ELSEVIER

Available online at www.sciencedirect.com
ScienceDirect

Inorganica Chimica Acta 359 (2006) 4723–4729

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Cationic copper(I) and silver(I) nitrile complexes with fluorinated weakly coordinating anions: Metal–nitrile bond strength and its influence on the catalytic performance

Yanmei Zhang [a], Wei Sun [a], Christelle Freund [a], Ana M. Santos [a],
Eberhardt Herdtweck [a], Janos Mink [b,c], Fritz E. Kühn [a,*]

[a] *Lehrstuhl für Anorganische Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*
[b] *Molecular Spectroscopy Department, Chemical Research Centre of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary*
[c] *Faculty of Informational Technology, Research Institute of Chemical and Process Engineering, Analytical Chemistry Research Group of the Hungarian Academy of Sciences, Veszprém University, P.O. Box 158, H-8201 Veszprém, Hungary*

Received 15 November 2005; accepted 11 December 2005

Dedicated to Professor Dr. Dr. h.c. mult. Wolfgang A. Herrmann.

Abstract

Copper(I) and silver(I) complexes of formulae $[Cu(NCCH_3)_4]^+[A]^-$ ($[A]^- = [B(C_6F_5)_4]^-$ (**1**), $\{B[C_6H_3(CF_3)_2]_4\}^-$ (**2**), $[(C_6F_5)_3B–C_3H_3N_2–B(C_6F_5)_3]^-$ (**3**), and $[Ag(NCCH_3)_4]^+[B(C_6F_5)_4]^-$ (**4**) are examined with particular emphasis on the strength of their M–N bond and its influence on the catalytic performance of these complexes in cyclopropanation and aziridination. To examine the strength of the M–N interactions, vibrational spectra of the related hydrogenated and deuterated species $[Cu(NCCH_3)_4]^+$, $[Cu(NCCD_3)_4]^+$, $[Ag(NCCH_3)_4]^+$, and $[Ag(NCCD_3)_4]^+$ are also determined. It is found that the metal–nitrile bond strength is an important factor for the catalytic activity of the respective complexes.

Keywords: Copper; Silver; Cyclopropanation; Aziridination; Vibrational spectroscopy

---

1. Introduction

Weakly or non-coordinating anions (WCAs) are of considerable interest as counterions for the synthesis of novel ionic compounds as well as counterions for cationic catalysts, due to their potential in enhancing reactivity of metal complexes [1]. Among the industrial applications requiring WCAs is, for example, the so-called metallocene process for the stereoregular polymerization of olefins [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 $[Cu(NCCH_3)_4]^+$ cation coordinated with some common counterions, such as BF_4^-, ClO_4^- and PF_6^-, is well known both with respect to its properties, its structure and its catalytic activity [3]. Particular attention was given to 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].

Three-membered carbocyclic rings hold a prominent position in organic chemistry both due to their interesting biological properties [4] and to their use as starting materials and intermediates in organic synthesis [5]. However, the

---

[*] Corresponding author. Tel.: +49 0 89 289 13080; fax: +49 0 89 289 13473.
E-mail address: fritz.kuehn@ch.tum.de (F.E. Kühn).

0020-1693/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2005.12.044

synthesis of small rings still poses some challenges. Accordingly, the catalytic cyclopropanation and aziridination of olefins, forming three-membered rings, have been attracting significant attention [6]. 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 [7].

We recently published our findings about the applications of Ag(I) and Cu(I) nitrile compounds, associated with several non-coordinating anions as intermediates in the synthesis of Mn(II)-based polymerization catalysts [8]. It had turned out, however, that these synthetic intermediates were not applicable as catalysts for the polymerization of isobutene or the copolymerization of isobutene and isoprene [8b]. However, Ag(I) compounds with WCAs could be successfully applied for the coupling of terminal alkynes with aldehydes and amines [8d] and Cu(I) complexes with WCAs were applicable for catalytic cyclopropanations and aziridinations, as we have communicated recently [8e]. These latter findings are described in this work in more detail and a comparison of the vibrational spectra of Cu(I) and Ag(I) complexes with WCAs is given.

2. Experimental

2.1. Materials

All solvents were dried using standard procedures unless otherwise stated. All manipulations were carried out using standard Schlenk techniques. Styrene, α-methylstyrene, *trans*-β-methylstyrene, *cis*-β-methylstyrene, *trans*-anulene, 1,2-dihydronaphthalene, *cis*-cyclooctene and ethyldiazoacetate (EDA) were purchased from Aldrich. PhI = NTs was synthesized according to a known literature procedure [12]. The potassium salts of anions for complexes **1**–**3** were prepared according to Ref. [4].

2.2. Physical measurements and calculations

IR spectra were recorded on a Perkin–Elmer FT-IR spectrometer using KBr pellets as matrix. ^{1}H NMR experiments were performed on a Bruker AVANCE-DPX-400 spectrometer. Elemental analyses were performed at the Mikroanalytisches Labor of the TU München (M. Barth). The MIR spectra were recorded on a Digilab FTS-60A spectrometer with a KBr beamsplitter and a MCT detector. FIR spectra were recorded on a Digilab FTS-40 spectrometer with high pressure Hg-lamp, wiremesh beamsplitter and DTGS detector. Raman spectra were recorded on a Digilab and partially on a Nicolet FT-Raman 950 spectrometer equipped with NdYAG laser (wavelength: 1064 nm; power: 50–150 mW). Some of the Raman spectra were measured on a Renishaw System RM1000 spectrometer equipped with a Leica DMLM microscope, a diode laser (782 nm) and a Peltier-cooled CCD detector. Calculations were performed using a published program [13].

2.3. Syntheses

2.3.1. $[Cu(NCCH_3)_4][B(C_6F_5)_4]$ (*1*)

CuCl (0.79 g, 7.98 mmol) was added to a 40 mL solution of $Ag[B(C_6F_5)_4]$ (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 colorless crystalline solid. Yield 6.0 g (83%). *Anal.* Calc. for $C_{32}H_{12}BCuF_{20}N_4$: 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).

2.3.2. $[Cu(NCCH_3)_4]\{B[C_6H_3(CF_3)_2]_4\}$ (*2*)

CuCl (0.052 g, 0.53 mmol) was added to a 20 mL solution of $Ag[B\{C_6H_3(CF_3)_2\}_4]$ (0.6 g, 0.53 mmol) in dry acetonitrile. The resulting solution was stirred overnight in darkness under an argon atmosphere. The solid (AgCl) was filtered off and the filtrate was evaporated to dryness under oil pump vacuum and recrystallized with dichloromethane and hexane in an 1:1 ratio. The desired product was obtained as a colorless crystalline solid. Yield 0.49 g (85%). *Anal.* Calc. for $C_{36}H_{18}BCuF_{24}N_2$: C, 44.04; H, 2.22; N, 5.14. Found: C, 43.64; 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_6H_3, 12H).

2.3.3. $[Cu(NCCH_3)_4][(C_6F_5)_3B–C_3H_3N_2–B(C_6F_5)_3]$ (*3*)

CuCl (0.022 g, 0.22 mmol) was added to a 20 mL solution of (0.3 g, 0.22 mmol) $Ag[(C_6F_5)_3B–C_3H_3N_2–B(C_6F_5)_3]$ 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 under oil pump vacuum and kept at −35 °C. The desired product was obtained as a colorless crystalline solid. Yield 0.26 g (89%). *Anal.* Calc. for $C_{47}H_{15}BCuF_{30}N_6$: C, 42.81; H, 1.15; N, 6.37. Found: C, 42.76; 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_2H_2, s, 2H) 7.43 (CH, s, 1H).

2.3.4. Typical procedure for cyclopropanation

(114 mg, 1.0 mmol) EDA in 2.0 mL dichloromethane was added slowly to a 2 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 completed within 1 h. The structure of the product was determined by GC–MS and 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 can be considered as equivalent to the yield.

2.3.5. Typical procedure for aziridination

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

2.4. X-ray crystallographic studies on $[Cu(NCCH_3)_4][B(C_6F_5)_4]$ (1)

Crystal data and details of the structure determination are presented in Table 1. Suitable single crystals for the X-ray diffraction study were grown by standard cooling techniques from a saturated solution of freshly prepared complex **1** in acetonitrile. A clear colorless fragment was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR951) and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 6517 reflections. Data collections were performed at 123 K (OXFORD CRYOSYSTEMS) within a θ-range of $1.67° < \theta < 25.34°$ and measured with 10 data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0°$. A total number of 82913 reflections were integrated. Raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.047$) a sum of 6267 (all data) and 5744 [$I > 2\sigma(I)$], respectively, remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and treated as riding atoms using SHELXL-97 default parameters. Full-matrix least-squares refinements with 527 parameters were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium IV PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97 [14].

Table 1
Crystallographic data for complex **1**

Formula	$C_{32}H_{12}BCuF_{20}N_4$
Formula weight	906.82
Color/habit	colorless/fragment
Crystal dimensions (mm^3)	0.53 × 0.61 × 0.81
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
a (Å)	11.4125(1)
b (Å)	16.2928(1)
c (Å)	19.1983(1)
β (°)	106.4778(2)
V (Å^3)	3423.15(4)
Z	4
T (K)	123
D_{calc} (g cm^{-3})	1.760
μ (mm^{-1})	0.779
$F(000)$	1784
θ Range (°)	1.67–25.34
Index ranges (h,k,l)	±13, ±19, ±23
Number of reflections collected	82913
Number of independent reflections/R_{int}	6267/0.047
Number of observed reflections ($I > 2\sigma(I)$)	5744
Number of data/restraints/parameters	6467/0/527
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0280/0.0715
R_1/wR_2 (all data)[a]	0.0314/0.0736
Goodness-of-fit (on F^2)[a]	1.046
Largest diff peak and hole (e Å^{-3})	+0.26/−0.25

[a] $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; Goodness-of-fit $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

3. Results and discussion

3.1. Syntheses and characterizations

3.1.1. Syntheses and structures

The WCAs for complexes **1** and **2** were prepared respectively from pentafluorobenzene bromide and 3,5-bis-(trifluoromethyl)-bromobenzene treated successively with *n*-butyllithium, borontrichloride and potassium chloride (Chart 1, Scheme 1). The resulting salts were then transformed to silver salts by reaction with silver nitrate. The WCA of complex **3** was synthesized according to the 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) (Eq.

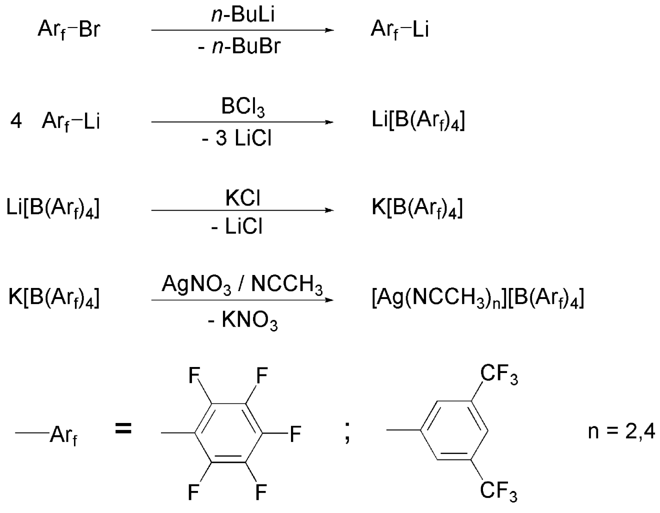
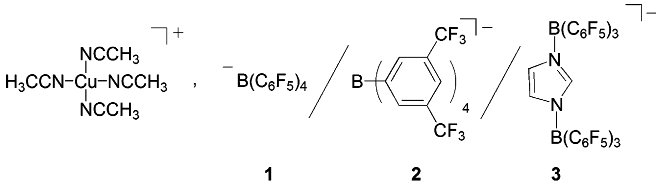


Chart 1.



Scheme 1.

(1)). The solvent stabilized complexes are stored at −35 °C under argon atmosphere to prevent decomposition and oxidation over long storage periods. However, they can be stored at room temperature for short periods of time and handled in laboratory atmosphere briefly.

$$\text{Ag[A]} + \text{CuCl} \xrightarrow[\text{r.t.}]{\text{NCCH}_3} \text{AgCl} + [\text{Cu(NCCH}_3)_4][\text{A}] \qquad (1)$$

The copper(I) complexes were characterized by IR spectroscopy, X-ray crystallography, elemental analysis and ^{1}H NMR. Suitable crystals were obtained from acetonitrile solution. The molecular structure of complex **1** was determined by single-crystal X-ray crystallography (Fig. 1). The crystallographic data are listed in Table 1, and selected bond lengths and angles are tabulated in Table 2.

As expected, the coordination environments around the monovalent copper ions in **1** are slightly distorted tetrahedral, with Cu(I)–N bond distances (2.000(2)–2.029(2) Å) and bond angles (N–Cu–N angles range from 103.13(7)° to 120.57(7)°). The acetonitrile ligands form nearly linear bonds to the copper atoms, and the bond distances of the acetonitrile ligands are longer than the analogs with common counterions such as BF_4^-, ClO_4^- and PF_6^-. There is nothing surprising about this slightly distorted tetrahedral geometry of the d^{10} cation. Table 2 gives the Cu–N bond lengths and N–Cu–N and Cu–N–C bond angles. The X-ray structure of a closely related Ag complex, namely of $[Ag(NCCH_2CH_3)_4]^+[B(C_6F_5)_4]^-$, had been described previously. In this case, the Ag(I)–N bond distances range between 2.265(3) and 2.298(3) Å, the N–Ag–N bond angles between 98.77(12)° and 125.53(12)° [8b].

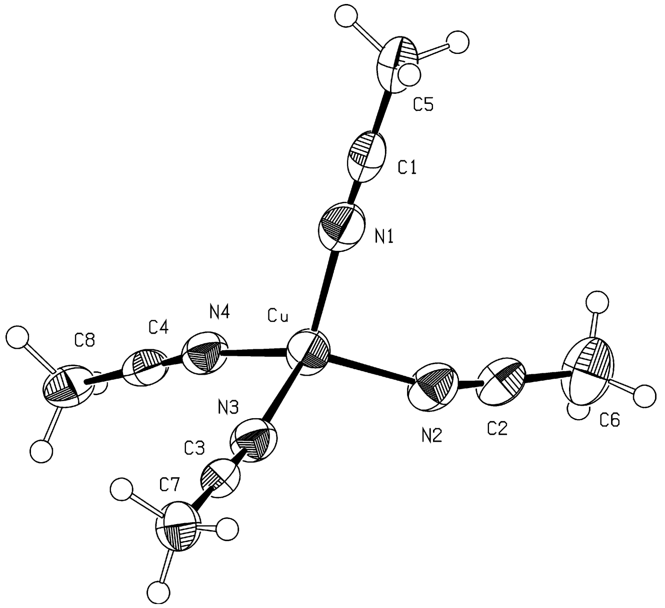


Fig. 1. ORTEP-style representation of the cationic part of the molecular structure of complex **1** as determined by single-crystal X-ray crystallography. The thermal ellipsoids are given at a 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**

Cu–N(1)	2.000(2)	N(1)–Cu–N(2)	103.13(7)
Cu–N(2)	2.021(2)	N(1)–Cu–N(3)	106.26(7)
Cu–N(3)	2.001(2)	N(1)–Cu–N(4)	119.81(7)
Cu–N(4)	2.029(2)	N(2)–Cu–N(3)	120.57(7)
		N(2)–Cu–N(4)	104.28(7)
		N(3)–Cu–N(4)	103.89(7)
		Cu–N(1)–C(1)	175.8(2)
		Cu–N(2)–C(2)	161.8(2)
		Cu–N(3)–C(3)	170.0(2)
		Cu–N(4)–C(4)	170.1(2)

3.1.2. Infrared spectra

Due to the interest in vibrational spectra of transition metal nitrile complexes [3d,3e] in general and due to the importance of such nitrile complexes as starting materials for a wide range of syntheses and catalyses in particular [9,10], the infrared spectra of copper(I) complexes **1**–**3** were investigated in detail and the bands are listed in Table 3. The IR shifts of the ν_{CN} absorption are observed at 2277 and 2308 cm^{-1} for complex **1**, 2286 and 2317 cm^{-1} for complex **2** and 2286 and 2318 cm^{-1} for complex **3**. Based on these IR data and the examinations on its analog containing only two (instead of four) nitrile ligands [9], it can

Table 3
Infrared bands of the $[Cu(NCCH_3)_4]^+$ complexes with different counterions

$[B(C_6F_5)_4]^-$ (**1**)	$[B(C_6H_3(CF_3)_2)_4]^-$ (**2**)	$[(C_6F_5)_3B–C_3H_3–N_2–B(C_6F_5)_3]^-$ (**3**)	Assignment
3028 w	3022w	3030 w	CH_3 asym str
2954 s	2946 s	2950 w	CH_3 sym str
2308 s	2317 w	2318 w	933 + 1380
2277 vs	2286 s	2286 s	CN str
1420 sh	1416 w	1408 sh	CH_3 asym def
1384 m	1380 sh	1380 sh	CH_3 sym def
1093 m	1094 w	1100 m, sh	
1037 vw	1071 sh	1031 vw	CH_3 rocking
1000 sh	1001 vw	1000 sh	
933 vw	933 w	935 vw	C–C str
545 vw	545 w	530 w,b	
402 w	405 sh	403 vw	δ(CCN)
389 m	395 s[a]	390 sh[a]	ν_a(CuN)
		375 sh	
345 sh	350 w		
		318 m	
227 w	230 w	252 m	δ(MCN)
154 m	105 m	203 m	δ(CMC)
147 m	146 w	[b]	
92 w	88 m	[b]	
74 w	70 w	[b]	

s, strong; m, medium; w, weak; v, very; sh, shoulder.

[a] Overlapping with anion bands.

[b] No FIR spectrum is available.

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 complexes **1**–**3**. The chemical shift of the acetonitrile protons in $CDCl_3$ of compound **1** ($\delta = 1.87$ ppm) is closer to the shift of free acetonitrile ($\delta = 1.83$ ppm) than the nitrile proton shift of the nitrile ligands of compounds **2** and **3** ($\delta = 2.02$ and 2.13 ppm, respectively).

In order to aid the assignments, the spectra of acetonitrile-d_3 copper(I) complexes of compound **1** (**1a**) prepared by the same method were recorded. Table 4 contains the measured and the calculated fundamental vibrations of related species such as hydrogenated $[Cu(NCCH_3)_4]^+$ and deuterated $[Cu(NCCD_3)_4]^+$. The force constant calculations have been performed with an updated computer program system [13]. As expected, the frequencies of $[Cu(NCCH_3)_4]^+$ are closely related to those of the $[Cu(NCCD_3)_4]^+$ cation.

The vibrational spectra of the corresponding silver compounds, $[Ag(NCCH_3)_4]^+$ (**4**) and $[Ag(NCCD_3)_4]^+$ (**4a**) (with the same counterion as **1** and **1a**), have been recorded for the sake of completeness. The results for $[Ag(NCCH_3)_4]^+$ and $[Ag(NCCD_3)_4]^+$ are summarized in Table 5. The two bands corresponding to the CN stretching vibrations of the Ag(I) complexes **4** and **4a** (2296 and 2295 cm^{-1}) show a stronger frequency shift from the vibration of the free acetonitrile (2261 cm^{-1}) than that observed for the Cu compounds **1** and **1a** (2294 and 2293 cm^{-1}, see Table 4), indicating a stronger metal–ligand interaction compared to the Cu(I) complex.

Table 4
Experimental and calculated frequencies of the Cu(I) complexes **1** and **1a** (cm^{-1}) (counterion $B(C_6F_5)_4^-$)

	$[Cu(NCCH_3)_4]^+$ (**1**)		$[Cu(NCCD_3)_4]^+$ (**1a**)		Potential energy distribution (PED)
	Experimental	Calculated	Experimental	Calculated	
A_1					
ν_1	2294*	2294	2293	2293	$40\nu_{CN} + 30\nu_{CC} + 10\nu_{CuN}$
ν_2	948	949	901	899	$50\nu_{CC} + 40\nu_{CuN} + 5\nu_{CN}$
ν_3	368	326	343	314	$80\nu_{CuN} + 12\nu_{CC} + 3\nu_{CN}$
E					
ν_4	401	401	400	401	$52\delta_{CCN} + 41\delta_{CCuC}$
ν_5	256	255	250	255	$100\delta_{CuNC}$
ν_6	92	91	88	89	$80\delta_{CCuC} + 10\delta_{CCN}$
F_2					
ν_7	2277	2277	2276	2276	$60\nu_{CN} + 30\nu_{CC} + 5\nu_{CuN}$
ν_8	933	933	882	880	$50\nu_{CC} + 25\ \nu_{CuN}$
ν_9	402	402	402	401	$100\delta_{CCN}$
ν_{10}	389	386	370	375	$50\nu_{CuN} + 40\nu_{CN} + 4\nu_{CC}$
ν_{11}	227	221	220	217	$70\delta_{CuNC} + 10\nu_{CuN} + 4\nu_{CC}$
ν_{12}	147	119	143	116	$60\delta_{CCuC} + 10\delta_{CuNC}$

* Fundamental bands for the A_1 and E species were observed in the Raman spectra.

Table 5
Experimental and calculated frequencies of the Ag(I) complexes **4** and **4a** (cm^{-1}) (counterion $B(C_6F_5)_4^-$)

	$[Ag(NCCH_3)_4]^+$ (**4**)		$[Ag(NCCD_3)_4]^+$ (**4a**)		Potential energy distribution (PED)
	Experimental	Calculated	Experimental	Calculated	
A_1					
ν_1	2296*	2296	2295	2295	$93\nu_{CN} + 8\nu_{CC} + 4\nu_{AgN}$
ν_2	948	948	901	901	$81\nu_{CC} + 16\nu_{AgN}$
ν_3	359	343	334	319	$80\nu_{AgN} + 12\nu_{CC} + 6\nu_{NC}$
E					
ν_4	394	394	393	392	$52\delta_{CCN} + 41\delta_{CAgC}$
ν_5	296	290	290	290	$100\delta_{AgNC}$
ν_6	118	109	114	106	$70\delta_{CAgC} + 20\delta_{CCN}$
F_2					
ν_7	2286	2286	2285	2285	$90\nu_{CN} + 10\nu_{CC} + 4\nu_{AgN}$
ν_8	932	932	880	879	$80\nu_{CC} + 10\nu_{AgN}$
ν_9	403	403	403	403	$100\delta_{CCN}$
ν_{10}	350	339	338	327	$80\nu_{AgN} + 10\nu_{CN} + 4\nu_{CC}$
ν_{11}	230	213	226	211	$70\delta_{AgNC} + 10\nu_{AgN} + 4\nu_{CC}$
ν_{12}	88	85	85	82	$60\delta_{CAgC} + 10\delta_{AgNC}$

* Fundamental bands for the A_1 and E species were observed in the Raman spectra.

Table 6
Infrared valence force constants of $[M(NCCH_3)_4]^+$ complexes of the types **1** and **4** (counterion $B(C_6F_5)_4{}^-$)

	$[Cu(NCCH_3)_4]^-$ (**1**)	$[Ag(NCCH_3)_4]^+$ (**4**)	Unit
K(CN)	18.803	18.873	a
K(CC)	4.989	4.960	a
K(MN)	2.224	2.347	a
F(CN, CN)	−0.021	−0.020	a
F(CC, CC)	−0.020	−0.049	a
F(MN, MN)	0.307	0.405	a
H(CNC)	0.859	0.102	b
H(MNC)	0.077	0.942	b
H(CMC)	0.402	0.436	b
h(CNC, CNC)	0.060	0.041	c
h(MNC, MNC)	0.091	0.087	c
h(CMC, CMC)	0.001	0.129	c

K, stretch; *F*, stretch–stretch; *H*, bend; *h*, bend–bend force constants.
[a] 10^2 N m^{-1}.
[b] 10^{-18} N m rad^{-2}.
[c] 10^{-8} N rad^{-1}.

The Cu–N stretching vibrations ($\nu_1 = 368$ and $\nu_{10} = 389$ cm^{-1}) are observed at higher wave numbers than those for the Ag–N stretching modes (Table 5). Based on these latter frequency differences, it could be easily misinterpreted that in the Cu(I) complexes the CH_3CN ligands are more strongly coordinated. The real explanation, however, results from force constant calculations where the Ag–N stretching force constants (2.347 N cm^{-1}) are higher than the Cu–N force constant (2.224 N cm^{-1}). As it can be seen in Table 6, the CN stretching force constant is higher in the Ag(I) complexes [13].

3.2. *Influence of the M–N bond strength on the catalytic behavior*

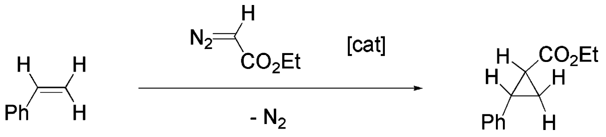
The use of complexes with weakly coordinated, easily displaceable ligands, has a positive effect on the catalytic activity, by rendering the intermediate species more accessible to substrate coordination. The negative effect of excess ligand in cyclopropanation catalysis with copper(I) complexes has been observed previously [3c]. It has been shown in the literature that nitrile ligated complexes may lose one or more of their acetonitrile ligands quite easily forming an under-coordinated, linear $[Cu(NCCH_3)_2]^+$-complex [9]. As we have communicated previously [8e] complexes **1**–**3** were tested as catalysts for cyclopropanation reactions using styrene as olefin (Eq. (2), Table 7).

Table 7
Cyclopropanation of styrene catalyzed by complexes **1**–**4** (reaction time 1 h)

Complexes[a]	Yield[b]	*cis*:*trans*[c]
$[Cu(NCCH_3)_4]^+[B(C_6F_5)_4]^-$ (**1**)	71	49:51
$[Cu(NCCH_3)_4]^+\{B[C_6H_3(CF_3)_2]_4\}^-$ (**2**)	42	36:64
$[Cu(NCCH_3)_4]^+[B(C_6F_5)_3–C_3H_3N_2–B(C_6F_5)_3]^-$ (**3**)	25	37:63
$[Ag(NCCH_3)_4]^+[B(C_6F_5)_4]^-$ (**4**)	0	

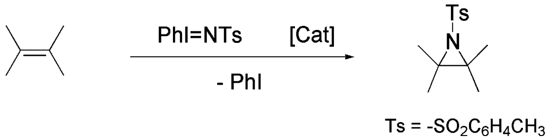
[a] Styrene: EDA = 2:1.
[b] Yield determined by GC (FID) with dodecane as standard.
[c] Determined by GC (FID) and GC–MS.

From these data, it is obvious that compound **1** is more efficient in the cyclopropanation reaction than its derivatives **2** and **3**. As a possible reason for this observation, the slightly weaker Cu–N bond in compound **1** in comparison to its derivatives **2** and **3** has been assumed. According to the vibrational spectroscopic results presented above, it is to be expected that the silver complex **4** also shows a lower catalytic activity than the copper complex **1**. This is indeed the case. Applied under the same reaction conditions as compound **1**, compound **4** shows no catalytic activity for olefin cyclopropanation reactions.



(2)

The aziridination of olefins has been very 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 compared the complexes **1** and **4** as catalysts for olefin aziridination reactions (Eq. (3)). Again, while **1** proved to be an active catalyst as communicated previously [8e], compound **4** was found to be catalytically inactive.



(3)

As a first step in such catalytic reactions, the removal (dissociation) of one or two ligands has been assumed in the literature [8e,11], to create an empty coordination site for the entry of a substrate molecule (Eq. (4)). It is interesting to note that a copper compound of composition $[Cu(NCCH_3)_2]^+[B(C_6F_5)_4]^-$ (**5**) has been described in the literature [9], while the corresponding Ag complex could not be isolated [8d]. Furthermore, compound **5** displays ca. 0.15 Å shorter copper–nitrile bond distances than compound **1**.

$$[Cu(NCCH_3)_4]^+ \underset{+\,2\,NCCH_3}{\overset{-\,2\,NCCH_3}{\rightleftharpoons}} [Cu(NCCH_3)_2]^+ \qquad (4)$$

4. Conclusions

Acetonitrile ligated copper(I) complexes **1**–**3** bearing weakly or non-coordinating anions are catalytically active toward cyclopropanation and aziridination of olefins. The related silver complex **4**, however, is inactive in both catalytic reactions. The catalytic activity corresponds very well with the strength of the metal–nitrile interaction as deduced from vibrational spectroscopic data. The stronger the metal–nitrogen interaction is, the lower is the catalytic activity of the complexes. This supports the assumption that the catalytic reaction starts with a metal–ligand dissociation, opening a free coordination site for the entry of a substrate.

Acknowledgments

The authors are grateful to the DFG (DFGKK1265/4-1) and the Fonds der Chemischen Industrie for financial support.

Appendix A. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC 296400 for **1**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 366 033, e-mail: deposit@ccdc.ac.uk or on the web www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.12.044.

References

[1] (a) I. Krossing, I. Raabe, Angew. Chem., Int. Ed. 43 (2004) 2066;
(b) S.H. Strauss, Chem. Rev. 93 (1993) 927.

[2] (a) L.D. Henderson, W.E. Piers, G.J. Irvine, R. McDonald, Organometallics 21 (2002) 340;
(b) I. Krossing, L. Van Wüllen, Chem. Eur. J. 8 (2002) 700;
(c) J. Zhou, S.J. Lancaster, D.A. Walker, S. Beck, M. Thornton-Pett, M. Bochmann, J. Am. Chem. Soc. 123 (2001) 223;
(d) S.V. Ivanov, J.J. Rockwell, O.G. Polyakov, C.M. Gaudinski, O.P. Anderson, K.A. Solntsev, S.H. Strauss, J. Am. Chem. Soc. 120 (1998) 4224.

[3] (a) J.M. Knaust, D.A. Knight, S.W. Keller, J. Chem. Cryst. 33 (2003) 813;
(b) C. Borrielo, M.E. Cucciolito, A. Panunzi, F. Ruffo, Tetrahedron-Asymmetr. 12 (2001) 2467;
(c) M.M. Díaz-Requejo, P.J. Pérez, J. Organomet. Chem. 617 (2001) 110;
(d) B.N. Storhoff, H.C. Lewis, Coord. Chem. Rev. 23 (1977) 1;
(e) F.D. Rochon, R. Melanson, H.E. Howard-Lock, C.J.L. Lock, G. Turner, Can. J. Chem. 62 (1984) 860.

[4] (a) C.J. Suckling, Angew. Chem., Int. Ed. 27 (1988) 537;
(b) H.M.L. Davies, T. Nagashima, J.L. Klino III, Org. Lett. 2 (2000) 823.

[5] H.N.C. Wong, M.-Y. Hon, C.-W. Tse, Y.-C. Yip, J. Tanko, T. Hudlicky, Chem. Rev. 89 (1989) 165.

[6] (a) M.P. Doyle, Chem. Rev. 86 (1986) 919;
(b) M.P. Doyle, D.C. Forbes, Chem. Rev. 98 (1998) 911;
(c) J.W. Herndon, Coord. Chem. Rev. 206 (2000) 237;
(d) P. Müller, C. Fruit, Chem. Rev. 103 (2003) 2905;
(e) J.B. Sweeney, Chem. Soc. Rev. 31 (2002) 247.

[7] (a) K. Guthikonda, J. Du Bois, J. Am. Chem. Soc. 124 (2002) 13672;
(b) T. Kubo, S. Sakaguchi, Y. Ishii, Chem. Commun. (2000) 625;
(c) Y. Chen, X.P. Zhang, J. Org. Chem. 69 (2004) 2431;
(d) W.J. Seitz, A.K. Saha, M.M. Hossain, Organometallics 12 (1993) 2604.

[8] (a) M. Vierle, Y. Zhang, E. Herdweck, M. Bohnenpoll, O. Nuyken, F.E. Kühn, Angew. Chem., Int. Ed. Engl. 42 (2003) 1307;
(b) M. Vierle, Y. Zhang, A.M. Santos, K. Köhler, C. Haeßner, E. Herdtweck, M. Bohnenpoll, O. Nuyken, F.E. Kühn, Chem. Eur. J. 10 (2004) 6323;
(c) A. Sakthivel, A.K. Hijazi, H.Y. Yeong, K. Köhler, O. Nuyken, F.E. Kühn, J. Mater. Chem. 15 (2005) 4441;
(d) Y. Zhang, A.M. Santos, E. Herdtweck, J. Mink, F.E. Kühn, New J. Chem. 29 (2005) 366;
(e) Y. Zhang, W. Sun, A.M. Santos, F.E. Kühn, Catal. Lett. 101 (2005) 35;
(f) S. Gago, Y. Zhang, A.M. Santos, K. Köhler, F.E. Kühn, J.A. Fernandes, M. Pillinger, A.A. Valente, T.M. Santos, P.J.A. Ribeiro-Claro, I.S. Gonçalves, Micropor. Mesopor. Mater. 76 (2004) 131.

[9] H.-C. Liang, E. Kim, C.D. Incarvito, A.L. Rheingold, K.D. Karlin, Inorg. Chem. 41 (2002) 2209.

[10] (a) P. Ferreira, F.E. Kühn, Trends Inorg. Chem. 7 (2001) 89;
(b) F.E. Kühn, D. Schön, G. Zhang, O. Nuyken, J. Macromol. Sci. Pure 37 (2000) 971;
(c) F.E. Kühn, J.R. Ismeier, D. Schön, W.-M. Xue, G. Zhang, O. Nuyken, Macromol. Rapid Commun. 20 (1999) 555;
(d) R.T. Henriques, E. Herdtweck, F.E. Kühn, A.D. Lopes, J. Mink, C.C. Romão, J. Chem. Soc., Dalton Trans. (1998) 1293;
(e) F.A. Cotton, F.E. Kühn, J. Am. Chem. Soc. 118 (1996) 5826;
(f) J.C. Bryan, F.A. Cotton, L.M. Daniels, S.C. Haefner, A.P. Sattelberger, Inorg. Chem. 34 (1995) 1875;
(g) F.A. Cotton, K.J. Wiesinger, Inorg. Chem. 30 (1991) 871;
(h) K.R. Dunbar, J. Am. Chem. Soc. 110 (1988) 8247.

[11] (a) T. Niimi, T. Uchida, R. Irie, T. Katsuki, Adv. Synth. Catal. 343 (2001) 79;
(b) T. Ikeno, I. Iwakura, S. Yabushita, T. Yamada, Org. Lett. 4 (2002) 517;
(c) J.M. Fraile, J.I. García, V. Martínez-Merino, J.A. Mayoral, L. Salvatella, J. Am. Chem. Soc. 123 (2001) 7616;
(d) B.F. Straub, I. Gruber, F. Rominger, P. Hofmann, J. Organomet. Chem. 684 (2003) 124;
(e) R.G. Salomon, J.K. Kochi, J. Am. Chem. Soc. 95 (1973) 3300;
(f) H. Fritschi, U. Leutenegger, A. Pfaltz, Helv. Chim. Acta 71 (1988) 154;
(g) T. Aratani, Pure Appl. Chem. 57 (1985) 1839;
(h) M.M. Díaz-Requejo, T.R. Belderrain, M.C. Nicasio, F. Prieto, P.J. Pérez, Organometallics 18 (1999) 2601.

[12] M.J. Södergren, D.A. Alonso, A.V. Bedekar, P.G. Andersson, Tetrahedron Lett. 38 (1997) 6897.

[13] J. Mink, L.M. Mink, Computer Program System for Vibrational Analyses of Polyatomic Molecules (in Lahey-Fujitsu Fortran Win32), Stockholm, 2004.

[14] (a) Data Collection Software for Nonius κ-CCD devices, Delft, The Netherlands, 2001;
(b) Z. Otwinowski, W. Minor, Meth. Enzymol. 276 (1997) 307ff;
(c) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435;
(d) A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992, Tables 6.1.1.4, 4.2.6.8, and 4.2.4.2;
(e) A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2001;
(f) G.M. Sheldrick, SHELXL-97, Universität Göttingen, Göttingen, Germany, 1998.