klaus Wurst^c and Michael R. Buchmeiser^{a,b,*}

^aLeibniz Institut für Oberflächenmodifizierung (IOM) e. V., Permoserstr. 15, D-04318 Leipzig, Germany

^bInstitut für Technische Chemie, Universität Leipzig, Linnéstr. 3, D-04103 Leipzig, Germany

^cInstitut für Allgemeine, Anorganische und Theoretische Chemie, Leopold-Franzens-Universität Innsbruck, Innrain 52a,

A-6020 Innsbruck, Austria

Received 1 July 2005; revised 31 July 2005; accepted 31 July 2005

Available online 28 October 2005

Abstract—The synthesis of novel copper (I) N-heterocyclic carbene complexes is described. Thus, reaction of CuX with 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene yields CuX(1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) (X = Cl, (1a), Br (1b)); however, reaction of CuCl with 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene yields the bis-N-heterocyclic carbene complex Cu(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) $^+_2$ CuBr $^-_2$ (2). A supported version of 1, i.e. PS-DVB–CH $_2$ –OCO–CF $_2$ –CF $_2$ –CF $_2$ –COOCu(1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) (3) was prepared from 1 and PS-DVB–CH $_2$ –OCO–CF $_2$ –CF $_2$ –COOAg. A copper loading of 4.15 µmol/g was realized. The new compounds were used as catalysts in carbonyl hydrosilylation and cyanosilylation reactions. Excellent reactivity was observed, giving raise to turn-over numbers (TONs) of up to 100,000. Compounds 1a, 1b, and 2 have also been used as catalysts for the atom transfer radical polymerization (ATRP) of methyl methacrylate (MMA). A linear conversion of monomer with time was observed, however, no control over molecular weight of PMMA was observed. © 2005 Elsevier Ltd. All rights reserved.

1. Introduction

N-heterocyclic carbenes (NHCs)¹⁻⁶ are currently among the most intensively investigated compounds since the corresponding transition metal complexes were found to possess good stabilities and high activities in various catalytic processes.^{7–14} Recently, our group reported on novel NHC complexes of Ag (I), Pd (II), Rh (I), Ir (I), and Ru (II) based on 1,3-R₂-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R=mesityl, 2-propyl).¹⁵⁻²² In this context, novel NHC-complexes of the general formula MX(1,3-R₂-3,4,5,6tetrahydropyrimidin-2-ylidene)(COD) (M=Rh, Ir; X=Cl, Br; R=2-Pr, mesityl; COD= η^4 -1,5-cyclooctadiene) have been used for carbonyl arylation and hydrosilylation reactions and were found to possess excellent activity.¹⁹⁻²¹ The same applies to the palladium complex $PdCl_2(1,3-(2-$ Pr)₂-3,4,5,6-tetrahydropyrimidin-2-ylidene) and ruthenium complexes RuCl₂(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene(=CHR)). Encouraged by the high reactivity of these complexes, we were interested in the synthesis and catalytic behaviour of the corresponding Cu (I) NHC compounds. So far, only few reports exist on Cu (I) complexes of N-heterocyclic carbenes.^{23–25} In the following, their synthesis, characterization, X-ray structures and catalytic activities are reported.

2. Results and discussion

2.1. Synthesis and X-ray structure of compounds 1a and 1b

Compound **1a** was prepared in 77% isolated yield from CuCl and 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene in THF (Scheme 1). The latter was generated from 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate and sodium *tert*-butoxide as described in the lit.¹⁷ Compound **1a** (Fig. 1) was characterized by X-ray crystallography. A summary of the data is given in Tables 1 and 2.

Compound 1a crystallizes in the orthorhombic space group

Keywords: N-heterocyclic carbenes; Tetrahydropyrimidin-2-ylidenes; Copper; Atom-transfer radical polymerization; Hydrosilylation; Cyanosilylation; Homogeneous catalysis; Heterogeneous catalysis.

^{*} Corresponding author. Tel.: +49 341 235 2229; fax: +49 341 235 2584; e-mail: michael.buchmeiser@iom-leipzig.de

^{0040–4020/\$ -} see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2005.07.116

Table I. Crystal data and structu	ire rennement for Ia and Z
--	--

	1a	2
Molecular formula	C ₁₀ H ₂₀ ClCuN ₂	C44H56Br1.74Cl0.26Cu2N4
Fw	267.27	916.27
Cryst syst	Orthorhombic	Monoclinic
Space group	Pnnm (No. 58)	C2/c (No. 15)
a (pm)	1220.30(6)	1540.04(3)
b (pm)	986.16(3)	1450.36(2)
c (pm)	1045.55(5)	1916.18(5)
α (deg)	90	90
β (deg)	90	95.088(2)
γ (deg)	90	90
Vol (nm ³)	1.25823(9)	4.26452(15)
Ζ	4	4
Temperature (K)	233(2)	233(2)
Density (calcd) (Mg/m ³)	1.411	1.427
Abs coeff (mm^{-1})	1.915	2.678
Color, habit	Colorless prism	Colorless prism
No. of rflns with $I > 2\sigma(I)$	1276	3156
Goodness-of-fit on F^2	1.057	1.047
R indices $I > 2\sigma(I)$	$R_1 = 0.0208$	$R_1 = 0.0347$
	$\omega R^2 = 0.0543$	$\omega R^2 = 0.0846$



Scheme 1. Synthesis of Cu-NHC complexes 1a, 1b and 2.



Figure. 1. X-ray structure of compound 1a.

Pnnm with a=1220.30(6) pm, b=986.16(3) pm and c=1045.55(5) pm, $\alpha=\beta=\gamma=90^{\circ}$, Z=4. The distance Cu(1)–C(1) is 191.50(19) pm, which is significantly shorter than the one reported for CuCl 1,3-(2,6-(2-Pr)₂-C₆H₃)(imidazol-

Table 2. Bond lengths (pm) and angles	(°)) for 1	a
--	-----	----------------	---

2-ylidene) (195.3 pm).²³ This finding underlines the fact that N-heterocyclic carbenes based on tetrahydropyrimidin-2-ylidenes are among the most basic ones. In due consequence, a pronounced trans-effect on the halogen ligand had to be expected and was in fact found. Thus, the distance Cu(1)–Cl(1) in **1a** (211.06(6) pm) is longer than the one observed in CuCl 1,3-(2,6-(2-Pr)₂-C₆H₃) (imidazol-2-ylidene) (208.90 pm).

In a similar way, **1b** was prepared in 75% yield from CuBr and 1,3-di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene in THF (Scheme 1). Due to structural similarity, no further discussion appears necessary.

2.2. Synthesis and X-ray structure of compound 2

Compound **2** was prepared in 88% isolated yield from CuCl and 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene in THF (Scheme 1). The latter was generated from 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium bromide and sodium *tert*-butoxide as described in the literature.¹⁷ The complex that forms is remarkable. Thus, a cationic Cu (I) bis-(NHC) compound with a CuBr₂ anion forms instead of the expected neutral CuBr(NHC) complex. So far, we have no conclusive explanation for this finding, the more, as the sterically demanding ligand should favor a Cu-mono-NHC-complex. Compound **2** (Fig. 2) was characterized by X-ray crystallography. A summary of the data is given in Tables 1 and 3.

Table 3. Bond lengths (pm) and angles (°) for 2

Cu(1)–C(1)	193.4(2)
Cu(1)-C(1)#1	193.4(2)
C(1)-Cu(1)-C(1)#1	178.73(13)
Cl(1)#2-Cu(2)-Br(1)	179.29(4)
Br(1)#2-Cu(2)-Br(1)	179.29(4)



Figure. 2. X-ray structure of compound 2.

Compound 2 crystallizes in the monoclinic space group C2/ c with a=1540.04(3) pm, b=1450.36(2) pm and c=1916.18(5) pm, $\alpha = \gamma = 90^{\circ}$, $\beta = 95.088(2)$, Z=4. As expected, the distances Cu(1)–C(1) and Cu(1)–C(1)# are identical (193.42(2) pm). This distance is only slightly longer than in the one found in **1a** indicating only minor, if any, steric repulsion of the two NHC ligands. The angle C(1)–Cu(1)–C(1)# is 178.73(13)°, illustrating an almost perfect alignment of the two NHC ligands. As expected, the CuBr₂ anion is almost perfectly linear with an angle Brl(1)– Cu(1)–Br(1)# of 179.29(4)°. It should be emphasized that the anion is in fact best described by the formula CuBr_{1.74}Cl_{0.26}. This irregularity may also account for the slight (calculated) deviation in the linearity of this anion.

2.3. Synthesis of an immobilized version of 1a/1b

In view of the high demand on supported catalysts,²⁶ we synthesized a supported version of **1a** respectively **1b** by reaction with a perfluoroglutaric acid-derivatized PS-DVB-based support according to an established procedure (Scheme 2).^{27,28} A catalyst loading of 4.15 μ mol/g was

accomplished. With this set of catalysts in hand, a series of catalytic reactions as outlined below were investigated.

2.4. Catalytic activity of compounds 1a, 1b and 2 in C=O cyanosilylation reactions

Compounds **1a**, **1b** and **2** were used in the cyanosilylation of various carbonyl compounds including aromatic aldehydes and ketones (Scheme 3). A summary of the results is given in Table 4, entries 1–8.



Scheme 3. C=O hydrosilylation, C=O cyanosilylation reactions and attempted ATRP of MMA.

As can be seen, catalyst **1b** showed excellent reactivity in this type of reaction. Yields were in the 22–100% range, TONs up to 50,000 were obtained. The more stable complex **2** resulted in even improved yields (80–100%), TONs reached 100,000. The supported version **3** gave significantly, however, still acceptable yields approaching 100% in selected cases. As a consequence of both the low copper loadings (12–71 µmol%) and the immobilization, products obtained with **3** were basically free of any copper residues (<1 ppm).

2.5. Catalytic activity of compounds 1a, 1b and 2 in C=O hydrosilylation reactions

Copper (I) catalyzed C=O hydrosilylation reactions (Scheme 3) were first described by Nolan and coworkers



Scheme 2. Immobilization of 1a on a PS-DVB-based support.

Table 4.	Cyanosilylation	of carbony	l compounds us	sing trimethy	ylsilylcyanide
----------	-----------------	------------	----------------	---------------	----------------

#	Educt/product	Time (h)	$1b^{a}$ /yield (%) ^b	TON	Time (h)	2^{c} /Yield (%) ^b	TON	µmol (%) 3	Yield (%) ^b	TON
1	4-Chlorobenzaldehyde/2-(4-Cl-phenyl)-2- trimethylsilyloxyacetonitrile	1	100	50,000	0.75	100	100,000	12	100	8600
2	4-Fluorobenzaldehyde/2-(3-F-phenyl)-2- trimethylsilyloxyacetonitrile	1	100	50,000	1	100	50,000	2.2	93	42,300
3	3-Hydroxybenzaldehyde/2-(3-trimethylsilyl- oxyphenyl)-2-trimethylsilyloxyacetonitrile	1	80	40,000	1	98	98,000	20	100	4900
4	Benzoin/1,2-diphenyl-1,2-bis(trimethylsilyl- oxy)propionitrile	6	22	11,000	6	80	80,000	71	4	60
5	Benzoylacetone/1-trimethylsilyloxy-1-methyl-3- benzoylpropionitrile	1	80	40,000	1	80	80,000	54	81	1500
6	4-Bromoacetophenone/2-(4-Br-phenyl)-2-tri- methylsilyloxypropionitrile	24	0	0	48	80	80,000	66	0	0
7	Benzaldehyde/1-phenyl-trimethylsilyloxy- acetonitrile	1.5	90	45,000	1	99	99,000	18	80	4500
8	Diphenyldiketone/2,3-diphenyl-2,3-bis(trimethyl-silyloxy)butanedinitrile	1.5	99	49,500	1	100	100,000	70	93	1300

^a 0.002 mol% of **1b**.

^b Determined by GC-MS. Reactions were run in dichloroethane at 75 °C.

^c 0.001 mol% of **2**.

for Cu-imidazol-2-ylidenes.^{23,24} With their systems, excellent yields approaching 100% were achieved using 3 mol% of the corresponding catalyst, translating into maximum turn-over numbers (TON_{max}) of 33.

As can be deduced from Table 5, entries 1–9, catalyst **1b**, if used on a 0.002 mol% scale, allowed for TONs up to 50,000. Yields were in the 80–100% range. Even better, catalyst **2**, used on a 0.001 mol% scale, allowed for TONs up to 100,000, yields for all substrates investigated were in the 70–100% range. The supported version **3** showed again reduced, however, still acceptable activity, allowing for TONs up to 42,500 and yields up to 100%.

Table 5. Hydrosilylation of carbonyl compounds using triethylsilane

2.6. Differences in catalyst structure accounting for differences in reactivity

From the set of data presented above, three important conclusions may be drawn. Firstly, ALL catalysts presented here are by far the most reactive Cu (I)–N-heterocyclic carbene complexes that have been prepared for the abovementioned reactions. Secondly, no change in selectivity is observed upon immobilization of **1a**, respectively **1b** on a Merrifield type support. However, presumably due to diffusion issues, reactivity is reduced, however, still exceeds any system reported so far. Thirdly, complex **2** is by far the more reactive one. This is believed to be a direct

#	Educt/product	Time (h)	$1b^{a}/Yield$ (%) ^b	TON	Time (h)	2^{c} /Yield (%) ^b	TON	µmol% of 3	Yield (%) ^b	TON
1	4-Chlorobenzaldehyde/4-Cl-phenyl- 1-triethoxysilylmethane	1 h	100	50,000	45 min	100	100,000	29	100	38,800
2	4-Fluorobenzaldehyde/4-F-phenyl- triethoxysilylmethane	45 min	100	50,000	0.5	100	100,000	1.1	23	21,000
3	4-Bromoacetophenone/2-(4-Br-phenyl)- 1-triethoxysilylethane	24 h	0	0	1	100	100,000	33	0	0
4	Benzophenone/diphenyltriethoxy- methane	1.5 h	90	45,000	1.5	98	98,000	30	20	660
5	4- <i>N</i> , <i>N</i> -Dimethylaminobenzaldehyde/4- <i>N</i> , <i>N</i> -dimethylaminophenyl-triethoxy- silvlmethane	2 h	90	45,000	1	98	98,000	12	40	3200
6	4-Chloroacetophenone/2-(4-Cl-phenyl)- 1-triethoxysilylethane	24 h	0	0	5°	98	98,000	26	0	0
7	Benzaldehyde/4-Cl-phenyl-triethoxy- silvlmethane	1 h	98	49,000	1	100	100,000	24	100	42,500
8	Norborn-5-ene-2-carbaldehyde/ norborn-5-ene-2-yltriethoxysilyl- methane	1 h	80	40,000	1	80	80,000	102	54	5300
9	Benzoin/1,2-diphenyl-2-triethoxysilyl- ethanol	1.5 h	0	0	1.5	70	70,000	35	0	0

Room temperature.

^a 0.002 mol%.

^b Determined by GC–MS. Reactions were run in THF at 65 °C using 0.15 mmol% of NaO-tert-Bu.

^c 0.001 mol%.



Scheme 4. Proposed mechanism for the cyanosilylation (left) and C=O hydrosilylation (right). Bromide may (in part) be replaced by tert-butoxide.

consequence of the structure of **2**. As a matter of fact, it consists of a cationic Cu (I) species, well protected by the two N-heterocyclic carbenes, and a 'naked' dibromocuprate. However, according to the mechanism proposed by Nolan et al. (Scheme 4), the formation of CuBr(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) and Cu(*tert*-butoxy)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene), respectively, in course of the reaction is proposed. Here the copper center is well-protected by the large N-heterocyclic carbene ligand and the mesityl moieties, respectively, leaving still enough space for the substrates to coordinate. Unfortunately, we were not able to retrieve unambiguous experimental evidence for this assumption so far.

2.7. Attempted ATRP of MMA using compounds 1b and 2

Atom transfer radical polymerization (ATRP) is a welldeveloped polymerization technique for the synthesis of narrow disperse polymers.²⁹ The polymerization mechanism involves a metal complex, where the metal changes reversibly its oxidation state. In addition, some additional free metal has been identified to play a positive role. In due consequence, the new copper (I) complexes and in particular complex **2** were expected to be suitable. However, **2** failed to provide an ATRP system capable of controlling



Figure. 3. Graph showing monomer conversion versus time for the polymerization of MMA by 1b.

the molecular weight. Instead, PMMA with similar molecular weights in the range of 70,000–90,000 g/mol was produced. The reason for this behavior apparently lies in the insolubility of **2** in the polymerization medium. Thus, once polymerization commences, the back reaction, forming the 'dormant species' is hindered, resulting in the rapid production of polymer. Once the deactivation step is successfully accomplished, reactivation of the polymer chain does not occur. Instead, the initiator forms new growing polymer chains facing the same fate.

Therefore, **1b** was used. This complex is more soluble and in fact allowed for a more controlled polymerization of MMA. Graphs of monomer conversion versus time as well as a graph showing M_n versus the number of monomer equivalents added (*N*) are shown in Figs. 3 and 4, respectively. Polymerization results are summarized in Table 6.

As can be seen, monomer consumption proceeded linearly over time. Similarly, molecular weights developed linearly up to a monomer:catalyst ratio of 300 and then remained unchanged. However, molecular weights, as determined by light scattering, were about twice as high as calculated. This clearly indicates an initiation efficiency of roughly 0.5. In view of this finding and the comparably high polydispersity



Figure. 4. Graph of number of monomer equivalents added (*N*) versus M_{n} . The line shows the theoretical values for M_{n} .

Table 6. Summary of polymerization results for MMA using 1b

Entry	Ν	$M_{\rm n}$ (calcd)	$M_{\rm n}$ (found)	PDI	
1	100	10,000	4700	1.39	
2	200	20,000	7400	1.53	
3	300	30,000	8600	1.55	
4	400	40,000	8708	1.82	

N, number of monomer equivalents added. Polymerizations were carried out at 90 °C in diphenyl ether.

indices (1.4–1.8, Table 6), the polymerization certainly does not fulfil the stringent criteria of a true, controlled ATRP. However, it should be emphasized, that this is the first report on the use of an N-heterocyclic carbene–Cu system for these purposes.

3. Experimental

3.1. General

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further purification. Pentane, diethyl ether, toluene, methylene chloride and tetrahydrofurane (THF) were dried using a solvent dry system (SDS, MBraun). Chloroform- d_1 was distilled from calcium hydride. Styrene and methyl methacrylate (MMA) were dried over CaH₂ overnight, distilled under vacuum and stored under argon at -15 °C. The initiator ethyl-2-bromo isobutyrate (EBIB) was distilled under reduced pressure prior to use. Diphenyl ether was dried over molecular sieves (3 Å) and distilled prior to use.

NMR data were obtained at 300.13 MHz for proton and 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded on a Bruker Vector 2000 using ATR technology. Elemental analyses were carried out at the Mikroanalytisches Labor, Anorganisch-Chemisches Institut, TU München, Germany. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by GPC at 30 °C on Polymer Laboratories columns (PLgel 10 µm MIXED-B, 7.5×300 mm) in THF at 25 °C using a Waters Autosampler, a Waters 484 UV detector (254 nm), a light scattering detector (Wyatt) and an Optilab Rex refractive index detector (685 nm, Wyatt). The flow rate was 0.7 mL/ min. A dn/dc of 0.086 was used for the determination of M_w by light scattering.

3.1.1. Synthesis of CuCl(1,3-di(2-Pr)-3,4,5,6-tetrahydropyrimidin-2-ylidene) (1a). In a 100 mL Schlenk flask were added copper (I) chloride (0.28 g, 2.82 mmol), 1,3-bis(2propyl)-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate (0.70 g, 2.73 mmol) and sodium *tert*-butoxide (0.27 g, 2.82 mmol). Dry THF was added (25 mL) under argon and the mixture was stirred for 24 h at room temperature. The reaction mixture was filtered through celite and the solvent was evaporated in vacuo. A light green colored solid was obtained, which was recrystallized from dichloromethane/pentane to yield 0.56 g (77%) of the desired compound. FTIR (ATR): 2965 (m), 2929 (m), 2868 (m), 1677 (m), 1518 (s), 1311 (s), 1169 (m). ¹H NMR (CDCl₃) δ 1.19 (d, 12H, CH₃), 1.86 (q, 2H, CH₂), 3.0 (t, 4H, NCH₂), 4.59 (m, 2H, NCH). ¹³C NMR (CDCl₃) δ 194.7 (C:– N), 60.3 (N–H), 37.1 (N–H₂), 20.5 (CH₂), 20.4 (CH₃).

3.1.2. Synthesis of CuBr(1,3-di(2-Pr)-3,4,5,6-tetrahydropyrimidin-2-ylidene) (1b). In a 100 mL Schlenk flask were added copper (I) chloride (120 mg, 1.21 mmol), 1,3-bis(2propyl)-3,4,5,6-tetrahydropyrimidinium bromide (300 mg, 1.20 mmol) and sodium tert-butoxide (118 mg, 1.23 mmol). Dry THF was added (25 mL) under argon and the mixture was stirred for 24 h at room temperature. The reaction mixture was filtered through celite and the solvent was removed in vacuo, leaving a brown coloured precipitate behind. Recrystallization from dichloromethane/pentane yielded 285 mg (75%) of **1b**. FTIR (ATR): 2968 (m), 2932 (m), 2869 (m), 1517 (s), 1311 (s), 1169 (s). ¹H NMR (CDCl₃) δ 1.19 (d, 12H, CH₃),1.84 (q, 2H, CH₂), 3.0 (t, 4H, NCH₂), 4.6 (m, 2H, NCH); ¹³C NMR (CDCl₃) δ 195.1 (C:-N), 60.7 (N-H), 38.4 (N-H₂), 20.5 (CH₃), 20.7 (CH₂); elemental analysis calcd for C₁₀H₂₀BrCuN: C, 38.41; H, 6.77; N, 8.96; found, C, 38.81; H, 6.12; N, 9.04.

3.1.3. [Cu(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2ylidene) $_{2}^{+}$ CuBr $_{2}^{-}$] (2). In a 100 mL Schlenk flask were added copper (I) chloride (0.370 g, 3.74 mmol), 1,3dimesityl-3,4,5,6-tetrahydropyrimidinium bromide (1.50 g, 3.74 mmol) and sodium tert-butoxide (0.36 g, 3.75 mmol). Dry THF was added (40 mL) under an inert atmosphere and the mixture was magnetically stirred for 24 h at room temperature. The reaction mixture was filtered through a plug of celite and the solvent was evaporated in vacuo, leaving a light pink colored precipitate behind. Recrystallization from dichloromethane/pentane yielded 2.3 g (88%) of the desired compound. FTIR (ATR mode): 3275 (br), 2944 (br), 2912 (br), 1608 (br), 1509 (s), 1481 (br), 1443 (br), 1302 (s), 1205 (s), 1034 (br), 993 (br), 856 (s), 722 (br), 649 (br), 611 (br) cm⁻¹. ¹H NMR (CDCl₃) δ 1.74 (24H, O–H₃ of mesityl), 2.10 (m, 4H of CH₂), 2.27 (s, p-CH₃ of mesityl), 3.10 (t, 8H, N-H₂), 6.89 (s, 8H, aromatic); ¹³C NMR (CDCl₃): δ 18.2 (o–CH₃ of mesityl), 21.2 (p-CH₃ of mesityl), 20.0 (CH₂), 44.3 (N-H₂), 130.1, 135.1, 138.7, 141.9 (aromatic C), 198.9 (C:-N); elemental analysis calcd for C₄₄H₅₆Br₂Cu₂N₄: C, 56.96; H, 6.08; N, 6.04. Found: C, 57.63; H, 6.14; N, 6.05.

3.1.4. PS-DVB-CH₂-OCO-CF₂NCF₂NCF₂-COOCu(1,3di(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene) (3). PS-DVB-CH₂-OH (1.00 g, 1.1 mmol OH/g) was suspended in dry THF (20 mL). Perfluoroglutaric anhydride (1.00 mol equiv, 246 mg, 1.10 mmol) was added. Stirring was continued for 2 h, then the product was filtered off and washed three times with THF. It was dried in vacuo resulting in a white solid (1.35 g). FT-IR (ATR-mode): 3024 (br), 2 920(br), 1773 (s), 1600 (br), 1492 (s), 1451(s), 1306 (br), 1240 (br), 1174 (br), 1141 (br), 1046 (br), 1028 (br), 942 (br), 871 (br), 823 (w), 747 (s), 696 (s) cm⁻¹. The solid was re-suspended in THF (10 mL) and 1.0 equiv of NaOH (46 mg) dissolved in 25 mL of water was added. The mixture was stirred for 2 h, then the solid was filtered off, washed three times with water and re-suspended in 20 mL of water. AgNO₃ (1.30 mol equiv, 230 mg,

1.43 mmol), dissolved in 10 mL of water, was added and stirring was continued for a further 4 h. The product was filtered and washed three times each with water, diethyl ether and pentane. Drying in vacuo gave a white solid (1.52 g). FT-IR (ATR-mode): 3058 (br), 3024 (br), 2918 (br), 2848 (br), 1772 (br), 1654 (br), 1600 (br), 1510(s), 1492 (s), 1450 (s), 1372 (w), 1177 (w), 1153 (w), 1027 (w), 906 (br), 841 (w), 820, (w), 749 (m), 696 (s). The solid was re-suspended in THF (25 mL) and 2 (65 mg, 0.20 mmol) was added. Stirring was continued for a further 4 h. The product was filtered off, washed with THF, dichloromethane and pentane and dried in vacuo to yield a brown colored powder (1 g). FT-IR (ATRmode): 3057 (br), 3023 (br), 2918 (br), 2848 (br), 1657 (br), 1600 (br), 1491 (s), 1450 (br), 1370 (br), 1285 (br), 1155 (w), 1055 (w), 1027 (w), 947 (br), 835 (br), 749 (m), 696 (s) cm⁻ Cu content as determined by ICP-OES after dissolving a 20.0 mg sample in aqua regia: 4.15 µmol/g.

3.2. Typical procedure for hydrosilylation reactions

In a 50 mL Schlenk tube the catalyst (1.0 mmol%) was dissolved in 1 mL of THF, sodium *tert*-butoxide (5.5 mg, 15 mmol%) and 4 mol equiv of triethylsilane (166 mg, 1.42 mmol) were added and the solution was stirred for 5 min. Then, the carbonyl compound (0.20–0.40 mmol), dissolved in 2 mL of THF, was added to the reaction mixture. The solution was heated to 65 °C. Product conversion was monitored by GC–MS at defined time intervals. Compounds were identified by GC–MS. Quantification was accomplished using an internal standard (*tert*-butylbenzene).

3.3. Typical procedure for cyanosilylation reactions

In a 50 mL Schlenk tube the catalyst (1.0 mmol%) was dissolved in 1 mL of dichloroethane, then 2 mol equiv of trimethylsilylcyanide (71 mg, 0.71 mmol), dissolved in 2 mL of dichloroethane, as well as the carbonyl compound (0.20–0.40 mmol) were added. The solution was heated to 75 °C. Product conversion was monitored by GC–MS at defined time intervals. Compounds were identified by GC–MS. Quantification was accomplished using an internal standard (*tert*-butylbenzene).

3.4. Typical procedure for the ATRP of MMA

A 50 mL Schlenk flask was charged with 5 mL of diphenyl ether and the corresponding catalyst (0.5 mmol%), MMA (3.0 mL 28.3 mmol), EBIB (1.0 mmol%) and 0.500 mol equiv of tert-butylbenzene (internal standard for monitoring of monomer conversion) were added. 0.200 mL of the reaction solution was withdrawn, mixed with acetone, and used as reference solution. Then the reaction mixture was heated to 90 °C. At appropriate timed intervals, 0.500 mL aliquots of the solution were withdrawn and 3.0 µl thereof were dissolved in acetone. Acetone solutions were analysed by GC-MS, percent conversions were calculated relative to the reference solution. The rest of the 0.500 mL samples were mixed with methanol, the polymer that precipitated was filtered off, washed with methanol and re-dissolved in THF, passed through 0.2 μ m Teflon filters and analysed by GPC.

3.5. X-ray measurement and structure determination of 1a and 2

Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo-K_{α}-radiation (λ =0.71073 Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.³⁰ Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F² SHELX97.³¹ The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Positions of hydrogen atoms were calculated and refined isotropically.

3.6. Supporting information available

The crystallographic data for **1** and **2** have been deposited with the CCDC-No. xxx and xxy, and at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. (fax: +44 1223 336033; e-mail: deposit@ ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

4. Summary

In summary we have developed new copper (I)-1,3- R_2 -3,4,5,6-tetrahydropyrimidin-2-ylidene-based catalysts. Immobilization was accomplished at a Merrifield type support. All catalysts showed unprecedented high activity in the cyanosilylation and C=O hydrosilylation reactions resulting in TONs up to 100,000. Unfortunately, all catalysts failed to provide suitable ATRP systems capable of polymerizing methyl methacrylate (MMA) in a perfectly controlled way.

Acknowledgements

Our work was supported in part by a grant of the Austrian Science Fund (START Y-158).

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.07.116

References and notes

- Wanzlick, H.-W.; Schikora, E. Chem. Ber. 1961, 94, 2389–2393.
- 2. Wanzlick, H.-W.; Kleiner, H.-J. Angew. Chem. 1961, 73, 493.

- 3. Wanzlick, H.-W. Angew. Chem. 1962, 74, 129-134.
- Arduengo, A. J., III.; Harlow, R. L.; Kline, M. J. Am. Chem. Soc. 1991, 113, 361–363.
- Arduengo, A. J., III.; Rasika Dias, H. V.; Harlow, R. L.; Kline, M. J. Am. Chem. Soc. 1992, 114, 5530–5534.
- 6. Regitz, M. Angew. Chem. 1996, 108, 791-794.
- Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. Angew. Chem. 1995, 107, 2602–2605.
- Herrmann, W. A.; Elison, M.; Fischer, J.; Köcher, C.; Artus, G. R. J. Chem. Eur. J. 1996, 2, 772–780.
- Herrmann, W. A.; Cornils, B. Angew. Chem. 1997, 109, 1074–1095.
- Herrmann, W. A.; Köcher, C. Angew. Chem. 1997, 109, 2256–2282.
- 11. Cowley, A. H. J. Organomet. Chem. 2001, 617–618, 105–109.
- 12. Herrmann, W. A. Angew. Chem. 2002, 114, 1342-1363.
- 13. Muehlhofer, M.; Strassner, T.; Herrmann, W. A. Angew. Chem. 2002, 114, 1817–1819.
- Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. Angew. Chem. 2001, 113, 3500–3503.
- Krause, J. O.; Zarka, M. T.; Anders, U.; Weberskirch, R.; Nuyken, O.; Buchmeiser, M. R. Angew. Chem. 2003, 115, 6147–6151.
- Mayr, M.; Buchmeiser, M. R. Macromol. Rapid. Commun. 2004, 25, 231–236.
- Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. Chem. Eur. J. 2004, 10, 1256–1266.

- 18. Mayr, M.; Wurst, K.; Ongania, K.-H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 2622.
- Imlinger, N.; Mayr, M.; Wang, D.; Wurst, K.; Buchmeiser, M. R. Adv. Synth. Catal. 2004, 346, 1836–1843.
- Imlinger, N.; Wurst, K.; Buchmeiser, M. R. Monatsh. Chem. 2005, 136, 47–57.
- Imlinger, N.; Wurst, K.; Buchmeiser, M. R. J. Organomet. Chem. 2005, 690, 4433–4440.
- Yang, L.; Mayr, M.; Wurst, K.; Buchmeiser, M. R. Chem. Eur. J. 2004, 10, 5761–5770.
- 23. Kaur, H.; Kauer Zinn, F.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2004**, *23*, 1157–1160.
- Díez-González, S.; Kaur, H.; Kauer Zinn, F.; Stevens, E. D.; Nolan, S. P. J. Org. Chem. 2005, 70, 4784–4796.
- Larsen, A. O.; Leu, W.; Oberhuber, C. N.; Campbell, J. E.; Hoveyda, A. H. J. Am. Chem. Soc. 2004, 126, 11130–11131.
- 26. Polymeric Materials in Organic Synthesis and Catalysis; Buchmeiser, M. R., Ed.; Wiley-VCH: Weinheim, 2003.
- Krause, J. O.; Lubbad, S.; Mayr, M.; Nuyken, O.; Buchmeiser, M. R. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 2003, 44, 790–791.
- Krause, J. O.; Lubbad, S. H.; Nuyken, O.; Buchmeiser, M. R. Macromol. Rapid Commun. 2003, 24, 875–878.
- 29. Matyjaszewski, K.; Xia, J. Chem. Rev. 2001, 101, 2921-2990.
- Otwinowski, Z.; Minor, W. In *Methods in Enzymology*, Vol. 276; Academic Press: New York, 1997.
- Sheldrick, G. M. Program package SHELXTL V.5.1, Bruker Analytical X-Ray Instruments Inc, Madison, USA, 1997.