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Synthesis, characterization, and catalytic application of copper(I) nitrile cations with perfluorinated weakly coordinating anions

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Complexes of the type $[Cu(CH_3CN)_4]^+[A]^-$ ($[A]^- = [B(C_6F_5)_4]^-$ (**1**), $[B\{C_6H_3(CF_3)_2\}]^-$ (**2**), $[(C_6F_5)_3B–C_3H_4N_2–B(C_6F_5)_3]^-$ (**3**)) are synthesized and characterized. Their utilization as catalysts in cyclopropanation and aziridination reactions of olefins, forming three membered rings is explored. The compounds are found to catalyze both reactions in moderate to good yields being the best results obtained with compound **1**. The more weakly the nitrile ligands are coordinated to the metal center, the better is the catalytic performance of the catalyst.

KEY WORDS: weakly coordinating anions; three-membered carbocyclic rings; cyclopropanation; aziridination; copper(I) complexes.

1. Introduction

Weakly or non coordinating anions (WCAs) are of significant current interest as counter ions both in synthesis and in catalysis, due to their potential in enhancing reactivity of metal complexes [1]. An important industrial application requiring WCAs, is for example the metallocene process for the stereo regular polymerization of olefins currently being under close examination by several groups [2].

Although copper-based complexes have played a prominent role in the *in situ* generation of metal carbenes (or carbenoids) from diazo compounds and of nitrenes from the corresponding sources, comparatively little attention has been paid to the development of Cu(I) complexes with WCAs and to their potential catalytic applications. The $[Cu(I)(NCCH_3)_4]^+$ cation coordinated with some common counter ions such as BF_4^-, ClO_4^- and PF_6^- is well known both with respect to its structure and its catalytic activity [3]. Particular attention has been paid to such Cu(I) compounds especially as precursors for catalysts in the asymmetric catalytic cyclopropanation/aziridination [3b]. Copper(I) complexes bearing anionic polypyrazolylborate ligands have also been reported as catalysts for both cyclopropanation and aziridination of olefins [3c].

We synthesized Cu(I) complexes having as ligands easily displaceable solvent molecules (acetonitrile) with particularly bulky WCAs containing fluorinated phenyl groups and examined their behavior as catalysts for different chemical reactions. The use of catalysts based on copper is particularly attractive due to their relatively low cost if compared with catalysts based on rhodium or ruthenium.

Three-membered carbocyclic rings hold a prominent position in organic chemistry both due to their interesting biological properties [5] and to their use as starting materials and intermediates in organic synthesis [6]. However, the synthesis of small rings still poses some difficulties. Accordingly, the catalytic cyclopropanation and aziridination of olefins, forming three membered rings have been attracting significant attention [7]. The development of new and more efficient catalysts for these reactions as well as the study of their mechanism has been under investigation in several groups [8].

2. Results and discussion

2.1. Synthesis and characterization

The WCAs for complexes **1** and **2** were prepared by the reaction of pentafluorobenzene bromide and 3,5-bis(trifluoromethyl)-bromobenzene, resp., with *n*-butyllithium (chart 1, equation (1)) forming the corresponding potassium salts. The potassium salts were transformed to silver salts by reaction with silver nitrate. The WCA of complex **3** was synthesized according to literature procedures [4] and then transferred to the respective silver salt with silver nitrate as in the case of the anions of complexes **1** and **2**.

The copper(I) complexes **1**–**3** were synthesized by reacting copper(I) chloride with the silver salts of the corresponding anions in acetonitrile (anion exchange) (equation (2)). The solvent stabilized complexes are stored at −35 °C under Argon atmosphere to prevent decomposition and oxidation over long storage periods.

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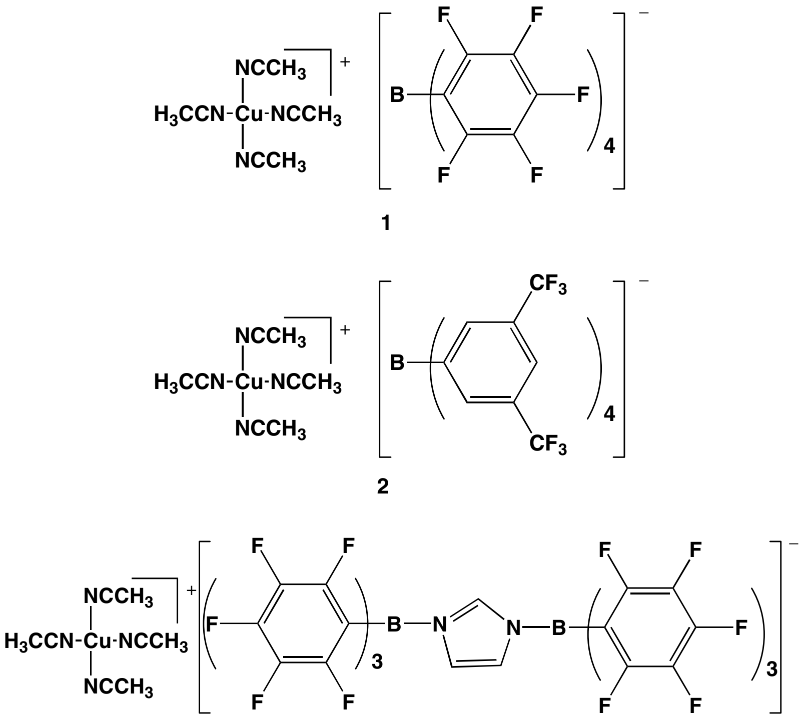


1

2

3

Chart 1.

However, they can be stored at room temperature for short periods of time and handled in laboratory atmosphere briefly.

$$4\text{R-Br} + \text{BuLi} + \text{BCl}_3 + \text{KCL} \xrightarrow[-78^\circ\text{C, r.t.}]{\text{Dry Ether}} \text{K[B(R)}_4] \tag{1}$$

R = Pentafluorobenzene bromide or
3,5-bis(trifluoromethyl)bromobenzene

$$\text{Ag[A]} + \text{Cu(I)Cl} \xrightarrow[\text{r.t.}]{\text{acetonitrile}} \text{AgCl} + [\text{Cu(NCCH}_3)_4\text{[A]} \tag{2}$$

Copper(I) complexes **1**–**3**were characterized by IR spectroscopy, elemental analysis and ^{1}H-NMR. The IR shifts of the ν_{CN} absorption are observed at 2277 cm^{-1} and 2308 cm^{-1} for complex **1**, 2286 cm^{-1} and 2317 cm^{-1} for complex **2** and 2286 cm^{-1} and 2318 cm^{-1} for complex **3**. These IR-data are in good agreement with those given in the literature for compound **1**, the only compound among the three described here, which was described already previously [9]. Based on these IR data and the examinations on compound **1** and its analogue containing only two (instead of four) nitrile ligands [9], it can be concluded that compounds **2** and **3** bind their nitrile ligands slightly stronger than compound **1**. This assumption is supported by the ^{1} H-NMR data of the acetonitrile ligands of the complexes **1**–**3**. The chemical shift of the acetonitrile protons in CDCl$_3$ of compound **1** (δ = 1.87 ppm) is more closely to the shift of free acetonitrile (δ = 1.83 ppm) than the nitrile pronton shift of the nitrile ligands of compound **2** and **3** (δ = 2.02 ppm and 2.13 ppm, resp.).

Table 1
Cyclopropanation at different ratios of styrene: EDA catalyzed by **1**

Ratio[a]	Time (h)	Yield(%)[b]	*cis*:*trans*[c]
1:1.2	1	55	40:60
2:1	1	71	49:51
3:1	1	78	38:62

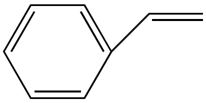
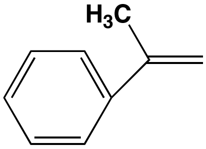
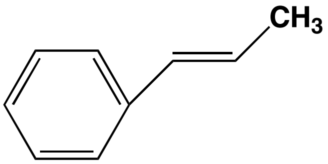
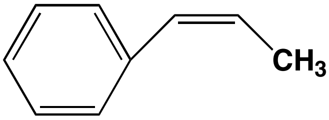
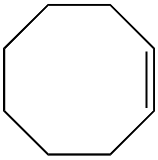
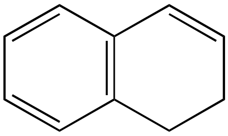
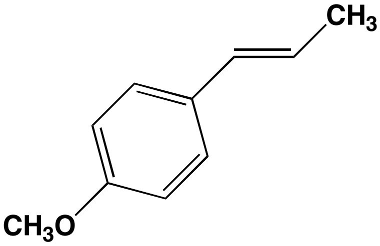
[a] Ratio = styrene:EDA.
[b] Yield determined by GC (FID) with dodecane as standard.
[c] Determined by GC (FID) and GC-MS.

Table 2
Cyclopropanation of styrene catalyzed by complexes **1**–**3**

Complexes[a]	Time (h)	Yield[b]	*cis*:*trans*[c]
1	1	71	49:51
2	1	42	36:64
3	1	25	37:63

[a] Styrene:EDA = 2 :1.
[b] Yield determined by GC (FID) with dodecane as standard.
[c] Determined by GC (FID) and GC-MS.

Table 3
Cyclopropanation of several olefins catalyzed by **1**

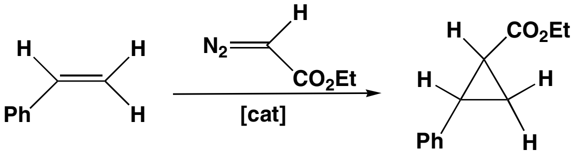
Entry	Olefins[a]	Yield[b]	*cis*:*trans*[c]
1		71	49:51
2		71	38:62
3		72	40:60
4		60	63:27
5		62	25:75
6		15	28:72
7		76	40:60

[a] Olefin:EDA = 2 :1, reaction time 1 h.
[b] Yield determined by GC (FID) with dodecane as standard.
[c] Determined by GC (FID) and GC-MS.

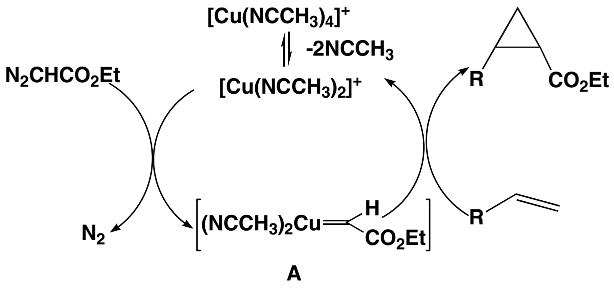
2.2. Catalysis

2.3. Cyclopropanation reactions

The use of complexes with weakly coordinated, easily displaceable ligands, should – in principle – have a positive effect on the catalytic activity, by rendering the intermediate species more accessible to substrate coordination. The negative effect of excess ligand in cyclopropanation catalysis with copper(I) complexes has been



Equation 3.



Scheme 1.

observed previously [3c]. It has been shown in the literature, however [9,10], that nitrile ligated complexes may lose one or more of their acetonitrile ligands quite easily forming, in the case of $[Cu(I)(NCCH_3)_4]^+$ as the starting compound, an under-coordinated, linear $[Cu(I)(NCCH_3)_2]^+$-complex. Complexes **1**–**3** were tested as catalysts for cyclopropanation reactions using styrene as olefin (equation (3)).

The influence of the styrene:ethyldiazoacetate (EDA) ratio on the reaction yield was studied preliminarily for compound **1**. The reactions were carried out at room temperature using 2 mol% of catalyst (with respect to EDA) in dichloromethane (a non coordinating but polar solvent), yielding a mixture of *cis* and *trans* cyclopropanes. The test reactions were completed within 1 h and the results are shown in table 1. For the subsequent catalytic reactions with compounds **2** and **3**, a styrene:EDA ratio of 2:1 was applied, since on going from 2:1 to 3:1 the improvement in the yield is not very significant. The same reaction conditions were applied and the results are summarized in table 2. For complex **1** (showing the highest activity among the three complexes studied), the cyclopropanation reaction was performed using several other olefins, including several styrene derivatives and cyclic olefins (table 3). The results achieved were similar or better than the ones achieved for styrene, except in the case of 1,2-dehydronaphtalene, which could only be converted to the corresponding cyclopropane in a trace amount under the conditions applied. All the α and β substituted styrene derivatives could be successfully converted to the desired cyclopropanes in moderate to good yields, even in the case of entry 7 bearing a CH_3O- electron-withdrawing group in the phenyl ring (known to have a negative effect in the reactivity). Higher selectivities could be obtained with cyclic olefins (entries 5 and 6).

In all the reactions of EDA with an excess of olefin in the presence of complexes **1**–**3** to give corresponding cyclopropanes, fumaric acid esters were detected as by-products, but no by-products containing styrene were found. This had already been reported in the literature for other metal-catalyzed cyclopropanations of olefin systems [11].

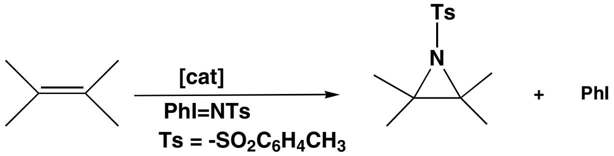
Several mechanistic studies on catalytic cyclopropanation reactions have been performed recently [12]. The fact that Cu(II) complexes are reduced to Cu(I) derivatives during the catalytic cycle, lead to the general agreement that the active species is a Cu(I) species regardless the oxidation state of the copper complex used as a pre catalyst [13]. Furthermore, it is also generally accepted that transition metal catalyzed cyclopropanation reactions involve the existence of a metal-carbene complex, formed by association of the diazo compound with the catalyst under liberation of N_2. The formation of the copper–carbene intermediate was shown to be the rate-determining step of the cyclopropanation reaction [13a,14]. The cyclopropanation catalyzed by the complexes **1**–**3** is therefore assumed to proceed via a similar mechanism to that already proposed for other copper(I) complexes [3c]. We assume the displacement of one, or even more likely, two of the acetonitrile ligands. The observation that compound **1** is the most active catalyst among the three examined complexes fits well with the finding, derived from the spectroscopic data, that the acetonitrile ligands are most weakly coordinated in case of complex **1**. Additional evidence for the ease of losing two nitrile ligands in the cases of compounds **1**–**3**, particularly for compound **1**, comes from the successful isolation and characterization of a linear, coordinatively unsaturated $[Cu(NCCH_3)_2]\ [B(C_6F_5)_4]$ complex, displaying only two acetonitrile ligands [9]. To the best of our knowledge, no evidence exists so far for a complex with three acetonitrile ligands around the Cu(I) center.

The reaction of copper(I) with EDA very likely generates the copper–carbene intermediate **A** with simultaneous release of nitrogen. The carbene transfer from intermediate **A** to the alkene substrate affords the cyclopropane product and regenerates the copper(I) complexes as shown in scheme 1.

Table 4
Aziridination of styrene catalyzed by **1**–**3** using PhI = NTs

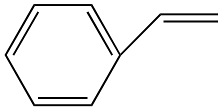
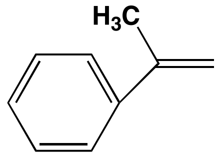
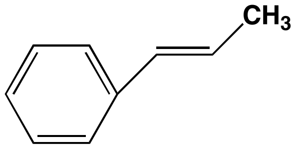
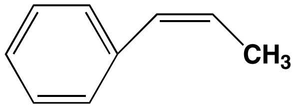
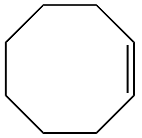
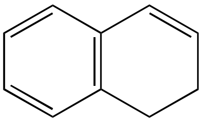
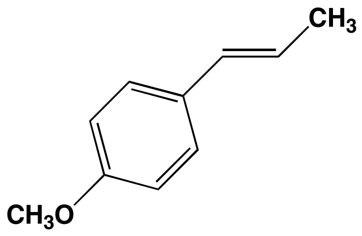
Complex[a]	Time (h)	Isolated yield (%)[b]
1	20	74
2	20	61
3	20	46

[a] Olefin:PhI = NTs ratio 2.5.
[b] Product identified by GC-MS and ^{1}H-NMR after isolation.



Equation 4.

Table 5
Aziridination of a variety of olefins catalyzed by **1** using PhI = NTs

Olefins[a]	Time (h)	Isolated yield (%)[b]
	20	74
	20	65
	20	88
	20	90
	20	95
	20	55
	20	60

[a]Olefin:PhI = NTs ratio 2.5.
[b]Product identified by GC-MS and ^{1}H-NMR after isolation.

2.4. Aziridination reactions

The aziridination of olefins has been often considered to be a similar reaction to cyclopropanation, in the sense that a nitrene group is transferred to the olefin, generating the three membered ring. We also investigated the complexes **1**–**3** as catalysts for olefin aziridination reactions (equation (4)).

As nitrene source we have used *p*-(toluensulfonyl)imino-phenyliodinate (PhI = Nts) in alternative to an azide. The catalytic studies involved 2% catalyst loading with regard to PhI = Nts and a styrene:PhI = NTs molar ratio of 2.5 in the presence of 4 Å molecular sieves at room temperature. Complex **3** reacts slowly and leads to low yields, while complexes **1** and **2** are found to be much more reactive and styrene can be converted to the corresponding aziridines in moderate to good yields. The catalytic results are displayed in table 4. As in the case of the cyclopropanation (see above), complex **1** is the best catalyst for aziridination of styrene with PhI = NTs among the complexes examined in this work, given the same experimental conditions. This again fits well with the conclusion drawn above, that the weaker the nitrile ligands are coordinated to the metal, the more smoothly the catalytic reaction runs.

We have also explored the conversion of simple mono and di substituted olefins including those with electron-withdrawing groups attached to the C=C bond using complex **1**. The olefin aziridination reactions were carried out at room temperature in the presence of 4 Å molecular sieves using 4.0 mL acetonitrile and 2% **1** for 20 h. 1,2-Dihydronaphthalene reacted very slowly and could only be converted to the corresponding aziridine in low yield. However styrene, α-methylstyrene, *trans*-*β*-methylstyrene, *cis*-*β*-methylstyreneand *trans*-anulene were more reactive and could be converted to the corresponding aziridines in moderate to excellent yields. The results obtained with styrene derivatives are comparable to reported literature values obtained with polypyrazolylborate copper(I) complexes [3c]. Furthermore, *cis*-cyclooctene, possessing a weaker and more reactive C=C bond, could be converted into the corresponding aziridines almost quantitatively table 5.

3. Conclusions

Acetonitrile ligated copper(I) complexes **1**–**3** bearing WCAs are shown to be catalytically active towards cyclopropanation and aziridination of olefins. Both reactions can be performed at room temperature with low catalyst loading (2%) giving product yields between 15 and 95%. From the three complexes tested, complex **1** proved to be the most active in both cyclopropanation and aziridination. This may be related to the particularly weak coordination of its acetonitrile ligands, being easily replacable during the course of the catalytic reaction.

4. Experimental

All solvents were dried using standard procedures unless otherwise stated. All manipulations were carried out using standard Schlenk techniques. IR was recorded on a Perkin Elmer FT-IR spectrometer using KBr pellets as matrix. ^{1}NMR were performed on Brucker AVANCE-DPX-400 spectrometer. Elemental analysis were performed at the Mikroanalylytisches Labor of the TU München (M. Barth). Styrene, α-methylstyrene, *trans*-*β*-methylstyrene, *cis*-*β*-methylstyrene, *trans*-anulene, 1,2-dihydronaphthalene, *cis*-cyclooctene and EDA were purchased from Aldrich. PhI = NTs was synthesized according to a known literature procedure [16]. The potassium salts of anions for complexes **1**–**3** were prepared according to Ref. [4].

4.1. *[Cu(NCCH$_3$)$_4$][B(C$_6$F$_5$)$_4$]* (**1**)

CuCl (0.79 g, 7.98 mmol) was added to a 40 mL solution of Ag[B(C$_6$F$_5$)$_4$] (6.28 g, 7.98 mmol) in dry acetonitrile under Argon atmosphere. The resulting mixture was stirred overnight at r.t. in darkness. The formed precipitate (AgCl) was removed and the filtrate was concentrated to ca. 5.0 mL under oil pump vacuum and kept at −35 °C. The desired product was obtained as a white crystalline solid. Yield 6.0 g (83%). Calcd. for $C_{32}H_{12}CuBF_{20}N_4$: C 42.38; H 1.33; N 6.18. Found: C 42.13; H 1.28; N 6.74. Selected IR (KBr, cm^{-1}) ν_{CN}, 2277, 2308. ^{1}H-NMR (400 MHz, CDCl$_3$, r.t., δ(ppm)): 1.87 (CH$_3$, 12H).

4.2. *[Cu(NCCH$_3$)$_4$][BC$_6$H$_3$(CF$_3$)$_{24}$]* (**2**)

CuCl (0.052 g, 0.53 mmol) was added to a 20 mL solution of Ag[B{C$_6$H$_3$(CF$_3$)$_2$}$_4$] (0.6 g, 0.53 mmol) in dry acetonitrile. The resulting solution was stirred overnight in darkness under Argon atmosphere. The solid (AgCl) was filtered off and the filtrate was evaporated to dryness by oil pump vacuum and recrystalized with dichloromethane and hexane at 1:1 ratio. The desired product was obtained as a white crystalline solid. Yield 0.49 g (85%). Calcd. for $C_{36}H_{18}CuBF_{24}N_2$: C44.04; H 2.22; N 5.14. Found: C43.64; H 2.45; N 4.74. Selected IR (KBr, cm^{-1}): ν_{CN}, 2286, 2317. ^{1}H-NMR (400 MHz, CDCl$_3$, r.t., δ(ppm)): 2.02 (CH$_3$, 12H), 7.53–7.68 (C$_6$H$_3$, 12H).

4.3. *[Cu(NCCH$_3$)$_4$][(C$_6$F$_5$)$_3$B–C$_3$H$_3$N$_2$–B(C$_6$F$_5$)$_3$]* (**3**)

CuCl (0.022 g, 0.22 mmol) was added to a 20.0 mL solution of (0.3 g, 0.22 mmol) Ag[(C$_6$F$_5$)$_3$B–C$_3$H$_4$N$_2$–B(C$_6$F$_5$)$_3$] in dry acetonitrile under argon atmosphere. The resulting solution was stirred overnight at r.t. in darkness. The formed precipitate of AgCl was removed and the solution was concentrated to ca. 1 mL by oil pump vacuum and kept at −35 °C. The desired product was obtained as a white crystalline solid. Yield 0.26 g (89%). Calcd. for $C_{47}H_{15}CuBF_{30}N_6$: C42.81; H 1.15; N 6.37. Found: C42.76; H 1.34; N 6.47. Selected IR (KBr, cm^{-1}) ν_{CN}, 2286, 2318. ^{1}H-NMR (400 MHz, CDCl$_3$, r.t., δ(ppm)): 2.13 (CH$_3$, s, 12H), 6.74 (C$_2$H$_2$, s, 2H) 7.43 (CH, s, 1H).

4.4. *Typical procedure for cyclopropanation*

(114 mg, 1.0 mmol) EDA in 2.0 mL dichloromethane was added slowly to a 2.0 mL dichloromethane solution of styrene (208.0 mg, 2.0 mmol) and **1** (18.0 mg, 0.02 mmol) over 30 min. The reaction was finished within 1 h. The structure of the product was determined by GC-MS, the conversion of styrene was determined by GC (FID) from a calibration curve recorded prior to the reaction course with dodecane as internal standard. Since no by-products containing styrene were found, the conversion is then equivalent to the yield.

4.5. *Typical procedure for aziridination*

(130.0 mg, 1.25 mmol) styrene, (94.0 mg, 0.25 mmol) Ph-I = N-TS and (18.0 mg, 0.02 mmol) **1**were stirred in 4.0 mL acetonitrile for 20 h. Then the product was purified by silica gel column chromatography (hexane:ethyl acetate = 5:1) and yields were determined by weighing the isolated product. The structure of pure product was determined by ^{1}H-NMR and GC-MS.

Acknowledgments

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